Fertilizers

Heinrich W. Scherer, Agrikulturchemisches Institut, Universität Bonn, Bonn, Federal Republic of Germany (Chap. 1 and 2)

Konrad Mengel, Institute for Plant Nutrition, Justus-Liebig-Universität Giessen, Giessen, Federal Republic of Germany (Chap. 1 and 2)

Heinrich Dittmar, BASF Aktiengesellschaft, Ludwigshafen, Federal Republic of Germany (Chap. 3 and 5)

Manfred Drach, BASF Aktiengesellschaft, Limburgerhof, Federal Republic of Germany (Chap. 4.1, 4.2 and 4.3)

Ralf Vosskamp, BASF Aktiengesellschaft, Limburgerhof, Federal Republic of Germany (Chap. 4.1, 4.2 and 4.3)

Martin E. Trenkel, Eusserthal, Federal Republic of Germany (Chap. 4.4 and 4.5)

Reinhold Gutser, Lehrstuhl für Pflanzenernährung, Technische Universität München-Weihenstephan, Freising, Federal Republic of Germany (Chap. 4.6)

Günter Steffens, Landwirtschaftliche Untersuchungs- und Forschungsanstalt, Oldenburg, Federal Republic of Germany (Chap. 4.7)

Vilmos Czikkely, BASF Aktiengesellschaft, Ludwigshafen, Federal Republic of Germany (Chap. 6)

Titus Niedermaier, formerly BASF Aktiengesellschaft, Ludwigshafen, Federal Republic of Germany (Chap. 6)

Reinhardt Hähndel, BASF Aktiengesellschaft, Limburgerhof, Federal Republic of Germany (Chap. 7)

Hans Prün, formerly BASF Aktiengesellschaft, Limburgerhof, Federal Republic of Germany (Chap. 7)

Karl-Heinz Ullrich, BASF Aktiengesellschaft, Limburgerhof, Federal Republic of Germany (Chap. 8)

Hermann Mühlfeld, formerly Chemische Fabrik Kalk GmbH, Köln, Federal Republic of Germany (Chap. 8)

Wilfried Werner, Agrikulturchemisches Institut der Universität Bonn, Bonn, Federal Republic of Germany (Chap. 9)

Günter Kluge, Bundesministerium für Ernährung, Landwirtschaft und Forsten, Bonn, Federal Republic of Germany (Chap. 10)

Friedrich Kuhlmann, Institut für Betriebslehre der Agrar- und Ernährungswirtschaft der Justus-Liebig-Universität Giessen, Giessen, Federal Republic of Germany (Chap. 11.1)

Hugo Steinhauser, formerly Lehrstuhl für Wirtschaftslehre des Landbaues, Technische Universität München, Freising, Federal Republic of Germany (Chap. 11.1)

Walter Brändlein, BASF Aktiengesellschaft, Ludwigshafen, Federal Republic of Germany (Chap. 11.2)

Karl-Friedrich Kummer, BASF Aktiengesellschaft, Limburgerhof, Federal Republic of Germany (Chap. 11.3)

See also: Individual fertilizers are also described under the separate keywords → Ammonia, → Ammonium Compounds, → Nitrates and Nitrites, → Phosphate Fertilizers, → Potassium Compounds, and → Urea

Ullmann's Agrochemicals, Vol. 1

ISBN: 978-3-527-31604-5

Fertilizers are products that improve the levels of available plant nutrients and/or the chemical and physical properties of soil. An overview is given over the chemical and physical aspects of plant nutrition uptake and soil properties. The different categories of fertilizers are discussed, and special interest is given on production processes and analyses, including storage and transportation as well as environmental, legal, and economic aspects.

1. Introduction

Fertilizers in the broadest sense are products that improve the levels of available plant nutrients and/or the chemical and physical properties of soil, thereby directly or indirectly enhancing plant growth, yield, and quality.

Fertilizers are classified as follows in terms of their chemical composition:

1) Mineral fertilizers consist of inorganic or synthetically produced organic compounds.
2) Organic fertilizers are waste products from animal husbandry (stable manure, slurry manure), plant decomposition products (compost, peat), or products from waste treatment (composted garbage, sewage sludge).
3) Synthetic soil conditioners are products whose main function is to improve the physical properties of soils, for example, friability and water and air transport.

The following categories are distinguished with respect to nutrient content:

1) Straight fertilizers generally contain only one primary nutrient.
2) Compound (complex or multinutrient) fertilizers contain several primary nutrients and sometimes micronutrients as well.
3) Micronutrient fertilizers contain nutrients required in small quantities by plants, as opposed to macronutrients; quantities range from 1 to 500 g $ha^{-1}a^{-1}$.

Finally, fertilizers can be classified as solid or liquid fertilizers and as soil or foliar fertilizers, the latter being applied exclusively by spraying on an existing plant population.

History. Fertilizing substances were applied even in antiquity. Their use can be attributed to the observation in nature that plants developed especially well in locations where human or animal excreta, ash residues, river mud, or dying plants were left. For example, the Egyptians knew about the fertility of the Nile mud, and the Babylonians recognized the value of stable manure; for example, HOMER mentions manure in the *Odyssey*. PLINY reports that the Ubians north of Mainz used "white earth," a calcareous marl, to fertilize their fields. The Romans acknowledged the advantages of green manuring, cultivating legumes and plowing them under. At the end of the first millenium, wood ash was much used as fertilizer in Central Europe. Not until the beginning of the 19th century did guano, at the suggestion of ALEXANDER VON HUMBOLDT (1800), and Chilean caliche, on the recommendation of HAENKES (1810), come into use as fertilizers. Up to that time, however, it was still believed that the organic matter of soil, humus, was the true source of plant nutrition.

Around 1800, the nutrition problem entered a critical phase in Europe. In 1798, MALTHUS set forth his pessimistic theses, saying that the quantity of food could increase only in arithmetic progression while the population grew geometrically. Combining results obtained by others (SPRENGEL, BOUSSINGAULT) with his own pathbreaking studies, J. VON LIEBIG set forth the theoretical principles of plant nutrition and plant production in *Chemistry in Its Application to Agriculture and Physiology* (1840). He took the view, now considered obvious, that plants require nitrogen, phosphate, and potassium salts as essential nutrients and extract them from the soil. LIEBIG's *mineral theory* was well supported by experimental data of J. B. BOUSSINGAULT (1802 – 1887) in France. He and also J. B. LAWES (1814 – 1900) and J. H. GILBERT (1827 – 1901) in England showed that plants benefit from inorganic N fertilizers. LIEBIG thus became the founder of the theory of mineral fertilizers, and his doctrines led to an increasing demand for them. A number of companies were subsequently founded in Europe to produce phosphate and potash fertilizers. Superphosphate was manufactured for the first time in 1846, in England.

In Germany, this industrial development started in 1855. The importation of saltpeter on a large scale began in the area of the German Federation (56 000 t in 1878). Peruvian guano soon came into heavy use (520 000 t in 1870). Ammonium sulfate, a coke-oven byproduct, was later recognized as a valuable fertilizer, and the mining of water-soluble potassium minerals was undertaken in the 1860s [1].

The demand for nitrogen that developed at the end of the 19th century soon outstripped the availability of natural fertilizers. A crucial breakthrough came about with the discovery and large-scale implementation of ammonia synthesis by HABER (1909) and its industrial realization by BOSCH (1913).

Around the turn of the century, the technique of hydroponics led to the discovery of other essential plant nutrients. Research showed that plants in general require ten primary nutrients: carbon, hydrogen, oxygen. nitrogen, phosphorus, potassium, calcium, magnesium, sulfur, and iron. JAVILLIER and MAZE (1908) pointed out for zinc and AGULHON (1910) pointed out for boron the nutritional effects on plants. WARINGTON (1923) first described the symptoms of boron deficiency, and BRANDENBURG (1931) clearly recognized dry rot in the sugar beet as boron deficiency. Generally micronutrients were made available to the plant as liquid foliar fertilizer, a method first suggested for iron by GRIS in 1844. By 1950, this list of micronutrients had been expanded to include manganese, copper, and molybdenum.

Almost 70 years ago, serious research began on the best nutrient forms for individual plant species under various soil and climatic conditions. Besides the classical fertilizers, for example, controlled-release fertilizers, improved foliar fertilizers, nutrient chelates, and nitrification inhibitors have been developed in recent decades. This development of new nutrient forms is still in full swing in the special fertilizers sector.

In the developed market economies of Western Europe, the United States, and Japan, however, the level of mineral fertilizer use has not been increasing since the beginning of the 1980s. In some countries, genuine agricultural overproduction has occurred recently. Since better delivery of plant nutrients has led to increasing self-reliance even in the Third World economies (e.g., China, India, Brazil), these countries are not so important as purchasers of nutrients on the world market, so that surpluses cannot be exported without limit. The production of fertilizers is also on the increase in these countries.

Thus overproduction plus regional environmental problems (nitrates entering the ground water) are actually leading to a decrease in mineral fertilizer use in some areas. This decline will be limited by diminishing soil fertility in localities where fertility has been enhanced by decades of proper fertilization.

2. Plant Nutrition and Soil Science

The science of plant nutrition is situated between soil science and plant physiology. It comprises the definition of the elements nutritive for plants; the uptake of plant nutrients and their distribution in the plant; the function of the nutritive elements in plant metabolism; their effect on plant growth; yield formation and quality parameters in crops; soil nutrient exploitation by plant roots; factors and processes that control the plant nutrient availability in soils; toxic elements in soils and their impact on plant growth; the application of plant nutrient carriers (fertilizers) and their turnover in soils; nutrient balance; and the maintenance of soil fertility.

Plant nutrition is considered mainly from two aspects, an agronomic one and an ecological one. The former is focused on the question of fertilizing soil as an efficient means to increase crop yield and to maintain or even improve soil fertility. The latter, the ecological aspect of plant nutrition, is concerned with the nutritive condition of a soil and a location and with its effect on plant growth and plant communities. Since fertilizers are the topic of this article, the agronomic aspects of plant nutrition are treated with greater depth.

The science of plant nutrition is closely associated with the science of soils. The latter comprises a broad field of scientific activity and thus cannot be considered here in all its facets. In this article only those problems of soil science relevant to understanding plant nutrition are treated.

2.1. Plant Nutrients

2.1.1. Definition and Classification

From a scientific point of view, the term plant nutrient is not especially precise. More appropriate is to distinguish between nutritive elements of plants and nutritive carriers. Essential *nutritive elements* for plants are the chemical elements that are required for a normal life cycle and that satisfy the following criteria:

1) A deficiency of the element makes it impossible for the plant to complete its life cycle.
2) The deficiency is specific for the element in question.
3) The element is directly involved in the nutrition of plants because of either its chemical or its physical properties.

According to this definition, the following chemical elements are nutritive elements for plants: C, H, O, N, P, S, K, Ca, Mg, Fe, Mn, Cu, Zn, Mo, B. Further elements, such as Na, Cl, and Si, may affect plant growth positively, and there are particular plant species for which these elements are of great importance. Nevertheless, they are not essential nutritive elements for plants in the strict sense of the definition. Cobalt is required by some bacteria, e.g., by dinitrogen-fixing bacteria and thus may also benefit plant growth indirectly.

Generally it is not the element itself that is provided to and taken up by the plant, but an ion or a molecule in which the nutritive element is present, e.g., C is present in CO_2, P in $H_2PO_4^-$, N in NO_3^- or NH_4^+, and B in H_3BO_3. The particular molecule or ion in which the nutritive element is present is termed the *nutrient carrier*. In the case of metals, the corresponding ion or salts of ion species in question, e.g., K^+, Ca^{2+}, Zn^{2+}, can be considered the carrier. In this sense fertilizers are nutrient carriers.

Plant nutrients may be grouped into macronutrients and micronutrients. *Macronutrients* are required in high amounts and thus are present in plant tissues in much higher concentrations than the *micronutrients*. Carbon, H, O, N, P, S, K, Ca, and Mg belong to the macronutrients. Their concentration in the dry plant matter is in the range 1 – 50 mg/g, except for C, H, and O, which have much higher concentrations (see Table 2). The concentration of the micronutrients in the dry plant matter is in the range 1 – 1000 µg/g.

From the viewpoint of fertilization, those nutrients that are required by plants in high quantities and that must be regularly supplied by fertilization are of particular interest. These nutrients are N, K, P, and to a minor degree also Ca, Mg, and S. Calcium is a *soil nutrient*, which means that it is important for an optimum soil structure. Application of micronutrients is not a common practice, but they are applied at locations where soils are low in a particular micronutrient or where soils may bind this micronutrient very strongly. This is the case for heavy metals (Fe, Mn, Cu, Zn) and B in calcareous and alkaline soils (soils with a high pH value), while Mo is strongly fixed in acid soils. Acid organic soils are known for their low available Cu content.

According to the different quantitative requirements for macronutrients and micronutrients, the former are taken up in much higher quantities than the latter. Thus a wheat stand with a yield potential of 7 t of grain per hectare requires about 100 kg K but only 100 g Cu.

From a physiological point of view, plant nutrients are grouped into four groups, as shown in Table 1. The *first group*, comprising C, H, O, N, and S, includes all major elementary constituents of organic plant matter. Their carriers are present mainly in the oxidized form, and they must be reduced during the process of incorporation. The energy required for this reduction originates directly or indirectly from photosynthetically trapped energy. Assimilation of H is basically an oxidation process, namely, the oxidation of water with the help of light energy (photolysis):

$$H_2O \xrightarrow{h\nu} 2H^+ + 2e^- + 0.5\,O_2$$

The *second group* (P, B, Si) comprises elements that are taken up as oxo complexes in the partially deprotonated (P) and protonated (B, Si) form. The oxo complex is not reduced in the plant cell, but may form esters with hydroxyl groups of carbohydrates, thus producing phosphate, borate, and silicate esters.

The *third group* comprises metals that are taken up from the soil solution in ionic form. They are only partially incorporated into the organic structure of the plant tissue: Mg in the chlorophyll molecule, Mn in the electron donor complex of photosystem II, and Ca^{2+} as countercation of indiffusible anions in cell walls and particularly in biological membranes. Potassium is virtually not incorporated into the organic plant matter. It is only weakly adsorbed by Coulombic forces. There exist, however, some organic molecules that may bind K^+ very selectively (ionophores, see Section 2.4.1). These ionophores are likely to be involved in K^+ uptake.

The *fourth group* comprises heavy metals, of which Fe, Cu, and Zn are taken up as ions or in the form of soluble metal chelates, while Mo is taken up as molybdate. These molecules are easily incorporated into the organic structure, where they serve as essential elements of enzyme systems: Fe in the heme group and in ferredoxin, Mn in arginase [2], Cu in oxidases (polyphenol oxidase, cytochrome oxidase, ascorbate oxidase [3]), Zn in RNA polymerase [4], and Mo in nitrate reductase [5] and nitrogenase [6].

All nutritive elements of plants, therefore, are taken up in the form of inorganic complexes, mostly in oxidized form or as metal ions, i.e., in forms characterized by a low energy level. This is a unique feature of plants, and a feature in which they contrast sharply with animals and most kinds of microorganisms (bacteria and fungi). Animals and most microorganisms must take up food that is rich in chemical energy in order to meet their energy requirements. Plants, at least green plants, meet their energy requirement by converting radiation energy into chemical energy. This energy conversion process is manifest in the reduction of plant nutrient carriers (NO_3^-, SO_4^{2-}, CO_2) as already mentioned. Thus important processes of plant nutrition are closely linked with the unique function of plants in the great cycle of nature, i.e., the conversion of inorganic matter into organic form. Liebig [7] was correct in commenting on plant nutrition: “Die ersten Quellen der Nahrung liefert ausschließlich die anorganische Natur.” (The primary source of nutrition is provided exclusively by the inorganic materials in nature.)

2.1.2. Function of Plant Nutrients

Most plant organs and particularly plant parts that are metabolically very active, such as young leaves and roots, are rich in water (ca. 80 – 90 wt % of the total fresh matter), while their organic material is ca. 12 – 18 wt % and their mineral content is 2 – 6 wt %. As shown in Table 2, in the dry matter of plant material O and C are by far the most abundant elements, followed by H, N, and K. The elements C, O, H, and, to some extent, N are mainly structural elements in plant matter. They can, however, form chemical

Table 1. Physiological classification of plant nutritive elements, nutrient carriers, and form in which the nutrient is taken up

Nutritive element	Nutrient carrier	Uptake
First group		
C	CO_2, HCO_3^-	CO_2 by leaves, HCO_3^- by roots
H	H_2O	H_2O by leaves, H_2O and HCO_3^- by roots
O	CO_2, HCO_3^-, O_2	O_2 and CO_2 by leaves, HCO_3^- and O_2 by roots
N	NH_4^+, NH_3, NO_3^-, NO_x	NH_4^+ and NO_3^- by roots, NH_3 and NO_x by leaves
S	SO_4^{2-}, SO_2, SO_3, H_2S	SO_4^{2-} by roots, SO_2, SO_3, and H_2S by leaves
Second group		
P	$H_2PO_4^-$, HPO_4^{2-}	$H_2PO_4^-$ and HPO_4^{2-} by roots
B	H_3BO_3, borates	H_3BO_3 and $B(OH)_4^-$ by roots
Si	silicates	$Si(OH)_4$ by roots
Third group		
K	K^+, K salts	K^+ by roots
Mg	Mg^{2+}, Mg salts	Mg^{2+} by roots
Ca	Ca^{2+}, Ca salts	Ca^{2+} by roots
Mn	Mn^{2+}, Mn salts	Mn^{2+} by roots
Fourth group		
Fe, Cu, Zn, Mo	ionic form or metal chelates, minerals containing these elements	by roots in ionic form or in the form of soluble metal chelates, Mo in the form of the molybdate

groups that are directly involved in metabolic processes, e.g., carboxyl groups, amino groups, hydroxyl groups.

Table 2. Mean content of chemical elements in the dry matter of green plant material

Element	Content, g/kg
O	440
C	420
H	60
N	30
K	20
P	4
All other elements	26

Since in many soils the available N is low, *nitrogen* [*7727-37-9*] is the most important fertilizer element, and for this reason its function in plant metabolism deserves particular interest. Nitrogen is an essential element for amino acids, proteins, nucleic acids, many coenzymes, and some phytohormones. Basic biochemical processes of meristematic growth, such as the synthesis of proteins and nucleic acids, require N. If this nutrient is not supplied in sufficient amounts, the growth rate is depressed and the synthesis of proteins affected. Nitrogen-deficient plants are characterized by low protein and high carbohydrate contents. This relationship is shown in Table 3 [8].

Nitrogen is also essential for the formation of chloroplasts, especially for the synthesis of chloroplast proteins. Hence N deficiency is characterized by low chlorophyll content; the leaves, especially the older ones, are pale and yellow; the stems thin and the plants small. Nitrogen-deficient plants senescence earlier, probably because of a deficiency of the phytohormone cytokinin. Abundant N supply increases the protein content, especially the content of free amino acids, and often also the content of NO_3^- in plants. An example of this is shown in Table 4 [9]. Excess nitrogen nutrition results in luxurious plants that frequently are susceptible to fungi attack.

Table 3. Effects of N supply on yield of dry matter and the content of organic N and carbohydrates in the dry matter of young timothy plants (*Phleum pratense*) [8]

Yield and content	N supply	
	Low	Sufficient
Yield, g/pot	15.7	20.2
Content, mg/g		
Organic N,	20.5	31.5
Sucrose	46.9	22.6
Fructans *	22.2	9.2
Starch	32.8	11.7
Cellulose	169	184

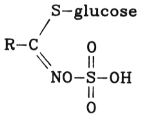
* Polysaccharides of fructose.

The ratio of N to S in plant matter is ca. 10 : 1. Hence *sulfur* [*7704-34-9*] is required in much lower quantities than N. Their functions are, however, similar. Sulfur is an elementary constituent of most proteins; the SH group in involved in various enzymatic processes and it is the reactive group of coenzyme A. Disulfide (S – S) bridges are essential structural elements in the tertiary structure of polypeptides and in many

Table 4. Relationship between N fertilizer rate and nitrogenous fractions in the dry matter of rye grass [9]

Nitrogen fertilizer rate, kg/ha	Nitrogenous fraction, g/kg			
	Total N	Protein N	Free amino acid N	NO_3^- and NO_2^- N
0	13.2	9.8	1.6	0.4
110	18.9	12.6	2.1	0.6
440	37.3	20.6	5.6	3.5

volatile S compounds, such as diallyl disulfide, which is the main component in garlic oil. Mustard oils occurring in many species of the Cruciferae contain a S-glycosidic bond and a sulfuryl group:



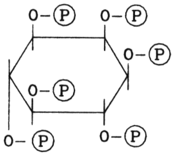
Insufficient S supply results in a decrease of growth rate with extremely low levels of SO_4^{2-} and high concentrations of free amino compounds and NO_3^- in the leaves, which is due to hampered protein synthesis. Sulfur plays an important role in the baking quality of wheat, since the concentration of S compounds in the gluten fraction is responsible for the linkages between the protein molecules [10]. Sulfur deficiency may also affect N_2 fixation of legumes by causing unfavorable conditions in the host plant or because of the relatively high S content of nitrogenase and ferredoxin [11]. Deficiency symptoms of S appear at first in the youngest leaves, which turn light green to yellow. Abundant supply with S results in an accumulation of sulfate in plant tissues.

Sulfur oxide can be taken up by the leaves and metabolized and thus can contribute to the S nutrition of plants. Too high SO_2 concentrations in the atmosphere may be toxic. The toxicity symptoms are necrotic spots in the leaves. According to SAALBACH [12], the critical SO_2 level in the atmosphere for annual plants is 120 $\mu g/m^3$. For trees and other perennials it is about half this level. The currently much discussed damage to trees in the forest of the Federal Republic of Germany (mainly spruce and silver fir) is not caused by toxic SO_2 levels.

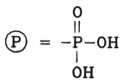
Phosphorus [*7723-14-0*] is an essential element in nucleic acids and various phospholipids (phosphoglyceride and phosphosphingolipids). In both cases. phosphate is esterified with sugars (nucleic acid) or with alcohol groups of glycerol or sphingosine. Phosphate is also present in various coenzymes; the most prominent is adenosine triphosphate (ATP), which carries a kind of universal energy that is used in a number of biochemical processes. Metabolites and enzymes can be activated by phosphorylation, a transfer of the phosphoryl group from ATP to the metabolite according to the following reactions:

Activation of glucose
Glucose + ATP $\longrightarrow$ Glucose-6-phosphate + ADP
Phosphorylation of an enzyme
Enzyme – OH + ATP $\longrightarrow$ Enzyme–OⓅ + ADP

Such reactions demonstrate the essential role of P not only in plant metabolism but also in all living organisms. Undersupply with P results in a reduced growth rate, and seed and fruit formation is affected. The leaves of P-deficient plants often show a gray dark green color; the stems may turn red. The P reserve in seeds is the Mg (Ca) salt of the inositol hexaphosphate (phytic acid):



Myo−inositol hexaphosphate



$$Ⓟ = -\overset{\displaystyle O}{\overset{\|}{\underset{\underset{\displaystyle OH}{|}}{P}}}-OH$$

Phosphoryl group

The physiological role of boron has remained obscure until now, and therefore various hypotheses with numerous modifications exist concerning the physiological and biochemical role of boron in higher plants. Depending on the pH of the soil, boron seems to be taken up mainly as undissociated boric acid or as the borate anion. Plant species differ in their boron uptake capacity, reflecting differences in boron requirements for growth. However, there is still some controversy about boron translocation in plants. At least in higher plants, a substantial proportion of the total boron content is complexed in the cell walls in in a *cis*-diol configuration [14]. According to Birnbaum et al. [13], B is involved in the synthesis of uracil and thus affects UTP formation. (UTP is an essential coenzyme for the synthesis of sucrose and cell-wall components.) Also the synthesis of ribonucleic acid is hampered in the case of B deficiency. Since uracil is an integral part of ribonucleic acid (RNA), the formation of RNA may also be related to the synthesis of uracil. Pollard et al. [15] suggest that B has a specific influence on plant membranes by the reaction of borate with polyhydroxy compounds.

Boron deficiency appears as abnormal or retarded growth of the apical growing points. The youngest leaves are misshapen and wrinkled and show a darkish blue-green color. The fact that B deficiency primarily affects the apex is in accord with the impaired synthesis of ribonucleic acids required for meristematic growth. High levels of available B in the soil may cause B toxicity in plants. This is mainly the case in arid areas; however, B toxicity can also be the consequence of industrial pollution [16]. The toxicity is characterized by yellow leaf tips followed by progressive necrosis. The leaves take on a scorched appearance and drop prematurely.

Silicon [*7440-21-3*] is not an essential element for plants; however, it has a beneficial effect on various plant species, mainly grasses [17]. In plants well supplied with Si, cuticular water losses are diminshed and resistance against fungal attack is improved [18]. The favorable effect of Si on rice growth is well known. Silicon-containing fertilizer is frequently applied in rice production.

Among the metal cation species, *the potassium* [*7440-09-7*] *ion*, K^+, is the nutrient plants take up from the nutrient medium at the highest rates. The K^+ concentration in the cytoplasm is about 100 mM and thus much higher than the concentration of other ion species [19]. Probably this high K^+ concentration has a favorable influence on the conformation of various enzyme proteins [20]. Potassium ions can easily penetrate plant membranes (see Section 2.4.1), which often leads to a depolarization of the membranes. Membrane depolarization, it is supposed, has a favorable effect on meristematic growth, photophosphorylation, aerobic phosphorylation, and phloem loading [21]. These basic processes are important for the long-distance transport of photosynthates, the synthesis of various organic compounds, and CO_2 assimilation.

The data in Table 5 show that with an increase of K^+ in alfalfa leaves (*Medicago sativa*), the CO_2 assimilation rate increased, while the mitochondrial respiration rate decreased [22]. In the case of low K, the respiration was about 2/3 of the CO_2 assimilation, while with high K the C gained by assimilation was about 11 times higher than the C lost by respiration. This typical behavior indicates that under the conditions of K^+ deficiency much of the stored carbohydrates must be respired in order to meet the ATP demand of the plant. Plants undersupplied with K^+ have therefore a low energy status. Such plants are highly susceptible to fungal attack, water stress, and frost damage.

Table 5. Relationship between K^+ concentration in the dry matter of alfalfa leaves, CO_2 assimilation, and mitochondrial respiration [22]

Concentration of K^+, mg/g	Carbon gain and loss, mg dm^{-2} h^{-1}	
	CO_2 assimilation	Mitochondrial respiration
13	11.9	7.56
20	21.7	3.34
38	34.0	3.06

Potassium is important in determining the osmotic pressure of plant fluids, and K^+-deficient plants are characterized by inefficient water use. Sodium ions may replace some K^+ functions, e.g., the less specific osmotic functions. Important counterions of K^+ in plant tissues are Cl^-, NO_3^-, and organic anions. The frequently observed favorable effect of Na^+ and Cl^- on plant growth is related to their osmotic functions.

Plants suffering from K^+ deficiency show a decrease in turgor, and under water stress they easily become flaccid. Plant growth is affected, and the older leaves show deficiency symptoms as necrosis beginning at the margins of tips and leaves. In K^+-deficient plant tissue, toxic amines such as putrescine and agmatine accumulate.

The most spectacular function of *magnesium* [*7439-95-4*] is its integral part in the chlorophyll molecule. Besides this function, Mg^{2+} is required in various other processes and, the Mg fixed in the chlorophyll molecule amounts only to about 20 % of the Mg present in green plant tissues. Magnesium is an essential ion in ribosomes and in the matrix of the cell nucleus. Here Mg^{2+} is bound by phosphate groups, since the Mg^{2+} is strongly electrophilic and thus attracts oxo complexes such as phosphate [23]. The magnesium ion activates numerous enzymatic reactions in which phosphate groups are involved. The activation is assumed to be brought about by bridging the phosphate group with the enzyme or with the substrate. This is an universal function of Mg^{2+} not only relevant for plant metabolism but also for practically all kinds of organisms.

Deficiency of Mg^{2+} affects chlorophyll synthesis: leaves turn yellow or red between the veins. The symptoms begin in the older leaves. Protein synthesis and CO_2 assimilation are depressed under Mg^{2+} deficiency conditions. Recent results [24] have shown that the yellowing of spruce needles in the Black Forest is due to a Mg^{2+} deficiency and can be cured by Mg^{2+} fertilizer application.

Calcium [*7440-70-2*] is the element of the apoplast (cell wall and "free space") and of biological membranes. Here it is adsorbed at the phosphate head groups of membrane lipids, thus stabilizing the membranes [25]. Most of the Ca^{2+} present in plant tissues is located in the apoplast and in the vacuole, some in the mitochondria and in the chloroplasts, while the cytoplasm is extremely low in Ca^{2+} (10^{-7} to 10^{-6}M). The maintenance of this low cytoplasmic Ca^{2+} concentration is of vital importance for the plant cell [26]. Higher cytoplasmic Ca^{2+} concentrations interfere with numerous enzymatic reactions and may even lead to a precipitation of inorganic phosphates. This low Ca^{2+} concentration suffices to form a complex with calmodulin, a polypeptide of 148 amino acids. The Ca – calmodulin complex is a universal enzyme activator. The activation is brought about by allosteric induction.

Direct Ca^{2+} deficiency in plants is rare, since most soils are relatively rich in Ca^{2+}. Physiological disorders as a consequence of an insufficient Ca^{2+} supply of particular plant parts, however, occur frequently. Calcium is mainly translocated by the transpiration stream. Hence plant parts such as fruits, which mainly feed from the phloem and less from the xylem sap, may suffer from an insufficient Ca^{2+} supply. Shear [27] cites a list of 35 such Ca^{2+}-related disorders in fruits and vegetables. Two of the most important ones involve storage tissues and result in poor crop qualities [28]: *bitter pit* in apples, characterized by small brown spots on the surface, and *blossom-end rot* in tomatoes, a cellular breakdown at the distal end of the fruit, which is then susceptible to fungal attack.

Manganese [*7439-96-5*] is an integral part of the superoxide dismutase and of the electron donor complex of photosystem II. Manganese may activate enzymes in the same way as Mg^{2+} by bridging the phosphate group with the enzyme or the substrate. Deficiency of Mn^{2+} leads to the breakdown of chloroplasts. Characteristic deficiency symptoms are smaller yellow spots on the leaves and interveinal chlorosis. Manganese toxicity may occur, especially on flooded soils, because of the reduction and thus solubilization of manganese oxides. Toxicity symptoms are generally characterized by brown spots of MnO_2 in the older leaves surrounded by chlorotic areas [29].

Iron [*7439-89-6*] is an essential element for haem and ferredoxin groups. Iron deficiency leads to chloroplast disorders; the synthesis of thylakoid membranes is disturbed and the photochemical activity affected [30]. Iron deficiency is characterized by yellow leaves. The symptoms are at first visible in the younger leaves. There is evidence that the deficiency, mainly occurring in plants growing on calcareous soils, is not induced by an insufficient Fe uptake from the soil but by a physiological disorder in leaves, affecting the Fe distribution in the leaf tissue [31].

Iron toxicity can be a problem under reducing soil conditions, which prevail in flooded soils. Under such conditions iron(III) oxides are reduced and the iron is rendered soluble. This may increase the Fe concentration in the soil solution by a factor of 10^2 to 10^3 [32] so that plants may suffer from Fe toxicity, characterized by tiny brown spots on the leaves, which later may turn uniformally brown. Iron toxicity is known as "bronzing."

Copper [*7440-50-8*] is an essential element of various enzymes, such as superoxide dismutase, polyphenol oxidases, plastocyanin of the photosynthetic transport chain, and cytochrome c oxidase, the terminal oxidase in the mitochondrial electron transport chain. Deficiency in Cu leads to pollen sterility and thus affects the fruiting of plants. Copper-deficient plants often are characterized by white twisted leaf tips and a tendency to become bushy.

Zinc [*7440-66-6*] is an integral part of carbonic anhydrase, superoxide dismutase, RNA polymerase, and various dehydrogenases. It is closely involved in the N metabolism of plants. In Zn-deficient plants, protein synthesis is hampered and free amino acids accumulate. There is evidence that Zn is involved in the synthesis of tryptophan, which is a precursor of indole acetic acid, an important phytohormone. Zinc deficiency is characterized by short internodes, small leaves, and chlorotic areas in the older leaves. Frequently the shoots die off and the leaves fall prematurely.

Molybdenum [*7439-98-7*] is present in the nitrate reductase and in the nitrogenase system that catalyzes the bacterial fixation (reduction) of dinitrogen. Deficiency of Mo frequently appears first in the middle and older leaves as a yellowish green coloration accompanied by a rolling of leaf margins. Cruciferae species are particularly susceptible to Mo deficiency. The most well-known Mo deficiency is the “whiptail” of cauliflower. For further information on the physiology of plant nutrition, see [3, 23, 33].

2.2. Soil Science

2.2.1. Soil Classes, Soil Types, and Parent Material

According to Schroeder [34], “soil is the transformation product of mineral and organic substances on the earth’s surface under the influence of environmental factors operating over a very long time and having defined organisation and morphology. It is the growing medium for higher plants and basis of life for animals and mankind. As a space-time system, soil is four dimensional.”

Soils are complex, quite heterogeneous, and may differ from each other considerably. Nevertheless, all soils have some common features. They possess a mineral, an organic, a liquid, and a gaseous component. In an ideal soil, the percentage proportions of these components are 45 %, 7 %, 23 %, and 25 %, respectively. The volumes of the liquid and gaseous components may change quickly. For example, in a water-saturated soil all pores are filled with water, and in a dry soil the soil pore volume is almost completely filled with air. The mineral and organic components contain plant nutrients and adsorb plant nutrients at their surfaces, and they are therefore of importance for the storage and retention of plant nutrients. The liquid phase of the soil is the soil solution. It contains dissolved plant nutrients and is the medium for the translocation of plant nutrients from various soil sites towards the plant roots. The gaseous soil component is essential for gas exchange, especially for the supply of plant roots with oxygen and for the release of CO_2 from the soil medium into the atmosphere.

For the description, comparison, and assessment of soils, a grouping according to general criteria is indispensable. There are two main grouping systems for soils: (1) soil classes or soil texture and (2) soil types. *Textural classes* are defined according to the particle size of soils. *Soil types* relate to the parent material of soils, to the pedological genesis, and to typical properties evident in the soil profile i.e., the horizontal layers of soils, called soil horizons.

Soil Classes. *Soil particle sizes* as a main characteristic of soil classes are grouped into four major groups as shown in Table 6. The major groups (sand, silt, and clay) are subdivided into coarse, medium, fine. Designation of the soil texture (soil class) depends on the percentage proportions of the sand, silt, and clay fraction in the total fine earth, which is sand + silt + clay. Soils in which the sand fraction dominates are termed *sandy soils*, soils consisting mainly of silt and clay are *silty clays*, and soils which contain all three fractions in more or less equal amounts are called *loams*. In the German terminology, abbreviations for the fractions are used (S = sand, U = silt, T = clay, L = loam). For example, if the major fraction is silt (U) and the next sand (S), the abbreviation is sU = sandy silt. Figure 1 shows the designations of the various soil classes according to the percentage proportion of the three main particle fractions.

In the farmer’s practice, sandy soils are called light soils, soils rich in clay heavy soils. This distinction relates to the force required to work (plough, cultivate) a soil. Soils rich in clay, but also silty soils, tend to compaction when dried and hence are heavy to work.

Table 6. Particle size of soil fractions relating to soil texture

Diameter, mm	Designation	Abbrevation
> 2	pebbles, gravels	
0.06 – 2	sand	S
0.002 – 0.06	silt	U
< 0.002	clay	T

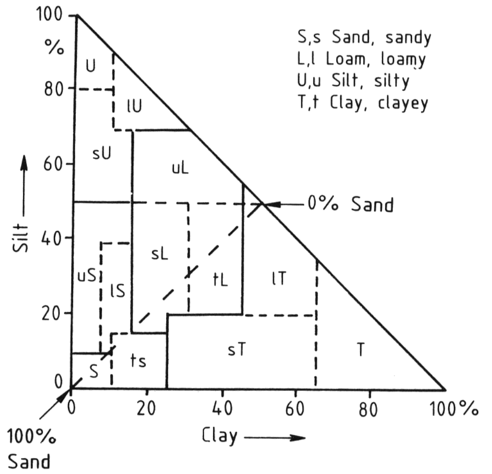


Figure 1. Diagram of soil textural classes, German system of SCHROEDER [34]
The vertical axis shows the percentage of silt, the horizontal the percentage of clay, and the dashed line the percentage of sand.

Although the grouping according to particle size is based on a physical factor, particle size is also associated with the chemical properties. This can be seen from Figure 2: the sand fraction consists mainly of quartz, which is a sterile material. Primary silicates (micas, feldspars) contain K, Ca, Mg, and other plant nutrients, which are released during the process of weathering. Clay minerals are less rich in plant nutrients than the primary silicates, but they possess large negatively charged surfaces that are of the utmost importance for the adsorption of plant nutrients and water.

The various soil particles form aggregates in which organic matter is also involved. This aggregation forming fine pores and holes in the soil is of relevance for soil structure. A good soil structure is characterized by a relatively high pore volume, ca. 50 % of the total soil volume. Soil structure depends much on the Ca saturation (see page 16). The richer the soil is in clay, the more important a good soil structure is.

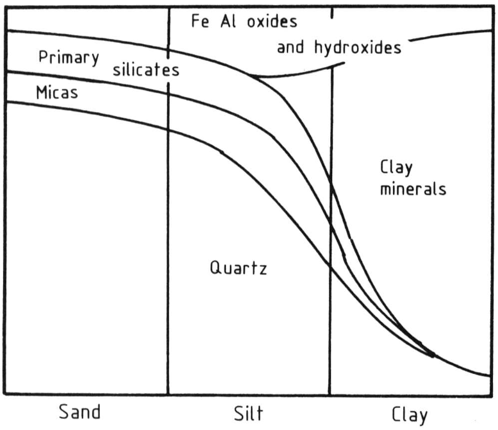


Figure 2. Mineral composition of the sand, silt, and clay fractions [34]

Soil Type. Soil type is related to the parent material from which a soil is developed and from the history of development, which is much influenced by climate and vegetation. Main groups of parent material are igneous rocks, sedimentary rocks, and metamorphic rocks. Also organic matter may be the main parent material. Content of plant nutrients, capacity to store plant nutrients, soil pH, and the rooting depth depend much on the parent material, but are also influenced by soil development.

In the following, a limited number of important soil types are considered according to the FAO World Soil Classification. Besides this system there are other systems, e.g., the U.S. Soil Taxonomy. The FAO classification comprises 26 classes.

A distinction can be made between young soils and old soils. The latter are generally highly weathered, their inorganic material consisting mainly of quartz and iron aluminum oxide hydroxides. Such soils are characterized by poor cation retention capacity (cation exchange capacity), low pH values, and a high phosphate fixing power. This soil type, called ferralsol, is frequent in the tropics, whereas in moderate climates highly weathered soils belong mainly to the podsols.

Young soils may be derived from the sedimentation of rivers and oceans (fluvisols) or from volcanic ash (andosols). These soils are generally rich in plant nutrients and thus form fertile soils. The most fertile soils belong to the black earths (chernozem). They are frequent in Russia, Central and East Europe as well as North America and are derived from loess. They are characterized by a neutral pH, by a well balanced content of clay and organic matter and by a deep rooting profile. They are naturally rich in plant nutrients and possess a high nutrient storage capacity. Soils in which the parent material loess is more weathered as compared with the chernozems belong to the luvisols. This soil type is common in Germany, Austria, and France where it represents the most fertile arable land. Gleysols are soils with a high water table, rendzinas are shallow soils derived from limestone, histosols are rich in only partially decomposed organic matter.

Under arid conditions salt may accumulate in the top soil layer. Solonchaks (white alkali soils) are saline soils with a pH of ca. 8 and with neutral anions as the most important anion component. Solonetz soils (black alkali soils) possess bicarbonate and carbonate as major anion component. Their pH is in the range 8 – 10. Crop growth on saline soils is extremely poor, and in many cases only a salt flora can grow under such conditions. This is particularly true for the solonetz soils.

For further information on soil texture and soil types, see [34 – 37], and the Soil Taxonomy of the Soil Conservation Service of U.S. Department of Agriculture [38].

2.2.2. Nutrient Retention in Soils

Nutrient retention is an important characteristic of fertile soil.

Cation Exchange. Cations are retained on soil colloids having a negative charge: the cations are bound at the surface of these particles by Coulomb forces. The most important cation species are Ca^{2+}, Mg^{2+}, K^+, Na^+, Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$, and H^+. This is represented in Figure 3. A distinction can be made between inorganic and organic soil colloids capable of cation adsorption. Inorganic particles belonging to the clay fraction are known as *secondary clay minerals* because they are mainly derived by weathering of primary minerals such as orthoclase, plagioclase, and particularly mica. Organic soil colloids capable of cation adsorption belong to the *humic acids*. The negative charge of the inorganic soil colloids originates from the so-called isomorphic substitution and from deprotonation. Isomorphic substitution is the replacement of Si^{4+} in the crystal lattice by Al^{3+}, Fe^{2+}, or Mg^{2+}, thus leading to a surplus of negative charge, because the anionic groups of the lattice are not completely balanced by Al^{3+}, Fe^{2+}, or Mg^{2+}. Such a negative charge is a permanent charge, in contrast to labile charges that result from deprotonation. Labile charges are typical for organic colloids (humic acids): carboxylic groups and acid hydroxylic groups of phenols may be protonated or not depending on the pH of the environment.

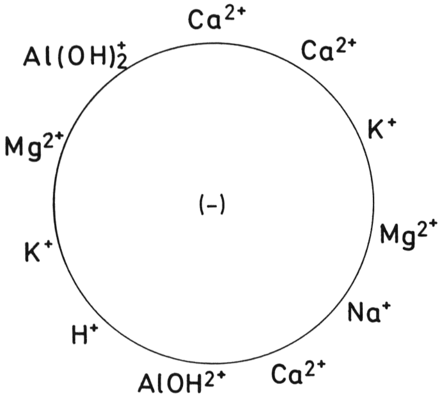


Figure 3. Schematic presentation of cations adsorbed to the negatively charged surface of a soil colloid

The secondary clay minerals are grouped into 1 : 1 clay minerals, in which a Si layer alternates with an Al layer, and 2 : 1 clay minerals, in which an Al layer is sandwiched by two Si layers. The most important representatives of the 1 : 1 clay minerals are the kaolinites. The 2 : 1 secondary clay minerals comprise the illite, transitional minerals, vermiculite, chlorite, and smectites (→ Clays). Most of these 2 : 1 clay minerals possess inner surfaces. They are therefore characterized by a high cation retention (= cation exchange) capacity.

These negatively charged soil colloids, often also called sorption complexes, function like a *cation exchanger*. Adsorbed cations can be replaced by other cation species. The cation exchange is stoichiometric. Adsorption and desorption depend on the concentrations of the cation species in the surrounding solution. If a soil colloid completely saturated by K^+ is exposed to increasing Ca^{2+} concentrations, for example, adsorbed K^+ is more and more replaced by Ca^{2+} until eventually the sorption complex is completely saturated by Ca^{2+} (Fig. 4). In soils, such exchange and equilibrium reactions are complex as numerous cation species and sorption complexes with differing preferences for particular cation species are involved. The principle, however, is that cations adsorbed by Coulomb forces at soil colloids equilibrate with free cations in the soil solution. Thus adding cations to a soil by fertilization, e.g., the application of a potassium salt, results in replacing adsorbed cations with the newly added cations until a new equilibrium is reached. The adsorbed cations are protected against leaching. but they are available to plant roots. The strength of cation adsorption increases with the the charge of the cation species and with the thinness of the hydration shell. Provided that there are no specific adsorption sites, the strength of cation adsorption follows Hofmeister's cation sequence:

$$Ca^{2+} > Mg^{2+} > K^+ > Na^+$$

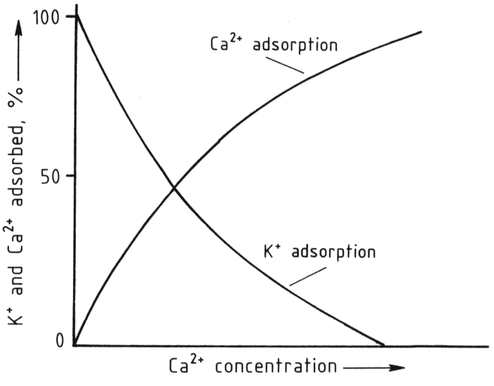


Figure 4. Ca^{2+} – K^+ exchange, K^+ desorption brought about by increasing Ca^{2+} concentration

At equilibrium, cation-exchange reactions are a helpful tool for predicting the distribution of ions between the adsorbed and solution phases of the soil as the amounts of cations present are changed. When a soil saturated with potassium is placed in a NaCl solution, the following equilibration occurs:

$$K_{soil} + NaCl \rightleftharpoons Na_{soil} + KCl$$

The exchange equation for this reaction is

$$\frac{[Na]\,(K)}{[K]\,(Na)} = k_1$$

Brackets refer to ions on the exchange site and parenthesis to the activity of ions in the solution. Since the proportionate strength of adsorption of the ions varies with the exchange site, values for k_1 differ for different exchange materials.

The divalent/monovalent system, which almost represents the situation in the soil, with K^+, Ca^{2+}, and Mg^{2+} as the dominant exchangeable cations, is more complex. The following equation, developed by GAPON [39], is widely used to describe monovalent/divalent exchange:

$$\frac{[K]\,(Ca)^{1/2}}{[Ca]\,(K)} = k_1$$

Cation exchange capacity (CEC) is defined as the quantity of cation equivalents adsorbed per unit soil or clay mineral. In Table 7 the exchange capacities of some soil classes are shown. The exchange capacity of the organic soil appears high if it is based on unit weight of soil. A more realistic picture is obtained, however, when the exchange capacity is based on soil volume, since under field conditions it is soil volume, not soil weight, that is related to a crop stand. Table 8 shows the cation exchange capacities of some important clay minerals and of humic acids in relation to the surface of these particles.

The cation exchange capacity of kaolinites and particularly of humic acids depends much on the pH of the medium. At low pH, most groups are protonated and hence the exchange capacity is low. Increasing soil pH, e.g., by liming, increases the cation exchange capacity if kaolinites and humic acids are the dominating exchange complexes.

Cation saturation of negatively charged soil colloids has some impact on soil structure, which is defined as the arrangement of soil particles

Table 7. Cation exchange capacity based on soil weight and soil volume as well as the specific weight of some soil classes

Soil class	Specific weight, kg/L	Cation exchange capacity *	
		cmol/kg	cmol/L
Sandy soil	1.5	3	4.5
Loam	1.5	15	22.5
Clay soil	1.5	30	45.0
Organic soil	0.3	75	22.5

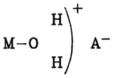
* cmol = centimole.

Table 8. Cation exchange capacity and inner and outer surfaces of some soil colloids

	Total surface, m^2/g	Inner surface, %	Cation exchange capacity, mol/kg
Kaolinite	20	0	10
Illite	100	0	30
Smectite	800	90	100
Humic acids	800	0	200

into aggregates. High percentage of adsorbed Ca^{2+} favors the formation of aggregates. In well structured soils, such as in chernozems, 70 to 80 % of the total cation exchange capacity is occupied by Ca^{2+}. In acid solids, H^+ and Al cations (Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$) and in saline soils Na^+ and Mg^{2+} are the dominating cation species adsorbed to soil colloids.

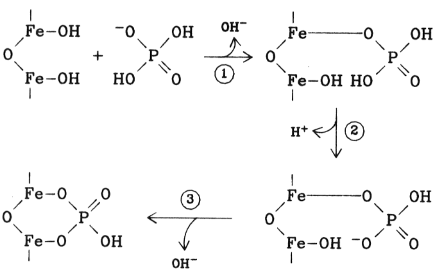
Anion Exchange. Soil particles may also adsorb anions. The adsorption occurs at the OH groups of aluminum and iron oxides as well as of some clay minerals. One may distinguish between a nonspecific adsorption and a specific anion adsorption. The nonspecific anion (A^-) adsorption originates from protonated hydroxylic groups.



$$M{-}O\left.\begin{matrix}H\\H\end{matrix}\right)^{+} A^-$$

Protonation depends on soil pH and is particularly high under acid conditions. Hence nonspecific anion adsorption only plays a role in acid soils.

The specific anion adsorption is a ligand exchange. This is, for example, the case for phosphate. In step 1 $H_2PO_4^-$ replaces OH^-, resulting in a *mononuclear bond* between the phosphate and the iron oxide. In step 2, a further deprotonation of the phosphate occurs, followed by a second ligand exchange (step 3) to form a *binuclear bond* between the surface of the iron oxide and the phosphate.



The final structure is supposed to be very stable, and the phosphate so bound is hardly available to plant roots. This reaction sequence explains why anion (phosphate) adsorption is promoted under low pH conditions. In mineral soils with pH < 7, the adsorbed phosphate represents a major phosphate fraction. Increasing the soil pH, e.g., by liming, increases phosphate availability [40]. The relationship between free and adsorbed anions can be approximately described by the Langmuir equation:

$$A = A_{\max}\frac{kc}{1+kc}$$

A = surface concentration of adsorbed anions
$A_{\max}$ = maximum surface concentration
c = concentration of free anion
k = constant related to adsorption energy, the adsorption strength increasing with k

Adsorption strength depends also on anion species decreasing in the order [41]:

$$\text{phosphate} > \text{arsenate} > \text{selenite} = \text{molybdate} > \text{sulfate} = \text{fluoride} > \text{chloride} > \text{nitrate}$$

Borate and silicate may also be adsorbed, but only at high pH. Under these conditions, boric acid and silicic acid may form anions according to the following equations:

$$H_3BO_3+H_2O \rightarrow B(OH)_4^-+H^+$$

$$H_2SiO_3+H_2O \rightarrow H_3SiO_4^-+H^+$$

This is why in neutral to alkaline soils boron can be strongly adsorbed (fixed) by soil particles, which may lead to boron deficiency in plants. The formation of a silicate anion can improve phosphate availability since $H_3SiO_4^-$ and phosphates compete for the same ligands at anion-adsorbing surfaces.

2.2.3. Soil pH, Buffer Power, and Liming

Proton concentration (pH) is of vital importance for all living organisms and also has an impact on soils and soil constituents. High H^+ concentrations ($pH<4$) attack soil minerals, dissolving metal cations out of the crystal lattice, and eventually lead to mineral degradation. Under low soil pH conditions ($pH<5$), bacterial life is suppressed while fungal life is relatively favored, which affects the decomposition of organic matter. Low soil pH ($pH < 4$) also affects root growth.

In many cases, however, it is not so much the H^+ but the toxic level of soluble Al species and Mn^{2+} associated with low pH conditions that considerably hamper root development and plant growth. A decrease in soil pH increases the solubility of aluminum oxide hydroxides and maganese oxides considerably. Under acid soil conditions Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$ are dissolved in the soil solution or adsorbed to soil colloids. Of the three Al species, $Al(OH)^{2+}$ is considered to be the most toxic. *Aluminum toxicity* of plants is characterized by poor root growth: root tips and lateral roots become thickened and turn brown [42]. In the cell, Al interferes with the phosphate turnover and may even be adsorbed on the DNA double helix.

A distinction is made between the *actual acidity*, which is determined by the H^+ concentration in the soil solution, and the *potential acidity*, which is determined by both the H^+ of the soil solution and the adsorbed H^+. The actual acidity is measured by hydrogen-ion electrodes; the potential acidity, by titration with a base. Titration includes the Al species, which also consume OH^-

$$Al^{3+}+OH^- \rightarrow Al(OH)^{2+}$$

$$Al(OH)^{2+}+OH^- \rightarrow Al(OH)_2^+$$

$$Al(OH)_2^++OH^- \rightarrow Al(OH)_3 \text{ (gibbsite)}$$

Potential acidity may be high in Al-rich soils as well as in soils with a high cation exchange capacity. Such soils are characterized by a high *hydrogen-ion buffer power*: a pH change in the soil solution requires a relatively large amount of H^+ or OH^-.

In soils, different buffer power systems can be distinguished. Soils containing carbonates are buffered according to the following equation:

$$CaCO_3+2\,H^+ \rightarrow Ca^{2+}+H_2O+CO_2$$

Reaction may be promoted by the presence of CO_2 originating from root and microbial respiration.

$$CaCO_3+CO_2+H_2O \rightarrow Ca(HCO_3)_2$$

$$Ca(HCO_3)_2+2\,H^+ \rightarrow Ca^{2+}+2\,H_2O+2\,CO_2$$

At lower pH levels soils are buffered by adsorbed cations (Fig. 5) and by Al complexes, e.g.,

$$Al(OH)_3+H^+ \rightarrow Al(OH_2)^++H_2O$$

Soil acidification results from different processes. Plant roots extrude H^+; net release of H^+ is especially high when plants are fed with NH_4^+, while NO_3^- nutrition results in a net release of OH^-. Leguminous species living in symbiosis with *Rhizobium* extrude H^+ at particularly high rates from their roots. Microbial oxidation of organic N, organic S, and elementary S leads to the formation of strong acids, such as HNO_3 and H_2SO_4, which have a marked acidifying effect on soils. Also SO_2 and NO_x as gases as well as the acid rain formed by these oxides have an acidifying effect. In Central Europe these pollutants carry ca. 3 – 5 kmol H^+ $ha^{-1}a^{-1}$ into soils.

Under anaerobic soil conditions, e.g., after flooding, protons are consumed by the reduction of Fe^{III} and Mn^{III} or Mn^{IV} as well as by the microbial reduction of NO_3^- (denitrification):

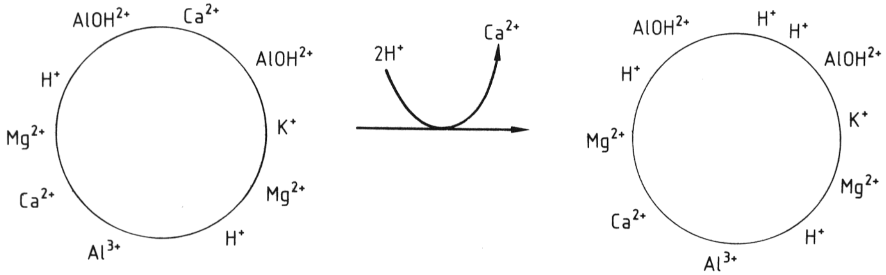


Figure 5. Principle of hydrogen-ion buffering by adsorbed cations

$$2\,NO_3^- + 10\,e^- + 12\,H^+ \rightarrow N_2 + 6\,H_2O$$

Some species of *Azalea, Calluna*, *Vaccinium*, and also tea (*Camellia sinensis*) are able to grow on acid habitats. These species can mask the Al with phenols and organic acids and thus avoid Al toxicity. Rye, potatoes, oats, and lupines tolerate weakly acid soils, whereas beets (*Beta vulgaris*), barley, rape, and most leguminous crops prefer more neutral soils. Wheat takes an intermediary position with regard to soil pH. In the case of leguminous crops, it is not so much the crop itself, rather it is the *Rhizobium* bacteria living in symbiosis with the crop that are affected by low soil pH. The mulitplication of the *Rhizobium* in the soil is depressed by soil acidity.

Low pH levels can be easily overcome by *liming*, the application of alkaline materials, mainly Ca/Mg oxides, carbonates, and silicates. They react with soil acidity as follows:

$$CaO + 2\,H^+ \rightarrow Ca^{2+} + H_2O$$

$$CaCO_3 + 2\,H^+ \rightarrow H_2O + CO_2 + Ca^{2+}$$

$$CaSiO_3 + 2\,H^+ \rightarrow H_2O + SiO_2 + Ca^{2+}$$

The quantity of lime required depends on the soil pH level and the buffer power. The lower the pH and the higher the buffer power, the more lime required.

Soil acidity is mainly a problem in humid zones, where the H^+ formed in the upper soil layer replaces the adsorbed metal cations (Ca^{2+}, Mg^{2+}, K^+), which are then leached. Under arid conditions, salts may accumulate in the top soil layer. If a major part of the anions accumulated are HCO_3^- and CO_3^{2-} (solonetz soils), high soil pH levels prevail, which affect plant growth and soil structure considerably. Such soils can be meliorated by heavy applications of elementary sulfur. Under aerobic conditions the S is oxidized to H_2SO_4 by soil microorganisms. The strong acid neutralizes the HCO_3^- and CO_3^{2-}

$$H_2SO_4 + 2\,HCO_3^- \rightarrow 2\,H_2CO_3 + SO_4^{2-} \rightarrow 2\,H_2O + 2\,CO_2 + SO_4^{2-}$$

$$H_2SO_4 + CO_3^{2-} \rightarrow SO_4^{2-} + H_2CO_3 \rightarrow H_2O + CO_2 + SO_4^{2-}$$

2.2.4. Soil Water – Plant Relationships

Plants continuously require water that is taken up from the soil by roots and transported from them to the upper plant parts, particularly to the leaves. From here water is released into the atmosphere. This last process is called *transpiration*. Water in the plant tissues is required to maintain optimum cell turgor, which is crucial for most metabolic processes.

Plants frequently have to overcome long dry periods during which they must feed from the soil water. Very crudely, the soil can be considered as a sponge that can store water in its pores and holes. The storage water in the soil must be retained against gravitation. The forces responsible for this retention are adsorption and capillary forces by which the water is sucked to the surface of the soil particles. This suction force can be considered as a negative pressure, and hence the strength of water binding in soils is measured in Pascals (Pa), the unit for pressure. The strength of water binding in soils is termed *water potential* (in older terminology, water tension). The higher the strength, the lower (more negative) the soil water potential. Water potentials in soils range from 0 to -1×10^6 kPa. Generally, however, soil water potentials of -10 to -1500 kPa prevail.

The total amount of water that can be adsorbed by a soil (all pores and holes filled with water) is called maximum water capacity. This is of minor importance; more relevant is the water quantity that can be retained against the gravitation force, the *field capacity*. Not all water of the field capacity fraction is available to plant roots. A proportion of the field capacity water is so strongly adsorbed that it can not be taken up by the roots. For most plant species this is water with a water potential < -1500 kPa: at such a low water potential, plants wilt. Therefore, this critical water potential is also called *wilting point*. The soil water fraction not available to plants is called *dead water*. The *available soil water* thus equals the difference between the field capacity and dead water.

Soils differ much in their capacity to store water. The higher the clay content of a soil, the larger the total surface of soil particles, and the more water that can be adsorbed. The water storage capacity of soils increases with the clay content. On the other hand, the water molecules are strongly adsorbed to the surface of clays and therefore the fraction of dead water increases with the clay content. For this reason, generally medium textured soils (loamy soils), and not the clay soils, possess the highest storage capacity for available soil water. Besides soil texture, also soil structure and the rooting depth of the soil profile determine the storage capacity for available soil water.

An important criterion of available soil water is the relationship between the percent water saturation of the soil and the water potential. This is shown in Figure 6 for a sandy, a loamy, and a clay soil. The section between field capacity (-10 kPa) and the wilting point (-1500 kPa) is the highest for the loamy soil.

The capability to use soil water economically differs considerably among plant species. A measure of this capability is the transpiration coefficient, the water quantity in kg (or L) required for the production of 1 kg plant dry matter:

Sorghum	277
Maize	349
Sugar beet	443
Spring wheat	491
Barley	527
Potatoes	575
Oats	583
Spring rye	634
Red clover	698
Flax	783
Alfalfa	844

Water loss under a vegetation cover results from evaporation (water release from the soil to the atmosphere) and transpiration (water release of the plant to the atmosphere). Evaporation is unproductive, transpiration productive. The relation between the two depends on plant nutrition, as can be seen in Table 9, which shows the favorable effect of N fertilizer on the productive use of soil water [43].

2.2.5. Organic Matter of Soils and Nitrogen Turnover

Organic matter of soils differs considerably. Soils can be classified according to the content of organic carbon in the soil (g/kg):

Low	<5
Medium low	5 – 10
Medium	10 – 20
High	20 – 40
Rich	40 – 80
Muck	80 – 150
Peat	>150

Soils with an organic carbon content of 50 g/kg are termed organic soils, in contrast to mineral soils. Enrichment of organic matter in soils depends on location and climatic conditions. Low temperature and a lack of oxygen favor the accumulation of organic matter in soils because these conditions hamper breakdown by soil microbes. Therefore, under cold continental climate conditions (frost, long winters) and under hydromorphic soil conditions (swamps, moors, bogs), organic matter accumulates.

The fertility status of organic soils differs considerably. Moors located on the tops of mountains are generally poor in nutrients, especially in N and K, since they are fed mainly from rain. Moors in lowland fed from rivers and streams may be rich in plant nutrients, especially

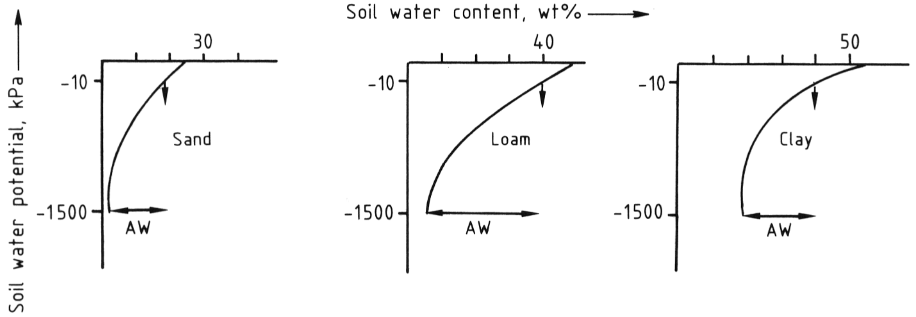


Figure 6. Relationship between the soil water content and the soil water potential and the resulting available water (AW) for three soil classes
Field capacity is −10 kPa; wilting point is − 1500 kPa.

Table 9. Relationship between N fertilizer rate, grain yield of barley, evaporation, and transpiration [43]

Nitrogen fertilizer rate, kg/ha	Grain yield, t/ha	Transpiration, * L/m^2	Evaporation,* L/m^2
30	1.02	85	235
125	1.65	121	278
225	2.69	217	212

* Transpiration and evaporation in liters per square meter of soil surface.

in N. The C : N ratio of the organic matter and soil pH are suitable indicators of the fertility status. Fertile soils possess C : N ratios of ca. 20 in their organic matter and pH values in the weak acid to weak alkaline range. Acid organic soils (highland moors) have much higher C : N ratios, ca. 50 or more in their organic matter. The C : N ratio has direct impact on the decomposition of organic N by soil microbes; the higher the ratio the lower the net release of mineral N by microbial activity.

Nitrogen turnover in soils is related not only to biological processes but also to physicochemical processes. In addition, there is a rapid exchange of N between the biosphere, the soil, and the atmosphere. The main processes of this nitrogen cycle are shown in Figure 7. Inorganic nitrogen, mainly NO_3^- and NH_4^+, including fertilizer N, can be easily assimilated by higher plants as well as by microbes (fungi, bacteria). Also dinitrogen (the N_2 of the atmosphere) can be reduced to NH_3 by some soil bacteria. The N_2 fixation capacity of the so-called free living bacteria, mainly species of *Azotobacter, Beijerinckia, Azospirillum,* and some species of the Cyanobacteria (*Anabaena, Nostoc, Rivularia*) is moderate, amounting to ca. 5 – 50 kg ha^{-1}a^{-1}. Symbiontic N_2-fixing bacteria, mainly species of *Rhizobium* and *Actinomyces*, have a fixation capacity about 10 times higher: for pulses (grain legumes) 50 – 100 kg/ha per growth period and for forage legumes even 200 – 500 kg ha^{-1}a^{-1}. They are of utmost importance in the N turnover and N availability in soils.

Inorganic nitrogen (N_2, NH_4^+, NO_3^-) assimilated by living organisms is mainly used for the synthesis of proteins, amino sugars, and nucleic acids. As soon as these organisms die, the organic N can be attacked by other microorganisms, which are able to convert the organic N into an inorganic form, a process called nitrogen mineralization. This starts with ammonification, and under aerobic conditions and favorable soil pH ammonification is followed by nitrification in the sequence:

$$\text{Organic N} \rightarrow NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$$

Ammonification is carried out by a broad spectrum of heterotrophic organisms; nitrification only by a small number of autotrophic bacteria [44]. The microbial oxidation of NH_4^+ to NO_2^- and NO_2^- to NO_3^- requires oxygen and hence proceeds only under aerobic conditions. The oxidation of NH_4^+ to NO_2^- is brought about by species of *Nitrosomonas, Nitrosolobus,* and *Nitrospira*, oxidation of NO_2^- to NO_3^- by species of *Nitrobacter*. They all require weak acid to neutral soil conditions; in acid soils nitrification is more or less blocked.

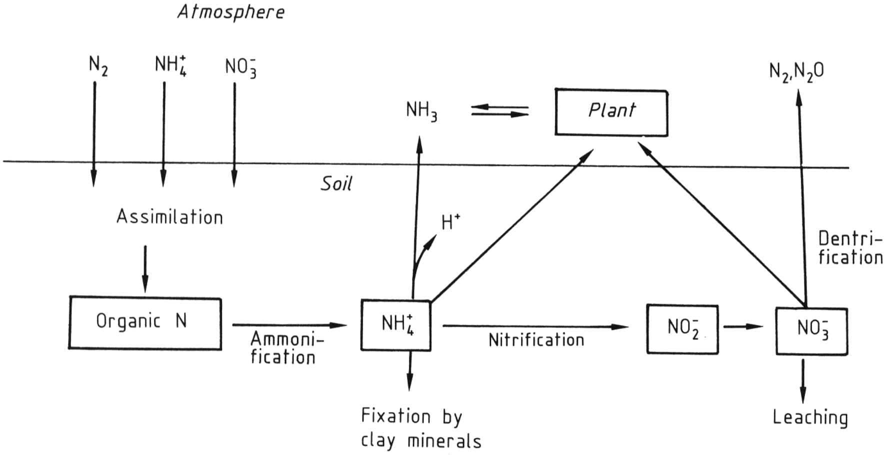


Figure 7. N cycle in nature. Transfer of N between soil, plant, and atmosphere

Ammonium ions produced by microbial breakdown of organic N, including urea, as well as NH_4^+ fertilizer can also be fixed by 2 : 1 clay minerals. In this form, NH_4^+ is protected against nitrification and leaching, but, depending on the type of clay minerals, may still be available to plant roots [45]. This fixed NH_4^+ fraction is of major significance for plant nutrition in soils derived from loess.

The concentration of ammonium ion in the soil solution is governed by the equilibrium

$$NH_4^+ \rightleftharpoons NH_3 + H^+ pK = 9.25$$

At pH < 6, there is virtually no NH_3 present; with an increase in pH the deprotonation of NH_4^+ increases, and so does the risk of NH_3 loss by volatilization. In alkaline and calcareous soils considerable amounts of N can thus be lost by the soil system [46]. High losses of NH_3 may also occur from the application of slurries, which generally have an alkaline pH [47].

Ammonium as well as NO_3^- are taken up by plant roots at high rates, and vigorous crop stands can deplete the NO_3^- concentration in the soil to a great extent. Nitrate is very mobile in soils since it is virtually unadsorbed on soil colloids. It can be leached by rainfall to deeper soil layers or even into the ground water (see Section 2.5.1). Nitrate losses may also occur under anaerobic soil conditions, for some bacterial species are able to use the oxygen of the NO_3^- as e^- acceptor for respiration. Nitrate is thus reduced to volatile NO, N_2O, and N_2 [49]:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO_{(g)} \rightarrow N_2O_{(g)} \rightarrow N_{2(g)}$$

This process, brought about mainly by species of *Pseudomonas*, *Alcalignes*, *Azospirillum*, *Rhizobium*, and *Tropionibacterium*, is called denitrification. It may cause considerable soil N losses particularly in flooded rice soils, in which anaerobic conditions prevail [50].

Loss of NO_3^- by leaching or denitrification can be reduced by blocking the NO_2^- formation by application of nitrification inhibitors such as Nitrapyrin (2-chloro-6-trichloromethylpyridine), AM (2-amino-4-chloro-6-trimethylpyrimidine), or terrazole (5-ethoxy-3-trichloromethyl-1,2,4-thiadizole). There are also some natural compounds that are nitrification inhibitors [51]. The most important is neem, which occurs in the seeds of *Azadirachta indica*, a tree common in the tropics.

Some of the organic N in the soil may be incorporated into a very stable organic form. This nitrogen, which mainly occurs in humic acids, is hardly mineralized. In most soils the humus-N fraction is by far the largest, comprising 80 – 90 % of the total soil N. It is of great importance for soil structure, but has hardly any relevance as a nutrient reserve.

The fraction of hydrolyzable soil N can be mineralized and thus may serve as a source for N absorbed by plants. The most important fraction in this respect is the N of the biomass, which comprises ca. 40 – 200 kg/ha, thus only a small fraction of total soil N, which may be 2000 – 8000 kg/ha in arable soils.

2.3. Nutrient Availability

2.3.1. Factors and Processes

From the total amount of N present in the soil, only a small proportion can be made available for plants (see above). This is also true for other plant nutrients. For example, in a clay-rich soil ca. 200 000 kg K^+ may be present in 1 ha within the rooting depth of 80 – 100 cm, but only 1 % may be available to plant roots.

Plant nutrient availability depends on physicochemical and biological factors. A young root pushing into a soil directly contacts only a small amount of macronutrients, which would contribute only a few percent of the total nutrient demand. By far the greatest proportion of nutrients (NO_3^-, NH_4^+, K^+, Ca^{2+}, Mg^{2+}) required by the plant must be transported towards the plant roots. This transport can be brought about by mass flow and/or diffusion. In *mass flow*, the nutrients are moved with the water flow from the soil towards the roots. Therefore mass flow depends much on water uptake and transpiration conditions. At zero transpiration (100 % relative humidity, rainy, or foggy weather) mass flow is also zero. Mass flow plays a major role for the transport of Ca^{2+}, Mg^{2+}, and also for NO_3^- in cases where the NO_3^- concentration of the soil solution is high, e.g., after fertilizer application.

Nutrients that are taken up at high rates by plant roots (K^+, NH_4^+; NO_3^-, phosphate) but that have relatively low total concentration in the soil solution are mainly transported by *diffusion*. Uptake of nutrients by roots decreases the nutrient concentration near the root surface and establishes a concentration gradient, which drives the diffusive flux of nutrients from the soil towards the plant roots. Absorbing roots thus act as a sink for plant nutrients. Typical depletion profiles are shown in Figure 8 for phosphate [52]. Phosphate and K^+ concentrations in the soil solution at the root surface may be as low as 1 μM, whereas in the bulk soil solution concentrations of 50 to 300 μM phosphate and 500 to 1000 μM K^+ may prevail. Fertilizer application increases the nutrient concentration of the soil solution and hence the concentration gradient that drives the nutrients towards the roots. Therefore, the level of the nutrient concentration in the bulk soil solution is an important factor of nutrient availability.

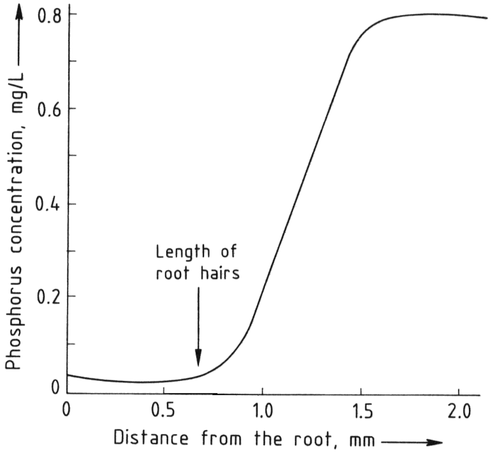


Figure 8. Phosphate depletion around a corn root: P concentration in the soil solution as a function of the distance from the root surface [52]

Diffusive flux and mass flow in the soil depend much on soil moisture. The dryer a soil, the smaller the water cross section (the size of soil pores that are still filled with water) and the more the nutrient flux is hampered. Therefore, soil moisture is another important factor of nutrient availability [53]. A third important factor of nutrient availability is the *nutrient buffer power* of a soil, a factor of particular relevance for phosphate, K^+, and NH_4^+. Here buffer power means the capability of a soil to maintain the nutrient concentration level in the soil solution (in analogy to the hydrogen-ion buffer power, see Section 2.2.3). In well-buffered soils nutrients absorbed from the soil solution by roots are replenished by nutrient desorption, e.g., by cation exchange.

The most important biological factor for nutrient availability is root growth [54]. For most plant nutrients, only the soil volume around the root can be exploited by the plant. For phosphate the depletion zone extends only a few millimeter from the root surface and depends much on the length of root hairs, as can be seen from Figure 8. For K^+ and NH_4^+, the depletion zone is more extended, ca. 1 – 4 cm from the root surface. Root mass, root length, and root hairs therefore are of great importance for the portion of soil volume that can be exploited by a crop stand.

Roots excrete organic materials such as organic acids, sugars, and slimes from which bacteria feed. As a result, the bacterial colonization in the rhizosphere (the volume around the root) is much denser than in the soil apart from the roots. These bacteria are involved in the N turnover, e.g., for the N_2 fixation of free-living bacteria and for denitrifying bacteria [55].

Proton excretion of roots affects bacterial activity in the rhizosphere, the dissolution of calcium phosphates, and the cation exchange. Net proton release of plant roots is strongly affected by the type of N supply. Ammonium nutrition results in a high net release of H^+, nitrate nutrition in release of OH^- and HCO_3^-. Leguminous species living in symbiosis with *Rhizobium* are known for a high H^+ release by roots and therefore have a strong acidifying effect on soils.

Nutrient deficiency, e.g., phosphate or Fe deficiency, also increases net release of H^+, which may contribute to the dissolution of iron oxides and calcium phosphates. The release of avenic acid and mugineic acid by plant roots is of particular importance for the mobilization of Fe in the rhizosphere [56].

Plant growth may be enhanced after infection with mycorrhizal fungi, which leads to increased nutrient uptake due to increases in the effective absorptive surface of the root, mobilization of sparingly available nutrient sources, or excretion of ectoenzymes or chelating compounds. Furthermore, mycorrhizal fungi may protect roots from soil pathogens [57] and and in this way enhance root growth and nutrient acquisition of the host plant. This is particularly important when considering the nutrition of plants with immobile nutrients such as phosphorus, as fungal hyphae are known to absorb P and translocate it into the host plant [58].

2.3.2. Determination of Available Plant Nutrients in Soils

The level of available plant nutrients in soils can be assessed by means of plant analysis and soil analysis. In the case of *plant analysis*, the nutrient content of a particular plant organ at a certain physiological stage may reflect the nutritional status of the plant, hence also the nutrient status of the soils [59]. Such diagnostic plant analysis is particularly common for perennial crops, including fruit trees and forest trees.

In *soil analysis*, soil samples are extracted with special extractants. The quantity of nutrients extracted reflects the level of available nutrients in the soil. Numerous soil extractants have been developed. In Central Europe the DL method (double lactate method) and the CAL method (calcium acetate lactate method) are widely used for the determination of available soil K and P. In the Netherlands, available P is extracted by water (P-water method). In the United States, the Olsen method (extraction with $NH_4F + HCl$) is used for the determination of available soil phosphate [60]. Ion-exchange resins are also useful tools for the determination of available plant nutrients [61].

Of particular interest is the determination of available soil N early in spring before the first application of N fertilizer. Mineral N (NO_3^-, exchangeable NH_4^+) is extracted with a $CaCl_2$ or K_2SO_4 solution [62]. This technique, called the N_{min} method, provides reliable information on the level of directly available soil N. The easily mineralizable N in the soil, which frequently is the important fraction for the release of available N during the growth period, is not obtained by the N_{min} method.

Electro-ultrafiltration (EUF method) has been used for the determination of available soil nutrients [63]. This method uses an electric field to separate nutrient fractions from a soil suspension. Most plant nutrients can be extracted. The advantage of this method is that, besides inorganic nitrogen, the readily mineralizable organic N fraction is extracted [64].

In the last decade S has attracted interest as a plant nutrient. Numerous procedures have been proposed for the determination of plant-available S in soils. The procedures include extraction with water, various salts and acids, and S mineralization by incubation [65].

The relationship between soil analysis data and the response of crops to fertilizer application is not always satisfying since other factors may interfere, such as rooting depth, root morphology, soil moisture, and particularly the clay content. These factors should be taken into consideration in interpreting soil test data.

2.4. Physiology of Plant Nutrition

2.4.1. Nutrient Uptake and Long-Distance Transport in Plants

Oxygen and CO_2 are mainly taken up by aboveground plant parts. The process of uptake is a diffusion of CO_2 and O_2 into the plant tissue. For the entry of these gases into the plant, the stomata are of major importance. Water and other plants nutrients are mainly absorbed from the soil solution. The rate of nutrient uptake increases with the concentration of the particular nutrient in the soil solution, the rate of uptake leveling off at higher soil-solution concentrations.

Plant nutrients in the soil solution, mainly present in ionic form, diffuse into the root tissue. The outer plasma membrane of the cells (plasmalemma) is a great diffusion barrier. The transport of nutrients across this barrier is the proper process of ion uptake. This transport is not mere diffusion, but is related to specific membrane components and to metabolic processes that allow selective uptake of the plant nutrients, which is often associated with an accumulation of the nutrient in the cell. For example, the K^+ concentration in the cell (cytoplasm) may be higher by a factor of 10^2 – 10^3 than the K^+ concentration in the soil solution.

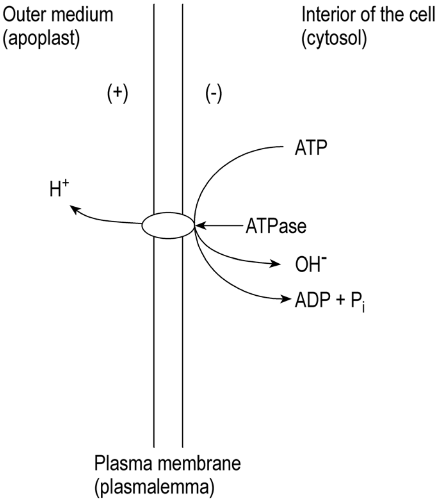


Figure 9. Scheme of plasmalemma-located ATPase, hydrolyzing ATP and pumping H^+ into the apoplast (proton pump)

Nutrient uptake is initiated by an enzyme located in the plasma membrane called ATPase (ATP hydrolase). Its substrate is ATP. Hydrolyzation of ATP results in the splitting of H_2O into H^+ and OH^-, from which the latter remains in the cytosol of the cell while H^+ is extruded into the outer medium (Fig. 9). Thus an electrochemical potential is created between the two sides of the membrane. The proton motive force (p.m.f.) obtained in this way is described by the following equation [66]:

$$\text{p.m.f.} = -50\,\Delta\text{pH}+\Delta\varphi \quad \varphi = \text{electrical charge}$$

The p.m.f. is the driving force for ion uptake. Cations are directly attracted by the negatively charged cell. Since the plasma membrane, however, represents a strong barrier, the entry of cation species must be mediated by particular carriers and ion channels. Little is known about these carriers and channels in plant membranes. These are assumed to be ionophores like valinomycin, nonactin, or gramicidin, which bind selectively to cation species and hence mediate a selective cation transport across the membrane. Such a type of carrier transport is shown in Figure 10. The carrier is hydrophobic and therefore quite mobile in the membrane, which consists mainly of lipids. At the outer side of the membrane it combines selectively with a cation species, e.g., K^+. The cation carrier complex then diffuses to the inner side of the membrane, where the K^+ is released. Release and combining with K^+ depend on the electrochemical difference between the two sides of the membrane. High K^+ concentration and a positive charge favor the combining process; low K^+ concentration and a negative charge favor the release of K^+. Net transport rate becomes zero as soon as the electrochemical equilibrium is attained, which is governed by the Nernst equation:

$$E = \frac{RT}{zF}\ln\frac{a_\text{o}}{a_\text{i}}$$

E = electrical potential difference between the two sides of the membrane

F = Faraday constant

z = oxidation state of the cation

a_o = activity of the cation species in the outer solution

a_i = activity of the cation species in the inner solution

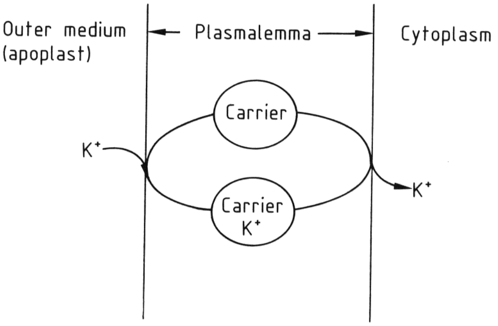


Figure 10. Scheme of K^+ carrier transport across the plasmalemma

The uptake of anions (NO_3^-, $H_2PO_4^-$) is also assumed to be driven by the plasmalemma-located ATPase. The anions presumably form protonated carriers at the outer side of the membrane and then are selectively tranported across the membrane. The protonated carrier – anion complexes are positively charged. Hence the electropotential difference between either side of the plasmamembrane represents the driving force for anion uptake.

Ion absorbed by cells of the root cortex are translocated via the symplasm in centripetal direction towards the central cylinder, where they are secreted into the xylem vessels. The actual process of this secretion is not yet understood. In the xylem the ions are translocated to the upper plant parts with the transpiration stream. They thus follow the vascular system of the plant and are distributed along the major and minor vein system of leaves from where they diffuse into the pores and intercellular spaces of cell wall (apoplast). The transport from the apoplast across the plasmamembrane into the cytoplasm of leaf cells is a process analogous to the nutrient uptake of root cells.

Some plant nutrients, such as N, P, K, and Mg, but not Fe and Ca, may also be translocated against the transpiration stream via the phloem tissue. These nutrients therefore may be transported from the tops to the roots or from older leaves to younger leaves.

2.4.2. Effect of Nutrition on Growth, Yield, and Quality

Meristematic growth requires plant nutrients: N and P for the synthesis of proteins and nucleic acids, K and Mg for the activation of enzymes and for membrane potentials, and all the other nutrients for various processes. The quantities required differ greatly but for practical purposes mainly N, K, and P, in some cases also Mg and Ca, limit plant growth. The growth rate is controlled by the nutrient with the lowest availability (LIEBIG's law of minimum). Application of this particular nutrient results in a growth response. This response is not linear, but rather follows a saturation type of curve (Fig. 11). Also crop yields as a function of increasing rates of fertilizer applicaton reflect this curve, which is also called the *Mitscherlich curve* since MITSCHERLICH [67] investigated these relationships extensively. The curve is described by the following equation:

$$\log(A-y) = \log(A-cx)$$

A = maximum yield
y = obtained yield
x = growth factor, e.g., fertilizer rate
c = constant

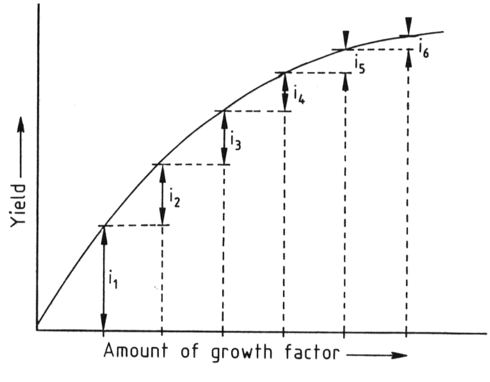


Figure 11. Mitscherlich curve, response curve of diminishing increments (i) with each further unit of growth factor

The term $(A - y)$ is the increment that is required to attain the maximum yield. This increment becomes smaller as the variable x (growth factor) becomes greater. Such growth factors include not only plant nutrients, including CO_2, but also light intensity and temperature. The growth response obtained by these factors also follows the saturation type of curve shown in Figure 11.

Growth and metabolic processes in plant tissues depend not only on the rates of plant nutrients supplied but also on the ratio in which the nutrients are provided. If the N supply is relatively high as compared with the supply of other nutrients, the synthesis of N-containing compounds, such as amino acids and proteins, is promoted. This may have a favorable effect on the protein synthesis in grains of cereals and hence improve their baking quality and their nutritional value. In grains for malting purposes and in particular barley, however, low protein content and high starch content are required. In this case, relatively high N rates have a detrimental effect on grain quality. An analogous case is the sugar beet, which should be high in sugar and low in N-containing compounds, especially amino acids. Relatively high N supply favors the synthesis of vitamins of the vitamin B group and the synthesis of carotenes in green plant tissue but has a negative effect on the content in vitamin C. High N rates may also increase the sensitivity of leaves and culms to fungi attack.

Phosphate and especially K^+ have a favorable impact on the energy status of plants. A relatively high supply of both nutrients promotes the synthesis of carbohydrates and the development of cell wall material, which increases the resistance against fungi attack.

2.5. Nutrient Balance

2.5.1. Gains and Losses of Plant Nutrients

In order to maintain the level of available plant nutrients in soils, the quantity of nutrients lost from the soil must be replenished. Nutrients may be lost by harvesting of plant material, leaching, transition into a non-available form in the soil, and volatilization. Nutrient gains result from fertilizer application, soil weathering, rainfall, and microbial dinitrogen fixation (see Section 2.2.5). In most soils, weathering provides enough of those nutrients that are only required in minor amounts, such as Fe, Mn, Cu, Zn, Mo, and B. Young soils being rich in primary minerals also may weather appreciable amounts of Mg, K, and phosphate. Generally, the contribution of plant nutrients released by weathering is more important if the yield level is lower. Up to the mid-1980s, sulfur supply to crops was to a large extent brought about by SO_2 in the atmosphere and by SO_2 dissolved in precipitation. However, in the last two decades increased global environmental concern has prompted reductions in SO_2 emissions, which in past years were beneficial for crop growth in many countries [68]. With the reduction in the sulfur supply from atmospheric emissions, the greater use of high-analysis S-free fertilizers, new high-yielding crop varieties, and declining use of sulfur as a fungicide, sulfur deficiency became widespread in various parts of the world.

The quantity of nutrients taken up by crops depends mainly on the yield level and on the kind of plant organs. For a rough calculation of *nutrient uptake by crops* the following figures may be used:

1 t of grain (cereals) contains	
20 – 25	kg N
5	kg K
4	kg P
1 t of dry matter of green plant material (leaves, stems) contains	
15 – 30	kg N
15 – 30	kg K
2 – 4	kg P
1 t of roots (beets) or tubers contains	
1.5 – 3	kg N
4 – 5	kg K
0.3 – 0.6	kg P

Nutrient losses only occur from plant parts removed from the field. For example, if only grain is harvested and the straw remains on the field, only the plant nutrients present in the grain are lost from the system.

High nutrient losses may occur by *leaching*. The quantities lost depend much on climate, weather conditions, and soil properties. In Central Europe, with a rainfall of about 700 mm/a, ca. 25 – 50 % of the precipitation passes through the soil profile to a depth >1 m. Plant nutrients dissolved in this drainage water are lost from the soil. Table 10 shows maximum and minimum leaching rates obtained during a period of eight years by Vömel [69]. Generally, leaching rates are low if the soil clay content is high. High leaching rates prevail in fallow soils, low rates in soils with a permanent plant cover, e.g., grassland. Phosphate is effectively not leached. Leaching occurs mainly with the winter or monsoon rainfall. Under such humid conditions plant nutrients present in plant residues (stubble, straw, roots, leaves) also may be leached.

Table 10. Leaching rates of plant nutrients from soils [69]

Soil	Plant nutrient, kg ha^{-1} a^{-1}			
	N	K	Ca	Mg
Sand	12 – 52	7 – 17	110 – 300	17 – 34
Sandy loam	0 – 27	0 – 14	0 – 242	0 – 37
Loam	9 – 44	3 – 8	21 – 176	9 – 61
Clay	5 – 44	3 – 8	72 – 341	10 – 54

Volatile losses only play a role for nitrogen, which may be lost in form of NH_3, N_2, and N_2O (see Section 2.2.5). Nutrient loss by conversion into a non-available form is only relevant for phosphate and in some cases for K^+.

2.5.2. Alternative Plant Nutrition

The terms “ecological agriculture” and “biological agriculture” are used as synonyms for “organic agriculture”. One of the main approaches of organic agriculture is a mixed farm system within a more or less closed nutrient cycle. With regard to plant nutrition the production system can be characterized by the following principles:

Nearly closed cycles of nutrients and organic matter within the farm
Predominant use of farmyard manure and compost
Slowly soluble P minerals, if necessary
K fertilizers not in the form of chloride

Besides nitrogen, which may be imported with manure, symbiotically bound nitrogen is the main N source. For this reason N_2 fixation by legumes is of great importance. Synthetic fertilizers are renounced. In the last few years major efforts were undertaken to quantify the cycles of nutrients as well as the organic matter cycles.

Organic agriculture has to deal with limited amounts of nutrients. Nutrient management, defined as systematic target-oriented organization of nutrient flow, is therefore considered as the optional combination of resources that are restricted or have to be released. Strategies must be adopted that make nutrients in the system internally available by achieving optimized utilization or which keep nutrients potentially available in the long term. The main nutrient flows in organic farm are fixed for the long term by organizing and optimizing the site-adapted crop rotation [70].

3. Standard Fertilizers

Standard fertilizers include the products used in large quantities worldwide. They are applied to agricultural and large-scale garden crops. They can be classified as solid and liquid fertilizers.

3.1. Solid Fertilizers

Solid fertilizers are the most important group of fertilizers. Worldwide, nearly 90 % of all the nitrogen applied in fertilizers is in solid form (season or fertilizer year 1996/97). In Germany about 83.5 % of total nitrogen is applied in the solid form, and the corresponding figure in the United States is 44 %. Phosphate and potash are applied mainly in solid form. Solid fertilizers include granular, prilled, and compacted products (see Chap. 5).

A summary of the most important fertilizers can be found in [71].

3.1.1. Straight Fertilizers

Straight fertilizers contain only one nutrient, for instance, urea (N) or triple superphosphate (P_2O_5). Straight solid fertilizers are listed in Table 11.

3.1.2. Multinutrient Fertilizers

Multinutrient or compound fertilizers contain two or more nutrients. The term complex fertilizer refers to a compound fertilizer formed by mixing ingredients that react chemically. In bulk-blend or blended fertilizers (see Chap. 5), two or more granular fertilizers of similar size are mixed to form a compound fertilizer.

There are several routes for manufacturing fertilizers. An important route is the Odda process, in which phosphate rock is digested with

Table 11. Straight fertilizers

Type	Production; main constituents	Analysis, wt %	Remarks	Ullmann keyword
Nitrogen fertilizers				
Calcium nitrate [*13477-34-4*]	synthetic	15.5 % N ($Ca(NO_3)_2$), NH_4 N, max. 1.5 %	fast acting; chiefly for special crops and refertilizing	→ Nitrates and Nitrites
Sodium nitrate [*7631-99-4*]	synthetic	16 % N ($NaNO_3$)	fast acting; chiefly for special crops and refertilizing	→ Nitrates and Nitrites
Chile saltpeter	from caliche; sodium nitrate	$\geq$ 15 % N	fast acting; chiefly for special crops and refertilizing	
Ammonium nitrate [*6484-52-2*]	synthetic; may contain additives such as ground limestone, calcium sulfate, dolomite, magnesium sulfate, kieserite	34 % N(NH_4NO_3)	special storage provisions (see Chap. 8)	→ Ammonium Compounds, Chap. 1
Calcium ammonium nitrate (CAN)	synthetic; may contain additives such as ground limestone, calcium sulfate dolomite, magnesium sulfate, kieserite	26 – 28 % N, $\geq$ 2 % $CaCO_3$	versatile fertilizer, both fast and slow acting	→ Ammonium Compounds
Ammonium sulfate nitrate (ASN)	synthetic	added as limestone or dolomite 26 % N ($NH_4NO_3^+$ and $(NH_4)_2SO_4$), $\geq$ 5 % NO_3 N	versatile fertilizer with both fast and slow action	→ Ammonium Compounds
Magnesium ammonium nitrate	synthetic; ammonium nitrate and magnesium compounds (dolomite, magnesium carbonate, or magnesium sulfate)	20 % N (NH_4NO_3)	for soils and crops requiring magnesium	
Ammonium sulfate [*7783-20-2*]	synthetic, often as byproduct	$\geq$ 6 % NO_3 N, 5 % MgO 21 % N ($(NH_4)_2SO_4$)	slow acting, for soils containing lime and/or high-precipitation areas	→ Ammonium Compounds, Chap. 2
Ammonium chloride [*12125-02-9*]	synthetic	$\geq$ 25 % N (NH_4Cl)	rice fertilization, chiefly in Japan and India	→ Ammonium Compounds, Chap. 3
Urea [*57-13-6*]	synthetic	46 % N ($CO(NH_2)_2$) biuret $\leq$ 1.2 %	optimal only when soil lime, heat, and moisture are appropriate; also suitable for foliar application; volatile losses are possible	→ Urea
Calcium cyanamide [*156-62-7*]	synthetic	20 – 22 % N; $\geq$ 75 % of total N from cyanamide; ca.40 % CaO 66 % N	slow acting, special requirements, also for weed control nitrification	→ Cyanamides, Chap. 1
Dicyandiamide [*461-58-5*]	synthetic		nitrification inhibitor, added pure to liquid manure; also as additive to straight and compound fertilizers containing ammonium	→ Cyanamides, Chap. 3

Table 11. (continued)

Type	Production; main constituents	Analysis, wt %	Remarks	Ullmann keyword
Phosphate fertilizers				
Basic slag (Thomas phosphate)	byproduct of steel production from ores containing phosphate; calcium silicophosphate	$\geq$ 12 % P_2O_5 soluble in mineral acid, $\geq$ 75 % soluble in 2 % citric acid	phosphate containing up to 45 % CaO, versatile phosphate fertilizer	→ Phosphate Fertilizers
Superphosphate	digestion of ground phosphate rock with sulfuric acid; monocalcium phosphate with calcium sulfate	16 – 22 % P_2O_5 soluble in neutral ammonium citrate solution, 93 % water soluble	for all soils	→ Phosphate Fertilizers
Triple superphosphate	digestion of ground phosphate rock with phosphoric acid; monocalcium phosphate	45 % P_2O_5; soluble in neutral ammonium citrate solution, 93 % water soluble	for all soils	→ Phosphate Fertilizers
Partly digested phosphate rock	partial digestion of ground phosphate rock with sulfuric or phosphoric acid; monocalcium phosphate, tricalcium phosphate, calcium sulfate	$\geq$ 20 % P_2O_5; soluble in mineral acid, 40 % water soluble	for all acidic soils ($pH < 7$)	→ Phosphate Fertilizers
Soft phosphate rock	grinding of soft phosphate rock; tricalcium phosphate and calcium carbonate	$\geq$ 25 % P_2O_5 soluble in mineral acid, 55 % soluble in 2 % formic acid	for acidic soils and low-precipitation areas	→ Phosphate Fertilizers
Dicalcium phosphate [*7789-77-7*]	neutralization of phosphoric acid with calcium hydroxide dicalcium phosphate dihydrate	$\geq$ 38 % P_2O_5 soluble in alkalized ammonium citrate; not water-soluble	for all soils	→ Phosphoric Acid and Phosphates
Thermal (fused) phosphate	thermal digestion of ground phosphate rock with alkali-metal compounds and silicic acid; alkali-metal calcium phosphate and calcium silicate	$\geq$ 25 % P_2O_5 soluble in alkalized ammonium citrate solution and in citric acid	for all soils and locations	
Aluminum calcium phosphate	thermal digestion and grinding; amorphous aluminum and calcium phosphates	29 – 33 % P_2O_5 soluble in mineral acid, 75 % soluble in alkalized ammonium citrate solution	for all soils and locations	
Potassium fertilizers				
Potash ore	run-of-mine potash	$\geq$ 10 % K_2O, $\geq$ 5 % MgO, contains sodium	for soils and crops where Na and Mg are important, especially cattle fodder	→ Potassium Compounds
Beneficiated potash ore	beneficiation of run-of-mine potash and mixing with potassium chloride	$\geq$ 18 % K_2O	for all soils	→ Potassium Compounds
Potassium chloride [*7447-40-7*]	beneficiation of run-of-mine potash	$\geq$ 37 % K_2O (up to 60 %)	for all crops not sensitive to chloride	→ Potassium Compounds
Potassium chloride with magnesium	beneficiation of run-of-mine potash and addition of Mg salts	$\geq$ 37 % K_2O, $\geq$ 5 % MgO	on Mg-deficient soils for all crops not sensitive to chloride	→ Potassium Compounds
Potassium sulfate [*7778-80-5*]	synthetic	$\geq$ 47 % K_2O, $\leq$ 3 % Cl	for all crops sensitive to chloride	→ Potassium Compounds
Potassium sulfate with magnesium	synthetic, from potassium sulfate, with addition of Mg salts; potassium sulfate and magnesium sulfate	$\geq$ 22 % K_20, $\geq$ 8 % MgO; $\leq$ 3 % Cl	deficient soils for all crops sensitive to chloride	→ Potassium Compounds

nitric acid. Calcium nitrate is crystallized by cooling and removed, and the mother liquor is neutralized by addition of gaseous ammonia (see → Phosphate Fertilizers, Chap. 11). Other important processes are based on digestion of phosphate rock with sulfuric acid and the so-called mixed-acid process [355]. For the production of NPK fertilizers, potassium compounds are added in the desired amount to the corresponding slurries. Magnesium (as kieserite or dolomite) and micronutrients may also be added.

NPK Fertilizers. According to the EEC Guidelines, NPK fertilizers must contain at least 3 % N plus 5 % P_2O_5 plus 5 % K_2O and at least 20 % total nutrients. The most commonly used grades (N-P_2O_5-K_2O, each in wt %) are

Nutrient ratio 1 : 1 : 1
15–15–15, 16–16–16, 17–17–17
Nutrient ratios 1 : 2 : 3 and 1 : 1.5 : 2
5–10–15, 6–12–18, 10–15–20
Nutrient ratio 1 : 1 : 1.5 – 1.7
13–13–21, 14–14–20, 12–12–17
Nutrient ratios 3 : 1 : 1 and 2 : 1 : 1
24–8-8, 20–10–10
Low-phosphate grades
15–5-20, 15–9-15

If additional numbers are given in a fertilizer grade, the fourth is the wt % MgO and the fifth is wt % S. Micronutrient contents may also be stated. In some countries the grade is expressed in terms of the elements rather than oxides.

The NPK fertilizers have the important advantage of simplified application, since all the important nutrients can be distributed in one operation. Each grain of fertilizer has the same content of nutrients. Serious errors are prevented by the harmonic nutrient ratio, provided the metering rate is correct. The nitrogen is usually present as nitrate and ammonium N in roughly equal parts. The phosphate is 30 – 90 % water-soluble, the rest being soluble in ammonium citrate solution. Most of the potassium is present as the chloride; the sulfate is used for chloride-sensitive crops.

In bulk-blended products (see Section 5.5), the individual fertilizers are combined in the desired nutrient ratio. The operational advantage is the same as that of synthetic NPK fertilizers. Because, however, the individual granular products may differ in grain-size spectrum, granule surface characteristics, and density, segregation may occur during handling, storage, packaging and even during application. These products are therefore suitable for practical use only when the individual components have similar physical qualities.

NP Fertilizers. The minimum analysis for NP fertilizers under the EEC Guidelines is 3 % N and 5 % P_2O_5 and at least 18 % total nutrients. Common grades are 20–20, 22–22, 26–14, 11–52, 16–48, and 18–46. These products are appropriate for potassium-rich soils or where potash is supplied as a separate fertilizer.

NK Fertilizers. The minimum analysis for NK fertilizers under the EEC Guidelines is 3 % N and 5 % K_2O and at least 18 % total nutrients. These products are suitable for phosphate-rich soils or where phosphate is distributed separately.

PK Fertilizers. In the group of PK fertilizers, all combinations of the straight phosphate and potassium components listed in Table 11 are possible. In general, the materials are first milled and then mixed and granulated, so that a fairly homogeneous mixture is obtained. Some products are also made by bulk blending. The EEC Guidelines set forth a minimum analysis of 5 % P_2O_5, 5 % K_2O, and at least 18 % nutrients. Magnesium and micronutrient boron can be added.

3.1.3. Lime Fertilizers

Solid fertilizers also include lime fertilizers. The main purpose of using lime is to optimize soil pH; a secondary purpose is to supply calcium as a plant nutrient. The use of large amounts of lime to increase the pH is referred to as soil-improvement liming. Use to maintain the present pH is called maintenance liming.

The starting materials for lime fertilizers are limestone [*1317-65-3*] and dolomite [*17069-72-6*]. These are marketed in various forms. National fertilizer regulations (e.g., the type list in the Federal Republic of Germany's fertilizer law, see Chap. 10) govern the fineness of grinding. Calcination at 900 – 1400 °C yields quicklime CaO; hydration with water gives slaked lime

$Ca(OH)_2$. The most immediately effective form is finely divided quicklime with a particle size of ca. 0.15 mm or less. If a lime grade contains at least 15 % MgO or $MgCO_3$, it can be called magnesium lime. The content of MgO depends on the starting material (proportion of dolomite) and may be up to 40 %.

Calcium carbonates [*471-34-1*], $CaCO_3$, act slowly. They are recommended above all for lighter soils. Unslaked and slaked limes are faster acting. They are suitable mainly for loamy and clayey soils.

Besides these lime products from natural rock, there are also limes from industrial processes. They include smelting lime and converter lime, which are steel-industry byproducts. Converter lime with phosphate must contain 40 % CaO + MgO and also at least 5 % P_2O_5. These products must also satisfy minimum requirements on fineness to ensure sufficiently fast action.

Finally, the refining of beet sugar yields a product containing lime. According to the fertilizer law in the Federal Republic of Germany, this lime form must contain at least 30 % CaO and 5 % MgO.

3.1.4. Magnesium Fertilizers

The following magnesium fertilizers are offered in commerce: kieserite [*14567-64-7*] (27 % MgO) for soil application, and Epsom salts [*7487-88-9*] (17 % MgO) for foliar application in liquid form.

3.2. Liquid Fertilizers

Only solid fertilizers were produced and used up to ca. 1950: lower production costs, higher nutrient concentrations, and the ease of making compound fertilizers were for a long time the reasons that development was limited to the solid fertilizers. Since then, liquid fertilizers have also been developed and supplied to agriculture. Particularly in the United States, liquid fertilizers have come into heavy use. Modern production methods have lowered production costs, even for liquid fertilizers with high nutrient concentrations.

Homogeneous liquid fertilizers, in contrast to solid fertilizers, present no special problems during application by the farmer. Furthermore the storage of liquid fertilizers is less difficult than that of solid ones. Small amounts of herbicides and insecticides can be mixed with liquid fertilizers far more easily. Production plants for solid fertilizers are much more costly than those for liquid fertilizers. Liquid fertilizers have the drawbacks that they usually have lower nutrient content and are sensitive to impurities, as well as to precipitation and crystallization, especially caused by magnesium and fluorine.

Liquid fertilizers are classified as (1) anhydrous ammonia [*7664-41-7*] with 82 wt % N at high pressure, (2) aqueous ammonia with up to 24 wt % N, (3) ammoniates (ammoniated ammonium nitrate and/or urea solutions) with up to 50 wt % N at moderate to atmospheric pressure, and (4) nonpressure urea – ammonium nitrate solutions with up to 32 wt % N [72]. Compound liquid fertilizers include both clear liquids and suspensions.

The growing interest in liquid fertilizers results in large part from the fact that field spraying can be used for specific, exactly meterable, inexpensive, clean application with an injector. Even low nitrogen rates of 15 – 30 kg/ha can be exactly and uniformly metered out in liquid form.

Liquid-fertilizer plants are classified according to type of operation as hot mix or cold mix. Hot-mix plants use phosphoric acid and ammonia, whereby hot mix refers to the heat of reaction. Cold-mix plants mix ammonium phosphate solution with other ingredients; no heat of reaction is evolved. Cold-mix plants are popular in the United States, because they are simple and inexpensive. They are essentially a blending and mixing operation, the liquid counterpart of the bulk-blend plants (see Section 5.5).

Table 12 lists the consumption of nitrogen in liquid fertilizers and their share of total nitrogen consumption by countries. In Germany consumption of nitrogen in liquids has risen since the season 1985/86, but total nitrogen consumption is decreasing [72]. The use of liquid ammonia plays no role in Germany and has strongly declined in Denmark. In the United States more nitrogen is consumed in liquid than in solid form.

Liquid fertilizers can be easily mixed with a variety of micronutrients and agricultural pesticides. The dissolving of micronutrients in clear liquid fertilizers is promoted by gelatinizing agents or by complexing with polyphosphates.

Table 12. Consumption of liquid fertilizers and their share of total nitrogen consumption

Country and fertilizer year *	Liquid ammonia direct application		Nitrogen solutions		Total liquids		Total N
	10^3 t N	%	10^3 t N	%	10^3 t N	%	10^3 t N
World							
1985/86	5022.2	7.13	3811.1	5.41	8833.3	12.54	70 461.6
1993/94	5052.4	6.97	3801.9	5.24	8854.3	12.21	72 497.7
1994/95	4122.8	5.69	3794.3	5.24	7917.1	10.93	72 454.8
1995/96	4649.2	5.92	4013.6	5.11	8662.8	11.03	78 592.5
1996/97 **	4688.1	5.67	4097.0	4.96	8785.1	10.63	82 645.6
United States							
1985/86	3400.5	35.96	1887.6	19.96	5288.1	55.92	9457.0
1993/94	4116.3	35.89	2543.0	22.17	6659.3	58.06	11 469.4
1994/95	3308.7	31.12	2514.0	23.65	5822.7	54.77	10 632.1
1995/96	3693.6	33.09	2642.8	23.68	6336.4	56.77	11 161.5
1996/97 **	3651.6	32.65	2651.3	23.71	6302.9	56.36	11 184.5
Germany							
1985/86	15.0	0.66	65.0	2.84	80.0	3.50	2285.7
1993/94	0.0	0.00	205.0	12.72	205.0	12.72	1612.0
1994/95	0.0	0.00	226.0	12.65	226.0	12.65	1787.0
1995/96	0.0	0.00	282.0	15.93	282.0	15.93	1770.0
1996/97 **	0.0	0.00	290.0	16.53	290.0	16.53	1754.0
France							
1985/86	31.0	1.29	482.0	20.02	513.0	21.31	2408.0
1993/94	37.0	1.67	560.0	25.20	597.0	26.87	2222.0
1994/95	35.7	1.55	566.4	24.54	602.1	26.09	2308.3
1995/96	42.7	1.79	577.0	24.13	619.7	25.92	2391.7
1996/97 **	44.8	1.78	643.2	25.48	688.0	27.26	2523.9
Denmark							
1985/86	102.0	26.69	0.0	0.00	102.0	26.69	382.1
1993/94	0.0	0.00	4.0	1.23	4.0	1.23	325.0
1994/95	0.0	0.00	6.0	1.90	6.0	1.90	316.0
1995/96	18.0	6.19	7.0	2.41	25.0	8.60	291.0
1996/97 **	17.0	5.94	7.0	2.45	24.0	8.39	286.0

* The fertilizer year (season) runs from July 1 to 30 next year.
** Preliminary.

The pulverized additions such as copper sulfate, sodium molybdate, sodium borate, zinc oxide, or manganese oxide, which are mixed with suspensions [73], can be suspended in water by stirring.

Nonpressure liquid fertilizers are generally stored in concrete or mild steel tanks [308, p. 129]. A corrosion inhibitor is required in the case of nonpressure urea – ammonium nitrate solution. Concrete tanks have the shape of vertical cylinders. The tanks should be lined with a film of a durable plastic such as poly(vinyl chloride). Before lining, the concrete tank must be protectively coated [74]. For pressurized liquid fertilizers, double-walled vessels with leak warning systems should be employed. When single-walled tanks are used, a retaining basin must be erected.

3.2.1. Nitrogen Liquids

Liquid Ammonia. Since 1950, liquid ammonia has found increasing use as a direct-application fertilizer, especially in the United States, since it can be produced in large amounts at low cost. Because of its high vapor pressure (6 bar at 10 °C, 9 bar at 20 °C, and 12 bar at 30 °C), anhydrous ammonia must be stored and transported in pressure vessels and applied with special equipment.

Ammonia is injected into the soil to a depth of roughly 15 cm with injection prongs. In general, the equipment suitable for this purpose deposits the fertilizer in a pipe whose diameter depends on the soil type and soil moisture content. Figures 12 and 13 show the ammonia loss as a function of the soil type, the soil water content, and the depth of application [75]. If the soil contains 15 % water, the NH_3 loss is virtually independent of depth and, at about the 1 % level, can be neglected. Despite some advantages, the application of liquid ammonia is too expensive for most farmers in the EC. A publication for farmers on the safe use of liquid ammonia is available [76]. For storage and transportation, see → Ammonia and [308, p. 73]

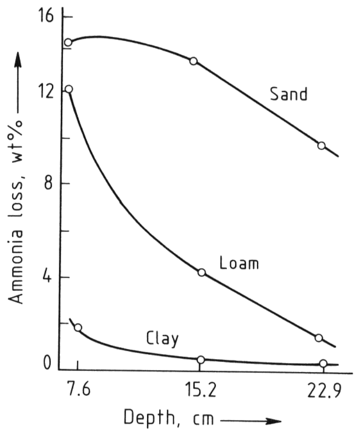


Figure 12. Ammonia losses as a function of application depth for three types of air-dry soils

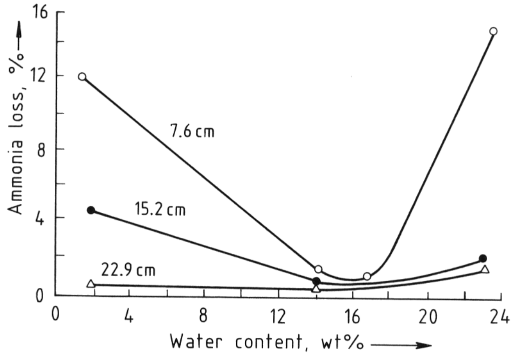


Figure 13. Ammonia loss as a function of soil water content for three depths of application

Pressurized Nitrogen Liquids. Together with ammonia, ammonium nitrate and/or urea can be converted into pressurized aqueous nitrogen fertilizers. The following categories are distinguished: low-pressure solutions (up to 1.3 bar) for direct application in agriculture, medium-pressure solutions (up to 7 bar), mostly used for ammoniating superphosphates or phosphoric acid, and high-pressure solutions (over 7 bar), used only for ammoniation. Table 13 lists some nitrogen solutions with their saturation temperatures and vapor pressures at 40 °C (313 K) [77].

Nonpressure Nitrogen Liquids. Nitrogen solutions that contain little or no ammonia have no significant vapor pressure at ambient temperatures. The most common nonpressure liquid nitrogen fertilizers comprise mixtures of ammonium nitrate, urea, and water (UAN), which are the most popular nitrogen fertilizers in the United States. A commercial solution might have the following composition:

Ammonium nitrate	39.5 % = 14 % N
Urea	30.5 % = 14 % N
Water	30.0 %
UAN	100.0 % = 28 % N

The density at 15 °C is ca. 1.28 g/cm^3, corresponding to 36 kg of nitrogen in 100 L of the product.

Figure 14 gives solubility isotherms and phase boundaries for the ammonium nitrate – urea – water system. In order to optimize the amount of UAN as a function of temperature during transportation and in the field, the UAN composition is adjusted to suit the conditions [77, 79]. This is especially important for winter application. Among almost-nonpressure nitrogen solutions, mixtures containing added NH_3 (see Table 14) should also be mentioned [80].

A urea – ammonium nitrate solution can be produced by dissolving solid urea in an ammonium nitrate solution. If the raw materials are solid urea and ammonium nitrate, UAN can be produced in a slightly modified dissolver. Figure 15 gives a simplified diagram of such a production unit.

The desired ammonium nitrate : urea ratio is obtained by mixing a 75 – 80 % urea solution at 120 °C with an 80 – 85 % ammonium nitrate solution at 40 °C, the quantities being controlled. After the addition of water, the liquid fertilizer is transferred to a storage tank after passing via a cooler. The mixer and cooler are made of stainless steel, and the equipment downstream of the cooler are made of carbon steel [94]

Table 13. Nomenclature and physical properties of some nitrogen solutions

% N × 10	Composition *	Vapor pressure at 40 °C, bar **	Saturation temperature, °C
410	22–65–0	0.7	− 6
410	26–56–0	1.2	−32
444	25–55–10	1.5	−29
453	31–0-43	3.4	+ 8
454	37–0-33	4.0	− 9
490	33–45–13	3.6	−27
490	34–60–0	3.4	−47
530	49–36–0	7.3	−73
580	50–50–0	10.1	−34

* $HN_3-NH_4NO_3-(NH_2)_2CO$, wt %.

** Multiply by 0.1 to convert to MPa.

Table 14. Composition, nitrogen concentration (N), and crystallization temperature (T_c) of nitrogen solutions [80]

Composition, wt %				N,	T_c,	Pressure at 10 °C,
NH_3	NH_4NO_3	Urea	H_2O	wt %	°C	bar *
24	56	10	10	44	−26	0.3
20	45	15	20	39.2	−32	0.2
19	58	11	12	41	−14	0.2

* Multiply by 0.1 to convert to MPa.

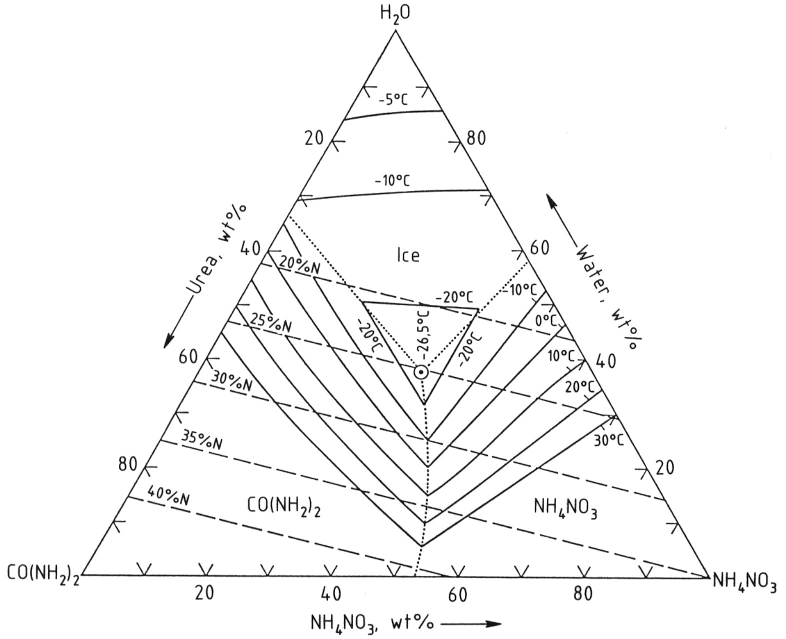


Figure 14. The ammonium nitrate – urea – water system [77, 78]
Solid lines are solubility isotherms; dotted lines show phase boundaries; dashed lines show constant nitrogen content.

Since urea – ammonium nitrate solutions attack ordinary steels, steel storage tanks and tank cars should be coated with Derakane-470, a poly(vinyl ester) [82], or lined with polypropylene or polyethylene [83]. This practice also prevents stress-corrosion cracking of the steels, especially in the presence of $(NH_4)_2CO_3$ [84]. Poly(vinylidene fluoride) provides excellent corrosion protection up to 120 – 130 °C [83]. The most common inhibitor for these solutions is anhydrous ammonia, which is used to adjust the pH to 7. Ammonium thiocyanate and ammonium phosphate are also effective [308, p. 129]

In the production and use of UAN, such solutions can explode if they are evaporated to $<5\,\%$ water and simultaneously heated, especially when the two components have become segregated [85].

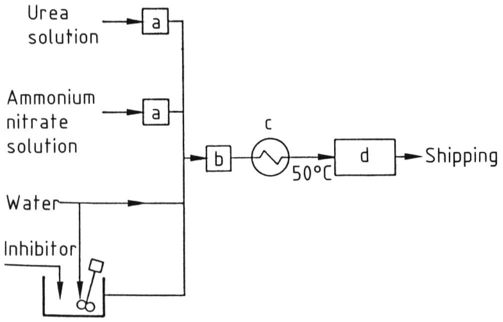


Figure 15. Production of urea – ammonium nitrate solution [112]
a) Ratio controller; b) Mixer; c) Cooler; d) Storage tank

3.2.2. Multinutrient Liquids

Liquid mixed fertilizers consist of aqueous solutions and dispersions of the nutrients nitrogen, phosphate, and potash. These liquid mixed fertilizers are produced mainly from phosphoric acid, anhydrous ammonia or aqueous ammonia, ammonium nitrate, urea, and potassium salts, chiefly KCl but also K_2SO_4 (hot mix). In most cases, fine-grained potassium chloride, with a somewhat higher potash content (62 % K_2O) than the normal fertilizer salt, is employed because it dissolves better. If only solid raw materials are used, the N-P-K grade of the liquid mixed fertilizer can be varied only over a narrow range. The following solid nitrogenous components are mainly employed: ammonium nitrate, urea, monoammonium phosphate, and diammonium phosphate (cold mix).

For intensive field and greenhouse cultivation of vegetables, etc., the nutrients can be introduced into the watering system in the form of a low-percentage nutrient solution. Because this solution is often delivered directly to the roots through hoses, it should have the lowest possible level of impurities.

3.2.2.1. NP Liquids

In the early 1950s the commercial production of mixed liquid fertilizers was started in the United States. Pure electric-furnace orthophosphoric acid was used as the phosphate source. The acid was ammoniated to give an 8–24–0 grade liquid which does not salt out at −8 °C. At mixing plants, this base solution was mixed with urea – ammonium nitrate solution to give a liquid containing ca. 28 – 32 % nitrogen. An additional potassium content was obtained by dissolving potassium chloride in the liquid. Maximum-mix grades attainable in this way included 13–13–0 and 7-7-7. A problem was the low concentrations of the 8–24–0 base solution and the final liquid mixes. Moreover, use of the cheaper wet-process orthophosphoric acid was not possible, because on ammoniation of such acids, iron, aluminum, magnesium and other impurities form voluminous, gelatinous, and crystalline precipitates that are difficult to handle.

In 1957 TVA introduced superphosphoric acid and base solutions made by ammoniation thereof [86]. The superphosphoric acid, initially produced by the electric-furnace process, contained ca. 76 % P_2O_5 as compared to 54 % P_2O_5 in commercial wet-process acid. At this higher P_2O_5 concentration, ca. 50 % of the P_2O_5 is in the form of pyrophosphoric, tripolyphosphoric, and tetrapolyphosphoric acids [88]. Because of higher solubility of the ammonium salts of these polyphosphoric acids, ammoniation of superphosphoric acid allowed production of higher grade base solution (10–34–0 instead of 8–24–0) and higher grade mixed fertilizer solutions. A further advantage was that the polyphosphates are effective sequestering agents that prevent precipitation of many metal ions. The kinetics of formation of ammonium polyphosphates are reported in [87].

Although the introduction of superphosphoric acid was an effective solution to the problem of low-grade liquids, there were still the high costs of the electric-furnace acid process. Studies were undertaken to produce usable superphosphoric acid by concentration of the cheaper (54 % P_2O_5) wet-process phosphoric acid to about 72 % P_2O_5 and a polyphosphate content of 45 – 50 %. Problems of the wet-process superphosphoric acid of this concentration were its high viscosity and the poor storage properties of the 10–34–0 base solution derived from it. Although the polyphosphate content of the liquid initially keeps impurities in solution in complexed form, precipitates may still form during storage if the acid used in ammoniation had too high an impurity level and the polyphosphate concentration is too low. A frequent problem with NP liquids is the precipitation of insoluble magnesium compounds. If 0.4 wt % magnesium (calculated as oxide) is present, the storage time before appearance of cloudy precipitates is only about one month. For magnesium oxide concentrations of 0.2 % and 0.1 %, the storage life is about 1 – 2 years [89].

The usual raw material for phosphoric acid productions, apatite, with its impurities and its variable composition, is not a simple raw material. In the production of phosphoric acid, however, most of the impurities (e.g., aluminum, iron, and magnesium compounds) remain behind in the acid slurry.

The removal of the impurities from the wet-process phosphoric acid (Fe, Al, Mg, Ca, SO_3, F) is necessary for storage and application of the liquid fertilizer. Two typical processes reduce the concentrations of the most troublesome impurities significantly (Table 15) [95]. Process B, which is used in Europe, reduces the impurity concentrations to lower levels than the U.S. Process A, while not reducing P_2O_5 concentration as much; however, Process B is more expensive.

The cleaning of the wet-process phosphoric acid by means of continuous extraction with ammonia and acetone has been described for the "green acid" from North Carolina phosphate rock and the "black acid" from Florida phosphate rock [90]. An extraction process is described in [91]. For the use of chelating agents, see [92, p. 58].

Addition of ammonium fluoride to aqueous aluminum phosphate-containing slurries precipitates aluminum as $(NH_4)_3$ AlF_6 and forms ammonium and diammonium phosphate:

$$6\,NH_4F + AlPO_4 \rightarrow (NH_4)_3AlF_6 + (NH_4)_2HPO_4 + NH_3$$

resulting in a filtrate that can be subsequently worked up to give a liquid fertilizer.

Figure 16 shows how the polyphosphate content and the N : P_2O_5 ratio affect the solubility of ammonium phosphates at 0 °C. The bottom curve represents the solubility of the orthophosphates. The middle and top curves demonstrate the increase in solubility as the polyphosphate content increases [93].

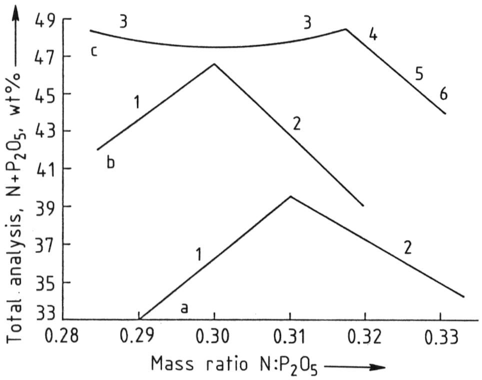


Figure 16. Effect of polyphosphate content and N : P_2 O_5 ratio on solubility of ammoniated phosphoric acids at 0 °C Polyphosphate contents as percent of total P_2O_5: a) 0; b) 45; c) 70
Crystallizing phases: 1) $(NH_4)H_2PO_4$; 2) $(NH_4)_2HPO_4$; 3) $(NH_4)_3HP_2O_7 \cdot H_2O$; 4) $(NH_4)_5P_3O_{10} \cdot 2\,H_2O$; 5) $(NH_4)_2HPO_4 \cdot 2\,H_2O$; 6) $(NH_4)_4P_2O_7 \cdot H_2O$

Table 16 characterizes NP base solutions made from superphosphoric acid. The two solutions are 10 – 34 from wet-process superacid and 11 – 37 from furnace-grade superacid. The 10 – 34 NP solution is used predominantly [77].

A large number of experimental data points were subjected to regression analysis. With the resulting equation, the total nutrient concentration in NP solutions made from ammonium

Table 15. Purification of wet-process phosphoric acid

	Raw acid	Purified acid	
		Process A	Process B
P_2O_2	52.5	40.4	48.9
Fe	0.6	0.2	0.07
Al	0.9	0.3	0.01
Mg	0.3	0.03	0.001
Fe	0.8	0.3	0.06

Table 16. Composition of NP base solutions [77]

Grade	Phosphoric acid, wt % P_2O_5	Percentage composition *				
		Ortho-phosphate	Pyro-phosphate	Tripoly-phosphate	Tetrapoly-phosphate	Higher phosphates
10–34–0	76	49	42	8	1	0
11–37–0	79 – 80	29	42	21	5	3
	80 – 81	20	37	23	10	10

* Distribution of P_2O_5 sources: of the total P_2O_5 present (34 or 37 wt %), the percentages given in the table are present in the form of orthophosphate, polyphosphate, etc.

phosphates and urea at 0 – 50 °C can be calculated with a relative error of 1 % or else determined with a nomograph [80].

Figure 17 shows schematically a plant for producing NP base solutions (tank reactor process).

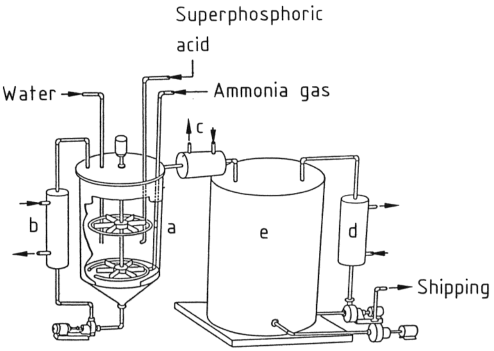


Figure 17. Plant for producing NP solution from superphosphoric acid [77]
a) Reactor; b, c, and d) Coolers; e) Storage tank

Superphosphoric acid, usually containing 40 to 50 % of the P_2O_5 as polyphosphates, ammonia, and water are continuously fed to a stirred-tank reactor. A heat exchanger operating in closed cycle holds the temperature in the reactor at roughly 70 °C. The solution concentration is controlled through density measurement, and the N : P_2O_5 ratio is controlled by means of the pH. The NP solution outlet from the reactor is cooled to 35 °C in another heat exchanger (c) before being transferred to a storage tank. To minimize hydrolysis of polyphosphate to orthophosphate, the product is further cooled to ca. 20 °C and the storage tank is protected from sunlight. The polyphosphate content of the product is always slightly lower than that of the feed acid. For example, a base solution containing about 50 % polyphosphate, which is about the minimum polyphosphate content of the product with acceptable storage properties, requires a feed acid containing 55 % polyphosphate.

Because of the expensive heat-exchange problems — heat must be supplied in the production of superphosphoric acid and removed in the subsequent ammoniation step — other techniques have been developed for producing ammonium polyphosphate solution from orthophosphoric acid in a *direct process*, thereby largely eliminating the expensive heat exchange. Two examples are the Swift process and the Tennessee Valley Authority (TVA) process.

In the Swift process (Swift Agricultural Chemical Corporation), ammonia gas reacts in a jet reactor (Fig. 18) with preheated wet-process phosphoric acid to produce ammonium polyphosphate. The phosphate melt inlet to the mixing tank is converted to liquid fertilizer by the addition of water; the grade produced is usually 10–34–0. The extent of polymerization depends on the temperature that prevails in the process reactor. At 300 °C, it is about 60 %. In addition to clear 10–34–0 liquid fertilizer, a 12–40–0 suspension can also be obtained with this process [94].

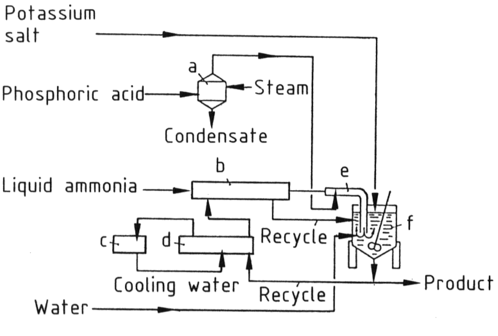


Figure 18. Swift process for producing NP (or NPK) solution from orthophosphoric acid [94]
a) Acid heater; b) Ammonia vaporizer; c) Cooling tower; d) Cooler; e) Pipe reactor; f) Mixing tank

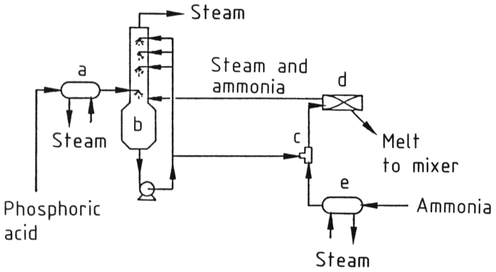


Figure 19. TVA process for producing NP solution from orthophosphoric acid [94]
a) Acid heater; b) Spray tower; c) T reactor; d) Rotating disengager; e) Ammonia preheater

The TVA process uses a T reactor (Fig. 19) to produce ammonium polyphosphate. Wet-process phosphoric acid (52 – 54 wt % P_2O_5) is preheated and then partly neutralized by ammonia in a simple spray washer (spray tower). The solution is then fed into the T reactor, which is also supplied with heated anhydrous ammonia from the other side. At the adjusted temperature of 232 – 243 °C, the reaction with ammonia goes to completion while the residual water is simultaneously vaporized and a foamy polyphosphate melt is formed [95]. After the product passes through a rotary separator (disengager), excess ammonia and steam are removed; the ammonia is scrubbed out, and the steam is discharged. From the melt, with a polyphosphate content of roughly 50 %, either clear liquid fertilizers such as 10–34–0 or suspensions such as 10–37–0 can be produced [95, 96].

The T reactor process has enabled reasonable equipment costs, process simplicity, and efficiency in the production of high-quality liquid fertilizers. The unique feature of the process is the conversion of a low-polyphosphate (20 – 35 %) superphosphoric acid to an high-polyphosphate (ca. 80 %) 10–34–0 or 11–37–0 base solution. The high polyphosphate content substantially improves the stability, storage life, and handling properties of the base solutions and NPK liquids. In contrast to the tank-reactor process the reaction is accomplished in a limited volume of the pipe reactor with minimal heat losses [97].

In the Ugine Kuhlmann process [98], clear NP liquid fertilizers with good storage properties are produced from *unpurified wet-process phosphoric acid* [90].

The crude acid is first treated with urea to yield urea phosphate, which is crystallized and separated. The mineral impurities remaining in the mother liquor can be used in the production of solid fertilizers. Thus there is no waste disposal problem. In the second reaction step, the urea phosphate is reacted with ammonia, yielding a urea – ammonium polyphosphate melt, which is dissolved in water to obtain a 16–30–0 liquid fertilizer.

3.2.2.2. NPK liquids

Liquid NPK fertilizers are produced by adding a potassium component, usually potassium chloride, to UAN and NP solutions. The amount of water needed to dissolve 100 g of a mixture of UAN, NP solution, and potassium chloride at a specific temperature, as well as the solid phase, can be shown conveniently in the form of three-component phase diagrams [80]. Other triangular diagrams show the solubility relationships in mixed liquid fertilizer systems [97]. While the clear NP solutions with polyphosphate have compositions corresponding to those of solid fertilizers, the contents must be kept lower in clear ternary NPK solutions because potassium nitrate, which is formed from ammonium nitrate and potassium chloride, has a low solubility.

Table 17 presents several three-component liquid fertilizers obtained by mixing a 10–34–0 base solution with potassium chloride powder. The added component lowers the nutrient content from almost 39 % to ca. 29 – 30 % [99].

Production takes place in either cold-mix or hot-mix plants [100], [312, p. 456]. Because cold-mix plants offer low investment costs and are easy to operate, they are in more widespread use. In a stirred vessel, the appropriate quantities of potassium chloride are added to the base solutions (e.g., 28–0-0 and 10–34–0) and mixed. Hot-mix plants, especially small-capacity ones, require relatively large investments and, because of their troublesome operation, must have well-trained personnel.

3.2.2.3. UAS Liquids

The use of high-analysis fertilizers containing little or no sulfur has led to soil sulfur deficiencies in areas far from industries. The critical level

Table 17. Three-component liquid fertilizers produced by mixing 10–34–0 base solution with KCl [99]

Fertilizer type	Salt composition, wt %						Total nutrient analysis, wt % *	Freezing point, °C
	Ammonium orthophosphate	Ammonium polyphosphate	Urea	NH_4NO_3	KCl	H_2O		
1 : 1 : 1	7.93	10.11	7.8	16.3	15.6	42.2	28.85	−21
1 : 2 : 2	9.20	12.4	5.0	10.4	18.7	44.4	29.54	−18.5
1 : 1.5 : 1	10.70	13.65	7.3	15.3	14.1	38.4	30.57	−23.5
2 : 1 : 1	5.75	7.33	11.9	24.8	10.7	39.5	27.89	−24.5
1 : 1 : 0	16.10	20.5	15.9	33.2	0	14.3	38.60	−33

* $N + P_2O_5 + K_2O$.

for sulfur in soil is 0.1 – 0.3 wt %. Sulfur deficiencies in the soil of Kuwait led to the development of a sulfur-containing liquid fertilizer: 21.2 wt % $(NH_4)_2SO_4$ + 37.6 wt % urea + 41.2 wt % water [101]. The total nitrogen content is 22 wt %, and the saturation temperature is 4 °C.

The reaction of urea with sulfuric acid

$$(NH_2)_2CO + H_2SO_4 \rightarrow (NH_2)_2CO \cdot H_2SO_4$$

yields liquid fertilizers with pH = 1. Because of corrosion, the plant must have polyethylene linings or else use expensive chrome – nickel – molybdenum steel. The following are typical UAS solutions [102]:

Sulfuric acid, wt %	N, wt %	S, wt %
28	9	27
17	16	49
15	17	52
10	18	55

Liquid fertilizers can be applied even in winter if ammonium thiosulfate is added in order to lower the salting-out temperature to − 18 °C. From the standpoint of nutrient content, this compound is better than water. Ammonium thiosulfate itself is a clear liquid fertilizer (12–0-0 + 26S) with a salting-out temperature of − 5 °C [102].

3.2.3. Suspensions

Suspension fertilizers contain solid nutrient salts, especially potassium chloride, suspended in a concentrated ammonium phosphate solution. Their development has made it possible to attain nutrient contents corresponding to those of solid NPK fertilizers:

Solutions	Suspensions
8–8-8	15–15–15
3–9-9	7–21–21
2–16–12	5–15–30
10–5-5	20–10–10

What is more, suspension fertilizers have the advantage that low-priced phosphates that are difficult to dissolve in water can also be employed.

The storage and application of suspension fertilizers, however, is more difficult than that of clear liquid fertilizers, since the former tend to undergo sedimentation. If an easily handled suspension is desired, the product must be stirred vigorously before use. Swellable clays such as palygorskite (attapulgite), a magnesium silicate-containing clay, have proved suitable as suspending agents. Suspensions thus make special demands on technique. The methods of storage, transportation, and spraying cannot be transferred directly from clear liquid fertilizer solutions. As a rule, substantial changes in equipment are needed, and these require additional investments. The quality of spray distribution does not match that for clear fertilizer solutions either. For all these reasons, suspensions have scarcely become established in Europe, despite efforts to introduce them. In the United States, on the other hand, a larger scale of farming, together with a well-developed distribution service sector, has allowed the successful introduction of suspensions.

A suspension fertilizer can be produced from *solid monoammonium phosphate* by intensive stirring in water and simultaneous adding of ammonia. The addition of swellable clay (1 – 2 %) ensures a fairly stable suspension. By dilution, a product of grade 9–27–0 is obtained. Applied in a comparable way, it behaves much like the commercial 10–30–0 liquid fertilizer [103].

Anhydrous ammonia is used to improve the solubility and mixing of monoammonium phosphate. Ammonium orthophosphate displays the highest solubility at a molar ratio $NH_3 : H_3PO_4$ of 1.5. A turbine mixer is suitable for homogenizing the suspension obtained by the addition of KCl and 1 or 2 wt % palygorskite [104].

A stable suspension is obtained by ammoniating *wet-process orthophosphoric acid* (54 wt % P_2O_5) at 71 °C and a pH between 7.5 and 8.5. The product is then adjusted to the desired pH with a small amount of acid. Because of the fineness of the solid particles, the suspension (8–24–0) remains stable. After cooling, it can be blended with urea – ammonium nitrate solutions (32 % N) and potassium chloride to produce various compositions of liquid fertilizers [105].

A two-step process developed by TVA yields low-priced, high-analysis suspension fertilizers in which the phosphate component is obtained by ammoniating orthophosphoric acid (Fig. 20). In the first reaction step, the acid is partly ammoniated with ammonia, and the solution is held for about 30 min at 106 °C. In the second step, ammoniation is completed. Then the product is cooled to 60 °C, and the suspension of fine diammonium phosphate crystals is stabilized with 1.5 wt % clay. A fluid NPK fertilizer of 15–15–15 grade can be produced from the 12–40–0 suspension [106]. Raising the acid concentration from 54 wt % to 70 – 73 wt % P_2O_5 (wet-process superphosphoric acid) gives useful suspension fertilizers. In general, however, the Mg content is so high that prolonged storage is excluded because of the precipitation of struvite, $MgNH_4PO_4 \cdot 6\ H_2O$.

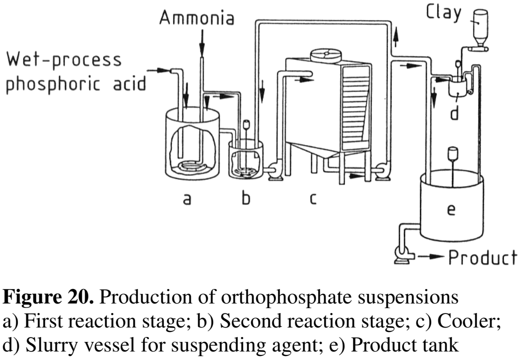


Figure 20. Production of orthophosphate suspensions
a) First reaction stage; b) Second reaction stage; c) Cooler; d) Slurry vessel for suspending agent; e) Product tank

This difficulty is avoided if *triple superphosphate* is employed as the sole phosphate source. Palygorskite is slurried with water in a mixing vessel, aqueous ammonia and urea – ammonium nitrate solution are added, and then finely-ground triple superphosphate and potassium chloride are incorporated. The suspensions made by this process have a typical grade of 12–12–12 [107]. The addition of palygorskite can be omitted if part of the triple superphosphate is first treated with aqueous ammonia to yield a voluminous precipitate, which then acts as a suspending agent for the other solid particles [108].

Suspensions from the Nitrophosphate Process. A low-cost process for producing a suspension fertilizer involves digesting crude phosphate with nitric acid. The slurry of phosphoric acid and calcium nitrate is inlet to a hot-mix plant and ammoniated to form an NP suspension fertilizer. Such processes have been developed in the United States, the USSR, and the Federal Republic of Germany [81, 109, 110]. Aside from the cheap raw material, the fixed costs of the fertilizer are relatively high. Since nitrophosphate processes yield suspension fertilizers with large amounts of calcium, the dilution effect of the calcium holds the nutrient content relatively low (e.g., 9–9-9 or 6–12–12).

High-Nitrogen Suspension Fertilizer. TVA has devised a promising method for producing a high-nitrogen suspension fertilizer (36 wt % N) [102]. This product is a mixture of microspray-crystallized urea and ammonium nitrate solution (76 wt % AN) with palygorskite. The composition is 57.5 wt % urea + 31.5 wt % ammonium nitrate + 10.0 wt % water + 1 wt % palygorskite [105, 108, 111].

Sulfur-Containing Suspensions. In regions where the effects of sulfur deficiency in the soil are pronounced in certain regions, sulfur in fertilizers not only increases yield but also can improve product quality. TVA has manufactured a 29–0–0–5S urea ammonium sulfate (UAS) suspension fertilizer in a pilot plant. The feedstocks are urea (70 % aqueous solution), sulfuric acid (93 %), anhydrous ammonia, and water. Clay (ca. 2 %) is added to the UAS solution to give the final product [102].

4. Special Fertilizers

The special fertilizers include water-soluble nutrient salts, foliar fertilizers, micronutrient fertilizers, slow- and controlled-release fertilizers, nitrification inhibitors, and organic fertilizers, including sewage sludge, compost and manure.

4.1. Water-Soluble Nutrient Salts

Especially for fertilization in commercial horticulture, but also for specialty field crops, water-soluble nutrient salts (e.g., ammonium nitrate, potassium nitrate, ammonium phosphate, magnesium sulfate) are preferably used with water-saving irrigation systems (drip irrigation/fertigation) and with soilless cultivation systems. Various crop-specific fertilizer recipes can be formulated with these salts. A convenient form for the consumer are multinutrient fertilizers made by mixing various water-soluble salts, which generally also include micronutrients. Such salt mixtures are available worldwide from most major fertilizer manufacturers.

From these salts and salt mixtures, the grower prepares highly concentrated master solutions, which for application are further diluted to render them plant-compatible and then fed into the irrigation system. By using appropriate automatic fertilizer systems it can be assured that irrigation intervals and concentration of the nutrient solution are adjusted to the crop's needs.

A distiction is made between urea-containing and urea-free nutrient salt mixtures. Since the application rate of nutrient salts is frequently monitored by means of conductivity, products containing urea cause problems as urea has no ionic conductivity and is therefore not detected. Therefore, products containing urea are mainly used for foliar fertilization (see Section 4.2) where these calibration problems do not exist and because urea nitrogen is the N form with the best uptake rate via the leaves.

A prerequisite for all nutrient salts is rapid dissolution in water without any residues. This is achieved by producing the salt mixtures from appropriate ingredients and by properly grinding them. Moreover, for special fields of application in horticulture (flood irrigation and soilless cultivation systems) they are rated by their nitrogen forms. For these fields of application, nitrate-based nutrient salts are preferred.

In principle, if appropriately diluted, all nutrient salts are suitable both for soil fertilization and for foliar fertilization.

4.2. Foliar Fertilizers

For over 100 years it has been known that nutrients can be taken up through the leaves. However, with some exceptions, plants cannot be provided with nutrients through the leaves alone, since even leafy plants such as potatoes cannot absorb sufficient nutrients through the leaves. Foliar fertilization, therefore, is usually a supplement to soil fertilization. However, it is often the case that proper foliar fertilization puts the plants in the position to utilize soil-derived nutrients better. Recent decades have seen foliar fertilizers come into use not only for special crops or in certain localities, but throughout agriculture.

Foliar fertilizers are substances that contain primary nutrients and/or micronutrients, are applied to the leaves, and are absorbed into the leaves. The most important foliar fertilizer is urea (46 % N) which is highly soluble in water and rapidly absorbed by plants via the leaves. Therefore, urea is frequently used as a component of fertilizer suspensions and solutions. In addition to nitrogen, other macro- and micronutrients can be added, frequently in a nutrient ratio tailored to the demand of specific target crops. Special raw materials and formulations ensure a good plant compatibility and optimum foliar nutrient uptake. Also used for foliar fertilization are solutions with organic ingredients (e.g., amino acids), readily soluble salts (e.g., potassium nitrate or micronutrients, mostly based on sulfate) and salt mixtures containing macronutrients and special micronutrient mixtures.

4.2.1. Production

Solid foliar fertilizers are produced by mixing salts that are readily soluble in water. Before application, the salts are dissolved for spraying. Liquid foliar fertilizers, which are made from readily soluble salts or solutions and adjusted to a given analysis, are also on the market. The production of suspensions for foliar application involves the use of dispersing agents, and in some cases ionic surfactants, to stabilize the spray.

4.2.2. Application

In order to achieve optimal utilization of nutrient uptake through the leaves, the nutrient salts must remain as long as possible in the dissolved liquid state on the leaf surface. For this reason, spraying in overcast weather or toward evening ("evening dew") gives better results than spraying on dry days in bright sunlight. Depending on the sensitivity of the leaves and the concentration of the spray liquid, application in hot, sunny weather may cause burning. Table 18 gives the time required for 50 % absorption of nutrients applied to the leaves of bean plants [113].

Table 18. Nutrient absorption rates [113]

Nutrient	Time for 50 % uptake
Nitrogen	1 – 6 h
Phosphate	2.5 – 6 days
Potash	1 – 4 days
Calcium	1 – 4 days
Sulfur	5 – 10 days
Magnesium	1 h (20 % uptake)
Iron	24 h (8 % uptake)
Manganese	1 – 2 days
Zinc	1 day
Molybdenum	10 – 20 days

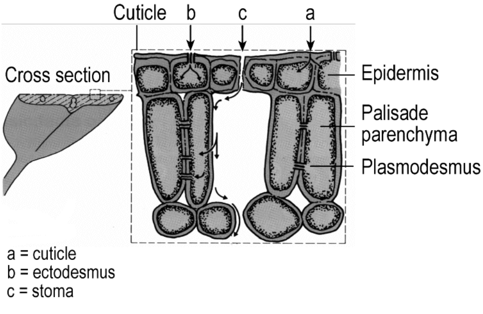


Figure 21. Access and transport paths for nutrients in leaves

Nutrients placed on the leaf surface follow three paths to the leaf cells [114 – 116]. After the cuticle has been wet by the nutrient spray, the cutin swells, which increases the distances between the wax plates in the cuticle. As a result, the nutrients are able to diffuse through the cuticle and into the cell wall (Fig. 21). The nutrients can then diffuse into the space around the epidermal cell and to the cell membranes, where they can be absorbed, or they can diffuse further along the cell wall of the epidermal cell and adjoining cells, deeper into the leaf, where they can be absorbed by a parenchymal cell. Nutrients that have been absorbed by an epidermal cell can be transferred to other cells by cytoplasmic strands connecting the cells, the plasmodesmata, a second path. If surfactants are included in the nutrient spray, a third path becomes available: the nutrients can pass through the stomata into the air spaces of the leaf.

Reasons for Using Foliar Fertilizers. Foliar fertilizers are applied to remedy obvious nutrient deficiencies. If a deficiency is recognized, the missing nutrient is supplied by spraying. If the deficiency is not well defined, complete foliar fertilizers or a mixed micronutrient fertilizer can be employed.

Another reason for foliar application is to remedy hidden (latent) nutrient deficiencies, which can seriously impair crop yield and quality.

Foliar fertilizers are also used to protect yield and quality, to meet peak nutrient demands (i.e., remedy latent deficiencies and stimulate the plants to absorb more nutrients from the soil), and to improve quality. The last point is especially important for special crops (wine, fruits, vegetables).

Advantages and Drawbacks of Foliar Fertilizers. Foliar application has a number of advantages over soil application: Nutrients act rapidly, nutrient utilization is high, nutrients are placed where they are needed, the risk of leaching losses and groundwater contamination is reduced. micronutrients are supplied to meet much of the demand for them, micronutrients are not fixed in the soil, application does not entail extra costs if fertilizers are combined with agricultural pesticides, and some nutritional problems can be cleared up only through application to the leaves or fruit (bitter pit in apples, stem necrosis in grapes).

The main disadvantages of foliar fertilization are that the action time is often short, the quantity of primary nutrients delivered is relatively small, and there are questions of compatibility in relation to concentration and prevailing weather conditions.

4.2.3. Combination with Agricultural Pesticides

Foliar fertilizers are usually applied along with agricultural pesticides for the following reasons [117]: to lower the cost of application, since pesticide spraying is required anyway; to reduce the stress due to the application of pesticide (e.g., certain herbicides); to improve the quality of pesticide spray liquids (lower the pH or increase the electrolyte content) and thus stabilize them; to reduce evaporation at low air humidity, so that most of the fine droplets reach the plant in liquid form; and to lower the surface tension of the water.

4.3. Micronutrients

The most important micronutrients (trace elements) are iron, manganese, boron, zinc, copper, and molybdenum. The delivery of micronutrients to plants is just as indispensable today as that of macronutrients or primary nutrients. Diseases resulting from an undersupply of micronutrients are seen more and more often as agriculture and gardening become more intensive, with a corresponding increase in plant nutrition [118]. For this reason, better and more specific micronutrient fertilizers have now been developed.

The term micronutrient also signifies that these substances are needed only in small quantities, often just 1 – 100 g per hectare and year. These small amounts are, however, absolutely necessary. But if the optimal dose is much exceeded, serious crop damage and loss of yield may occur. For boron, in particular, the difference between an adequate and an excessive amount is slight.

To work in the proper way, the micronutrients must be absorbed by the plants. Uptake is mainly in the form of ions: cations or metal – chelate ions of iron, manganese, copper, and zinc and anions in the case of boron and molybdenum (borates, molybdates). Absorption is through the leaves (foliar fertilizer) or the roots (soil solution).

4.3.1. Micronutrient Forms

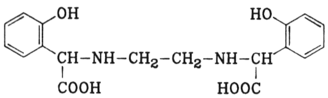
Micronutrients are used in the following inorganic forms:

1) Various metal salts (sulfates, chlorides, nitrates)
2) Milled oxides
3) Metal flours and metal slags

Table 19 lists only those micronutrient compounds that are in common use. The table also states the nutrient analyses, the solubilities in water, and the various types of fertilizers in which the compounds appear.

In addition to these, the nitrates and chlorides of iron, manganese, copper, and zinc are also used, especially in concentrated liquid fertilizers. The trace-element nitrates and chlorides have high solubilities (e.g., 268 g per 100 g H_2O for $Fe(NO_3)_2 \cdot 6\,H_2O$ or 400 g per 100 g H_2O for $FeCl_3 \cdot 6\,H_2O$; some of the nitrates and chlorides of manganese, copper, and zinc have still higher values). Because of the price and the handling qualities in the solid state, however, the sulfates are preferred. Many crops are sensitive to trace-element chlorides in large amounts. At the levels usual in foliar application, however, this is certainly not a major problem. Trace-element sulfates and nitrates provide two nutrient elements each.

Because soluble iron compounds are fixed as phosphates or oxides in calcareous soils, organic complexes were first developed for this element. One successful complexing agent is ethylenediamine di(*o*-hydroxyphenylacetic acid) (EDDHA):



Other compounds of trace metals with *N*-carboxylalkylamino acids are less effective in the soil, especially with soil pH values > 7, but if applied on the leaves are superior to the EDDHA compounds and to the simple salt solutions.

The *N*-carboxylalkylamino acids have also come into wide use today as chelating agents for manganese, copper, and zinc:

Table 19. Micronutrient fertilizers

Substances and products	Formula	Analysis, wt %	Solubility, g/100 g H_2O	Uses
Salts (technical)				
Iron(II) sulfate heptahydrate	$FeSO_4 \cdot 7H_2O$	19.5	62.3	liquid fertilizers,
Manganese(II) sulfate monohydrate	$MnSO_4 \cdot H_2O$	32	63.0	nutrient-salt
Copper(II) sulfate pentahydrate	$CuSO_4 \cdot 5H_2O$	25	36.0	mixtures, solid
Zinc(II) sulfate monohydrate	$ZnSO_4 \cdot H_2O$	35.5	63.7	straight and
Zinc(II) sulfate heptahydrate	$ZnSO_4 \cdot 7H_2O$	22	165.5	multinutrient
Boric acid	H_3BO_3	17		fertilizers,
Colemanite (boron mineral)	$Ca_2B_6O_{11} \cdot 5H_2O$	11		micronutrient and
Disodium octaborate tetrahydrate *	$Na_2B_8O_{13} \cdot 4H_2O$	20.8	9.5	multimicronutrient
Hexammonium heptamolybdate tetrahydrate	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	54		fertilizers
Oxides				
Manganese dioxide (mineral)	MnO_2	45		solid straight and
Zinc oxide (residual zinc)	ZnO	69		multinutirent
Molybdenum trioxide	MoO_3	60		fertilizers
Slags				
Copper slag flour		2.5 Cu, 0.05 Co		micronutrient fertilizers
Metal flours				
Manganese flour		20 Mn, 10 Fe, 0.5 Zn, 0.25 Cu		micronutrient
Copper flour		2.6 – 25 Cu		fertilizers

* Disodium octaborate is not a homogeneous substance. It has a $Na_2O : B_2O_3$ ratio of 1 : 4 and can be produced as a concentrated solution. It is sold by US Borax under the trade name Solubor.

EDTA	ethylenediaminetetraacetic acid
HEDTA	hydroxyethylethylenediaminetriacetic acid
DTPA	diethylenetriaminepentaacetic acid
EDDHA	ethylenediamine di(o-hydroxyphenylacetic acid)
EDDHMA	ethylenediamine di(*o*-hydroxy-*p*-methylphenylacetic acid)

Other chelating agents such as lignosulfonates and citric acid have so far been used only to a lesser extent.

4.3.2. Production

The list of fertilizers containing micronutrients comprises straight micronutrient fertilizers, combination micronutrient fertilizers, and ordinary fertilizers with micronutrients. All these types can be manufactured in either liquid or solid form. Among the solid micronutrient fertilizers, the powdered and fine-crystalline ones predominate, since nearly all of them can be dissolved in water and applied through the leaves. They generally consist of the several substances in Table 1 as well as the *N*-carboxyalkylamino acid chelates cited.

Solid micronutrient fertilizers for soil application include metal flours, metal slags, and micronutrient frits. Metal flours come from fabrication waste in the manganese production and processing industry and from specially prepared alloys. The source material is ground and granulated to between 0.25 and 1.5 mm. Metal slags such as copper slag flour are also won from waste products. The metal slags are quenched in water and comminuted to fine, powdery products.

Frits are made by melting glasses and incorporating the desired micronutrients (single-element and multi-element frits). The glasses are then finely milled [119].

Solid straight micronutrient fertilizers and multi-micronutrient fertilizers with complexing can be produced in various ways. One technique is to grind a metal sulfate with chelating agents, or several metal sulfates with chelating agents (in many cases borates, molybdates, and magnesium sulfate are added) and blending [120]. Chelation takes place when the material is dissolved in water before use. A second approach is to stir and thereby dissolve chelating acids and metal oxides (including magnesium oxide) in water at elevated temperatures; additives that cannot be chelated, such as borates and molybdates, are added; the product is further stirred, filtered, and spray-dried [121] or crystallized.

Liquid micronutrient fertilizers and combination micronutrient fertilizers can be prepared by the same technique but without the spray-drying step.

In the production of fertilizers with micronutrients, the micronutrients are usually added before granulation; in the case of liquid fertilizers, micronutrient compounds or chelates are dissolved along with the primary nutrient forms.

4.3.3. Commercial Fertilizers

Several firms in Western Europe manufacture pure micronutrients or combination micronutrient fertilizers, most of them in chelate form. Table 20 lists selected firms and examples of their products.

Urania (Germany) uses metal slags as raw material to produce granular copper fertilizers containing 2.5 % and 5 % Cu, as well as a copper – kieserite granular fertilizer with 2.5 % Cu and 21 % MgO. Similar micronutrient products and the same chelating agents are made in the United States and marketed as commercial fertilizers [119, pp. B68 to B83].

There are also fertilizers with micronutrient supplements, namely: granulated straight and multinutrient fertilizers, water-soluble nutrient salts, suspensions and solutions with micronutrients, which are chosen and added according to crop demand.

4.3.4. Use

In order to combat micronutrient deficiencies, either fertilization far exceeding actual depletion or directed foliar fertilization must be carried out [117, p. 128]. The annual depletion of micronutrients can be partly offset by the use of macronutrient fertilizers with micronutrients. On the basis of average micronutrient contents and average crops (rotation 70 % cereals, 20 % root crops, 10 % fodder), the following are withdrawn from the topsoil per hectare and year in central Europe [117, p. 122]: 400 – 700 g manganese, 260 – 400 g zinc, 150 – 200 g boron, 80 – 120 g copper. The amounts for grassland (per hectare and year) are 800 g manganese, 300 g zinc, 80 g copper, 50 g boron, and 0.5 g cobalt. In addition, leaching removes an average of 250 g manganese, 250 g boron, 100 g zinc, and 30 g copper per hectare and year [117, p. 122].

Table 20. Commercial fertilizers

Company	Products
ABM Chemical	Nevanaid Fe, finely powdered solid product with 9 % Fe (HEDTA)
(United Kingdom)	Nevanaid Fe, finely powdered solid product with 7 % Fe (DTPA)
	Nevanaid Mn, finely powdered solid product with 10 % Mn (EDTA)
Allied Colloids	Librel Fe-Dp, finely powdered solid product with 7 % Fe (DTPA)
(United Kingdom)	Librel Mn, finely powdered solid product with 13 % Mn (EDTA)
BASF	Fetrilon 13 %, spray-dried solid fertilizer with 13 % Fe (EDTA)
(Germany)	Fetrilon-Combi, spray-dried solid multimicronutrient fertilizer with 9 % MgO, 4 % Fe, 4 % Mn, 1.5 % Cu, 1.5 % Zn, 0.5 % B, 0.1 % Mo (all heavy metals as EDTA, boron as borate, Mo as molybdate)
	Nutribor, crystalline powder with 8 % B, 1 % Mn, 0.1 % Zn, 0.04 % Mo, 6 % N, 5 % MgO, 12 % S (EDTA)
	Solubor DF, microgranular with 17.5 % B
Ciba Geigy	Sequestrene 138, solid fertilizer with 6 % Fe (EDDHA), soil application
(Switzerland)	Ferrogan 330, solid fertilizer with 10 % Fe (DTPA)
Grace Rexoline	Rexene 224 Fe, powdered or granular fertilizer with 6 – 7 % Fe (EDDHMA), soil application
(Sweden)	Rexenol Cu, powdered solid fertilizer with 9 % Cu (HEDTA)
	Rexene Zn, liquid fertilizer with 6.5 % Zn (EDTA)

Normally, fertilization must more than make up for this consumption. Per hectare, boron-deficient soils must receive 1 – 2 kg of boron, and manganese-deficient soils must receive as much as 12 – 24 kg of manganese.

In order to prevent the development of latent deficiencies, micronutrients are often used in small quantities, especially for foliar application. This applies in particular to intensive cereal farming, where — even on well-supplied soils — the freely available micronutrients are soon consumed or else the nutrient flux at peak demand times cannot be covered from soil reserves. If relatively small amounts of a multi-micronutrient fertilizer are used in specific treatments during tillering and in the shoot and ear phases, latent deficiencies are generally eliminated and the yield potential is fully utilized [122, 123].

4.4. Slow- and Controlled-Release Fertilizers

4.4.1. Introduction

In plant nutrition, soil and plants are two antagonistic systems that compete for the nutrients available in or applied to the soil. This competition is the main reason why only a portion of nutrients is taken up and used by the plants and crops grown, while another portion is (temporarily) immobilized in the soil or lost by denitrification/volatilization and leaching (particularly of nitrogen) [124, p. 124]. The fertilizer industry has developed special types of fertilizers and fertilizer modifications which avoid or at least reduce such losses, such as:

- Foliar fertilizers
- Slow and controlled-release fertilizers
- Nitrification and urease inhibitors; stabilized fertilizers

The utilization rate of nutrients is improved considerably by leaf application. However, in practice it is impossible to supply all the necessary nutrients via plant leaves [124, pp. 125 – 127], [125, pp. 14 – 16]. A more practical route is the use of nitrogen fertilizers which release the nutrients according to the plants' requirements, that is, slow- and controlled-release fertilizers.

Terminology. The Association of American Plant Food Control Officials (AAPFCO) gives the following definition: "Delay of initial availability or extended time of continued availability may occur by a variety of mechanisms. These include controlled water solubility of the material (by semipermeable coatings, occlusion, or by inherent water insolubility of polymers, natural nitrogenous organics, protein materials, or other chemical forms), by slow hydrolysis of water-soluble low molecular weight compounds, or by other unknown means" [126].

There is no official differentiation between slow-release and controlled-release fertilizers. However, the microbially degradable N products, such as urea – formaldehydes (UFs and other urea – aldehyde compositions), are commonly referred to in the trade as slow-release fertilizers, and coated or encapsulated products as controlled-release fertilizers [127, p. 12].

Advantages and Disadvantages. Slow- and controlled-release fertilizers reduce toxicity, especially in use with seedlings. The toxicity of conventional soluble fertilizers is caused by the high ionic concentrations resulting from quick dissolution. Consequently, these slow and controlled-release fertilizers permit the application of substantially larger fertilizer dressings (depot fertilization). This results in significant savings in labor, time, and energy. They also allow the full nutrient requirements of crops grown under plastic cover to be met (protected crop cultivation). These fertilizers significantly reduce possible losses of nutrients due to the gradual nutrient release (particularly losses of nitrate nitrogen). They also reduce evaporative losses of ammonia. They further contribute to a reduction in environmentally relevant gas emissions (N_2O) [127, pp. 15 – 16].

There are no standardized methods for reliable determination of the nutrient release pattern available as yet due to the lack of correlation between laboratory tests and field conditions. With urea – formaldehyde fertilizers, a proportion of the nitrogen content may be released extremely slowly or not at all. With sulfur-coated controlled-release fertilizers the initial nutrient release may be too rapid and cause damage to turf or the crop. Repeated use of sulfur-coated urea may also increase the acidity of the soil. Polymer-coated or encapsulated controlled-release fertilizers can cause an environmental problem since undesirable residues of the coating material may accumulate in the fields. However, the main disadvantage is that the cost of manufacturing slow- and controlled-release fertilizers is still considerably higher than that of conventional mineral fertilizers. At present their cost/benefit ratio prevents their wider use in general agriculture. Consequently, the vast majority is applied in nonagricultural sectors such as nurseries and greenhouses, golf courses, professional lawn care, as well as by consumers (home and garden) and landscape gardeners [127, pp. 17 – 18]. Total world consumption of slow- and controlled-release fertilizers is estimated at 562 000 t (1995/96), amounting to only 0.15 % of world total consumption of $N + P_2O_5 + K_2O$ in the form of fertilizer material (ca. 380×10^6 t) [128].

Types of Slow- and Controlled-Release Fertilizers. The two most important groups are:

1) Condensation products of urea such as urea – formaldehydes (slow-release)
2) Coated or encapsulated fertilizers (controlled-release)

Of lesser importance are other organic chemicals, ion-exchange materials, and supergranules.

4.4.2. Urea – Aldehyde Slow-Release Fertilizers

Three types of urea – aldehyde condensation products (see also → Urea, Chap. 8.3) have gained practical importance:

1) Urea – formaldehyde (UF)
2) Urea – isobutyraldehyde (IBDU/Isodur)
3) Urea – acetaldehyde/crotonaldehyde (CDU/Crotodur)

At pH values below 2, crotonaldehyde and acetaldehyde can form cyclic condensation products [131]. For production of urea – aldehyde condensates, see [129, pp. 3 – 87], [130, pp. 1 – 137], [132, pp. 153 – 156], [133], [134, pp. 247 – 279].

The urea – formaldehyde products have the largest share of the slow- and controlled-release fertilizer market (40 % of world consumption in 1995/96); IBDU- and CDU-based products are less widely used (15 % in 1995/96), since their manufacturing costs are even higher than that of urea – formaldehydes [127, pp. 61 – 63].

4.4.2.1. Urea – Formaldehyde Condensation Products.

Ureaform, as defined by the American Association of Plant Food Control Officials (AAPFCO) is the oldest type of urea – formaldehyde condensate. As early as 1924, Badische Anilin- & Soda-Fabrik (now BASF) registered the first patent (DRP 431 585) on urea – formaldehyde condensation fertilizers [135]. In the United States they were patented for use as fertilizers in 1947; commercial production began in 1955.

Ureaforms are a mixture of methylene – urea oligomers of various molecular masses, polymer chain lengths, and hence varying water solubilities, such as methylene diurea (MDU), and dimethylene triurea (DMTU). They also contain a certain amount of unchanged urea.

Manufacture. The manufacture of urea – formaldehyde products is a two step process [136, p.13], [137 – 143]:

$$NH_2CONH_2 + CH_2O \rightleftharpoons HOCH_2NHCONH_2$$

$$CH_2O + HOCH_2NHCONH_2 \rightleftharpoons HOCH_2NHCONHCH_2HO$$

First, urea and formaldehyde are combined to give the intermediates monomethylol- [*1000-82-4*] and dimethylolurea [*140-95-4*]. Under acidic conditions these methylolureas react with further urea to give various oligomers of methylene urea:

$$NH_2CONH_2 + HOCH_2NHCONH_2 \rightarrow NH_2CONHCH_2NHCONH_2 + H_2O$$

In the production of granular urea – formaldehyde products, water must be removed by evaporation. The main problem in the manufacture of urea – formaldehyde slow-release fertilizers is the production of condensation oligomers in the desired proportions. A number of processes can be used to meet this target (e.g., dilute- and concentrated-solution processes). The procedure commonly applied is to use suspensions of methylene urea or solutions of urea and methylol urea as well as solid product. In this way the condensation reactions take place in the granulator itself (in situ process) [144].

Properties. The urea – formaldehyde products are separated into the following three fractions:

1) Fraction I: cold water (25 °C) soluble (CWS), containing residual urea, methylene diurea (MDU), dimethylene triureas (DMTU), and other soluble reaction products. Depending on soil temperature the availability of Fraction I nitrogen is slow.
2) Fraction II: hot water (100 °C) soluble (HWS), containing methylene ureas of intermediate chain length: slow-acting nitrogen.
3) Fraction III: hot water insoluble (HWI) containing methylene ureas of very long chain length, insoluble in both cold and hot water; extremely slow-acting or ineffective in plant nutrition.

How the proportion of the different methylene ureas affects the release of nitrogen and the nitrogen efficiency are expressed by the activity index (AI). The AI is calculated from the solubility fractions of the fertilizer under various conditions [127, p. 22]. In the past urea – formaldehydes had an AI of about 40 – 50; more recent formulations have AI values of 55 – 65.

In general, the nitrogen content of urea – formaldehyde condensation products ranges from 35 to 42 % N. The American Association of Plant Food Control Officials (AAPFCO) specifies a minimum AI of 40, with at least 60 % of the nitrogen as cold water insoluble nitrogen (CWI N), a total N content of at least 35 % N, and an unreacted urea nitrogen content of less than 15 % of total nitrogen. In the United States, Western Europe, the Former Soviet Union, and Israel research has been carried out to reduce the fraction of HWI nitrogen [148]. In the 1980s research resulted in the development of MDU/DMTU compositions which consist of shorter chain polymers with at least 60 % CWS polymer nitrogen. Although they have higher contents of CWS nitrogen, they still have safer agronomic and environmental properties than conventional nitrogen fertilizers. Commercial products are white, colorless powders or granules. In wet granulation, the pH value and temperature must be controlled to avoid hydrolysis and thus losses of formaldehyde. Under normal conditions the finished products are stable in handling and storage. Typical properties of urea – formaldehyde products are given in Table 21.

Application. The release of plant-available nitrogen from urea – formaldehyde products mainly involves decomposition through microbial activity and dissolution by hydrolysis. Consequently, factors affecting microbial activity, such as higher temperature, moisture, pH value and oxygen availability, also affect the release of nitrogen. These products are therefore widely used in warmer climates (in the Mediterranean region of Europe and in the southern and southwestern United States).

Table 21. Properties of typical ureaforms

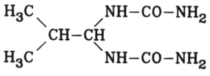
Property	Nitroform*	Azolon**
Total N, wt %	37.4	38.0
Insoluble in cold water, wt %	26.9	26.0
Soluble in hot water, wt %	15.4	10.4
Activity index	43	60
Bulk density, t/m^3		0.75
Granule size, mm	0.5 – 2.0	1.0 – 4

* Trademark of Nor-AM; BASF product analysis 1980.
** Trademark of Aglukon; analysis from [149].

4.4.2.2. Other Urea – Aldehyde Condensation Products

Due to the higher costs involved in the combination of urea with higher aldehydes, only two products have gained commercial importance. These are IBDU or Isodur (urea + isobutyraldehyde) and CDU or Crotodur (urea + acetaldehyde or crotonaldehyde).

IBDU (Isodur). Products derived through the combination of urea and isobutyraldehyde consist of mainly isobutylidene diurea [*6104-30-9*] (with small quantities of slow-acting by-products).



Isobutylidene diurea

Manufacture. Isobutylidene diurea is manufactured by condensation of liquid isobutyraldehyde with urea (either in solution or solid form). In contrast to urea – formaldehyde, the reaction of urea with isobutyraldehyde results in a single oligomer. To obtain an optimal proportion of IBDU it is important to stop the reaction by neutralization when the IBDU yield is at a maximum.

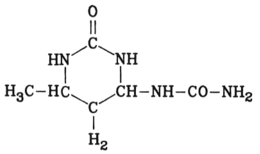
Isobutylidene diurea is produced in Japan and Germany [130, 150 – 152] (Mitsubishi, BASF).

In the BASF process urea reacts with isobutyraldehyde in an aqueous solution to give a high proportion of slow-release N [153]. A Mitsubishi-developed process is operated by IB Chemicals in Alabama.

Properties and Application. IBDU is a white crystalline solid with a theoretical N content of 32.18 wt % N. The official definition (AAPFCO) requires 30 wt % N, of which 90 % must be cold water insoluble prior to grinding. Since it is almost completely soluble in hot water, the N content is therefore nearly all slow-release N. It has a calculated AI of 90 – 99 (ureaform: 55 – 65). Nitrogen is released from IBDU by hydrolysis, which is affected by soil moisture and temperature. Both urea molecules of IBDU can be liberated. The rate of N release is mainly a function of particle size: the finer the particles, the more rapid the rate of N release. IBDU is unstable in an acid media, whereby it decomposes into the starting materials. Therefore, it tends to release its nitrogen more rapidly in strongly acid soils. This can also be counteracted by using larger, well-compacted granules [158, 159].

The safety margin and agronomic response from IBDU is good with turf; occasional phytotoxity has been observed in greenhouse use. Since it is independent of microbial activity, IBDU is particularly suited to low-temperature application. Properties of IBDU are given in Table 22.

CDU (Crotodur). Crotonylidene diurea [*1129-42-6*] is a mixture of 75 – 80 wt % crotonylidene diurea (2 mol urea + 2 mol acetaldehyde) and 15 – 20 wt % 5-oxyethylcrotonylidene diurea [*23048-84-2*] (2-oxo-4-methyl-5-oxyethyl-6-ureidohexahydropyridine), 2 mol urea + 3 mol acetaldehyde), [145] and 5 – 7 wt % K_2SO_4.



Crotonylidene diurea

Manufacture. Crotodur, which was patented as a slow-release fertilizer in 1959 [153], is produced by acid-catalyzed reaction of urea with acetaldehyde (Chisso Corp., Japan) or crotonaldehyde (BASF, Germany) [154, 155]. The mother liquor is neutralized, and the CDU isolated as a white powder by spray drying or filtration.

Properties (see Table 22). CDU or Crotodur contains 85 wt % to > 90 wt % pure crotonylidene diurea. It is almost completely insoluble in cold water, but soluble in hot water with a calculated AI of 90 – 99. In contrast to isobutylidene diurea, N release from crotonylidene diurea depends on hydrolysis and microbial activity. Only the urea molecule from the side chain (6-position) can be liberated by hydrolysis. The urea which forms part of the ring can only be released by microbial action [146]. The particle size also influences the N release; with large particles, release is strongly delayed.

Application. In Japan and Europe Crotodur is mainly used on turf and in speciality agriculture, either as a straight N fertilizer or in granulated NPK fertilizers.

4.4.2.3. Further Processing of Urea – Aldehyde Condensates

All commercial urea – aldehyde condensates such as ureaform, IBDU, Isodur, CDU, and Crotodur can be further processed by compaction or moist granulation with other conventional fertilizers with rapidly available plant nutrients, thus producing straight and compound fertilizers with both slow-release and rapidly available nitrogen. However, it is necessary to keep the pH between 5.4 and 6.2 [147], or preferably between 5.0 and 5.5 [156], the temperature below 90 °C, and the dwell time as well as the quantity of recycled material as low as possible [130, pp. 1 – 15], [156] to prevent hydrolysis and, particularly in the case of ureaform, further condensation to higher oligomers.

Commercial Products and Trade Names. There are a large number of various slow-release fertilizers based on ureaform 38–0-0, methylene ureas 40–0-0, IBDU 31–0-0, and CDU 31–0-0, which are formulated as straight fertilizers and in combination with P, K, and secondary and trace elements in solid form, as well as in solutions or suspensions: Scotts Granuform, Scotts MU-40, ProGrow, ProTurf (The Scotts

Table 22. Properties of CDU, IBDU, and Isodur

Property	CDU	IBDU	Isodur
mp, °C	245[a]	207 – 208	203 – 204[b]
Bulk density, kg/m^3	ca. 600	600 – 700	500 – 600
Solubility in water at 25 °C, g/L			
fertilizer grade		0.3 – 3.0	2.7
pure substance	1.3 (pH 2); 0.9 (pH 7)		1
Total N, wt %	31	31	31
pH (10 wt % suspension)	4 – 6	5 – 8	6 – 8
LD_{50} (rat, oral), g/kg[c]	10.0		10.0

[a] 259 – 260 °C for crotonylidene diurea (BASF).
[b] 236 °C for isobutylidene diurea (BASF).
[c] Toxicological data from BASF.

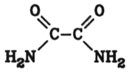
Company); Nitroform, Nutralene (Omnicology, Inc./AgrEvo); Plantosan, Nitroform, Nutralene, Azolon (Aglukon Spezialdünger). Hydroform, Hydrolene (Hydroagri US). Folocron, CoRoN (CoRoN Corp.); Isodur (Floranid), Crotodur (Triabon) (BASF); Azorit (EniChem); Urea – formaldehyde (Mitsui Toatsu Fertilizers); IBDU (Mitsubishi Kasei); CDU (Chisso).

Analyses of some typical fertilizers containing Isodur or Crotodur are listed in Table 23.

4.4.3. Other Organic Chemicals

Some other organic compounds such as oxamide, triazones, and melamine have also been used as slow-release fertilizers but have not obtained the commercial importance of urea – aldehyde products.

Oxamide [*471-46-5*], the diamide of oxalic acid, N content 31.8 wt %, M_r 88.08, *mp* 419 °C, ϱ^{20} 1.667 g/cm^3, is a nonhygroscopic, colorless compound that forms needle-shaped crystals.



Its solubility in water is only 0.4 g/L [41, p. 320]. By hydrolysis in the soil, it is transformed first into oxamic acid with liberation of ammonia, and then into oxalic acid. Oxalic acid is toxic to plants if it is not further converted into carbon dioxide by microbial activity. Because the nitrogen is released by hydrolysis, the slow-release effect is primarily a function of particle size. Oxamide is manufactured by oxidation of hydrogen cyanide with hydrogen peroxide to give cyanogen, which is then partially hydrolyzed [161]. It can also be produced directly in one step from hydrogen cyanide, oxygen, and water, with copper nitrate as the catalyst [162 – 164].

Table 23. Analysis and physical properties of typical fertilizers containing Isodur or Crotodur *

Property	Floranid permanent 15 + 9 + 15 (+ 2)**	Floranid N 32**	Triabon 16 + 8 + 12 (+ 4)**
Nitrogen content, wt %			
Total	15	32	16
IBDU	5	29	
CDU			11.0
Ammonium	5.8		4.0
Nitrate	4.2		
Carbamide		3.0	1.0
Phosphate (P_2O_5)	9		8
Potassium (K_2O)	15		12
Magnesium (MgO)	2		4
Granule size***	0.7 – 2.8	0.6 – 2.6	1.0 – 3.5
Bulk density, kg/m^3	960	600	820

* Floranid and Triabon are trademarks of BASF.
** Floranid Permanent and Triabon also contain trace elements.
*** 90 % within given range [157].

In Japan, production of oxamide as a slow-release fertilizer amounts to about 1000 t/a (1995, Ube Industries) [165].

Symmetrical Triazones. Some symmetrical triazones are used as slow-release nitrogen fertilizers [160], particularly in urea – triazone solutions with 28 % N for application to soil. Triazones are synthesized by condensation reactions of formaldehyde or other aldehydes with urea, organic amines, or ammonia [131, p. 251].

Commercial Products and Trade Names. Hickson Kerley, United States: N-Sure 28–0-0, N-Sure-Lite 30–0-0, Trisert 13–3-4.

Melamine, triaminotriazine [*108-78-1*], is a high-nitrogen (66 wt % N) crystalline powder. It is produced through heating urea under pressure in the presence of a catalyst. Melamine slow-release fertilizer material is available as a powder (Nitrazine 66 % N). Currently only small amounts are used in the fabrication of slow-release spikes and stakes for shrubs and trees.

4.4.4. Inorganic Compounds

Some sparingly soluble inorganic compounds such as metal ammonium phosphates and metal potassium phosphates [130, pp. 256 – 284] are also used as slow-release fertilizers. Their solubility in water at 25 °C is [166, 167]:

$MgNH_4PO_4 \cdot H_2O$	0.014 g/100 mL
$MgNH_4PO_4 \cdot 6H_2O$	0.018 g/100 mL
$MgKPO_4 \cdot H_2O$	0.21 g/100 mL
$MgKPO_4 \cdot 6H_2O$	0.23 g/100 mL

The release of nitrogen, particularly from the two ammonium compounds, again depends on particle size (slow release only with larger particles or granules).

The manufacturing processes for magnesium ammonium and magnesium potassium phosphates are described in [130, pp. 256 – 284], [168, 169].

Other sparingly soluble inorganic compounds which have been used as slow-release fertilizers are based on crystalline ammonium potassium polyphosphates [170], and on glassy melts of ammonium dihydrogenphosphate, potassium hydrogenphosphate, and dicalcium phosphate [171].

Commercial Products and Trade Names. MagAmp (magnesium ammonium phosphate; Grace Sierra Horticultural Products); EnMag (magnesium ammonium phosphate + potassium sulfate; ICI).

4.4.5. Coated and Encapsulated Controlled-Release Fertilizers

Coated fertilizers are conventional soluble fertilizer materials whose plant nutrients are rapidly available and which after granulation, prilling, or crystallization are given a protective coating to control water penetration and hence the rate of dissolution and nutrient release in the soil. The AAPFCO definition is: “A product containing sources of water soluble nutrients, release of which in the soil is controlled by a coating applied to the fertilizer”.

Coated fertilizers are the fastest growing group of slow- and controlled-release fertilizers in the United States and in Japan. They accounted for 24 % of total world consumption of slow- and controlled-release fertilizers in 1995/96 [127, pp. 61 – 63]. The growth is due to improved economics in production, the possibility of controlling the release of nutrients other than nitrogen, and the greater flexibility in determining the nutrient release pattern.

Many condensation polymers, drying oils, waxes, and bitumen were tested for their suitability as coating materials [129, pp. 102 – 263], [172, 173]. However, only three categories of coated/encapsulated controlled-release fertilizers have gained commercial importance:

1) Sulfur coatings
2) Polymer coatings (e.g., PVDC copolymers, polyolefins, polyurethanes, urea – formaldehyde resins, polyethylene, polyesters, alkyd resins)
3) Sulfur – polymer coatings (hybrid products with a multilayer coating of sulfur and polymer) [174 – 186]

4.4.5.1. Sulfur-Coated Controlled-Release Fertilizers

The only inorganic coating material which has achieved any importance is sulfur [129, pp. 102

– 263], [132, pp. 151 – 169], [193 – 196]. The sulfur coating can be regarded as an impermeable membrane which slowly degrades in the soil through microbial, chemical, and physical processes. Nutrient release depends on the thickness of the coating in relation to the size of the granule or prill and the quality of the urea substrate. The total N content of sulfur coated ureas varies with the amount of coating applied; products currently available contain 30 – 42 % N, 6 – 30 % S, and various sealants and conditioners. Commercial production started in 1972 when ICI commissioned a pilot plant in the United Kingdom.

Manufacture. Most of the modern industrial processes are still based more or less on the technology developed in the 1960s and 1970s by TVA [193, 194, 197] (now National Fertilizer and Environmental Research Center). Preheated (71 – 82 °C) urea granules (1.7 – 2.9 mm) are introduced into a horizontal rotating cylindrical drum. Molten sulfur (143 °C) is sprayed onto the urea granules and quickly solidifies on contact. The average target thickness is 40 µm, but there are various random proportions of granules having thin (< 30 µm), medium (30 – 50 µm) and thick (> 50 µm) sulfur coatings. Any pores and cracks are closed in a second step by addition of a polymeric hydrocarbon/petroleum-based wax or a high-viscosity polymeric paraffin oil with a polyethylene sealant (2 – 3 % of total weight). A flow conditioner such as diatomaceous earth, talc, clay, or silica (2 – 3 % of total weight) is added to give a dust-free, free-flowing product with good handling and storage properties.

Other straight and compound fertilizers can also be coated with sulfur. However, ammonium nitrates and fertilizers with high contents of nitrate nitrogen are excluded due to the risk of explosion.

Agronomic Properties. Generally, sulfur-coated urea products have good slow-release properties. However, resistance of the coating to impact and abrasion is low. The quality of sulfur-coated urea (SCU) is characterized by the rate of N release into the soil solution within seven days (TVA method). SCU-30 indicates a product that releases 30 % of its nitrogen within seven days, resulting in a rather rapid initial effect. If coated too thickly they may exhibit lock-off, i.e., no effective nutrient release. These disadvantages of sulfur-coated conventional fertilizers were the reason for the development of sulfur-coated, polymer encapsulated fertilizers.

Commercial Fertilizers and Trade Names. Sulfur-coated fertilizers are mainly distributed as straight nitrogen grades, e.g., Enspan 39 % N (Hydro Agri, North America), sulfur-coated urea, and sulfur-coated potassium (Nu-Gro Canada).

4.4.5.2. Sulfur-Coated, Polymer-Encapsulated Controlled-Release Fertilizers

Sulfur – polymer hybrid coatings combine the controlled-release performance of polymer-coated fertilizers with the lower cost of sulfur-coated fertilizers. Figure 22 [198] shows the flow diagram of the process developed by RLC Technologies. The process yields a sulfur-coated controlled-release granular urea fertilizer with a uniform, durable polymer coating over the sulfur coating. The hot-melt polymer liquid sealant of the conventional process is replaced by specific liquid monomers. When applied sequentially onto the surface of the hot sulfur-coated urea granules, they copolymerize to form a firm, tack-free, water-insoluble polymer coating sealant. The liquid monomers used in this process are diisocyanates, such as MDI (4,4-diphenylmethane diisocyanate), and a polyol mixture of DEG (diethylene glycol) and TEA (triethanolamine); the TEA acts both as a reactive polyol and a catalyst. The resulting product has improved impact resistance. The RLC sealant provides a substantial improvement over polymeric wax and solvent-dispersed sealants [198].

Commercial Products and Trade Names. The commercial products (in the United States) generally contain 38.5 to 42 % N, 11 to 15 % S and ca. 2 % polymer sealant: TriKote PCSCU 39–42N (Pursell Technologies), Poly-S PCSCU 38.5–40N (Scotts), and POLY PLUS PCSCU 39N (Lesco).

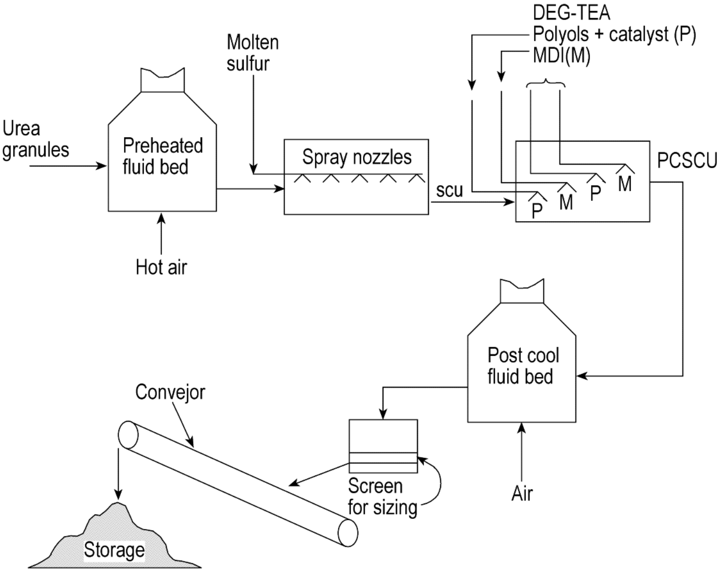


Figure 22. Flow diagram of the RLC Technologies process

4.4.5.3. Polymer-Encapsulated Controlled-Release Fertilizers

Application of controlled-release fertilizers to high-value crops requires precise control of nutrient release geared to plant requirements. Hence, a range of polymer-coated controlled release fertilizers has been developed, in which the rate of nutrient release can be altered by means of the composition and thickness of the coating, giving longevities from one to 24 months. The release pattern of these controlled-release fertilizers is significantly more linear than that of PCSCU.

Polymer coatings can be semipermeable membranes or impermeable membranes with tiny pores. Most polymers used in coating conventional fertilizers decompose extremely slowly or not at all in the soil and leave residues of up to 50 kg ha^{-1} a^{-1}). This may be considered as an environmental disadvantage even though the accumulation of 10 years (500 kg) only represents 200 ppm in dry soil. Nevertheless, extensive research is being carried out into the development of polymer coatings that are biodegraded after application. In the case of polyethylene, polypropylene, and ethylene copolymers, incorporation of ethylene – carbon monoxide copolymer promotes photochemical degradation of the coating, and coatings that contain a poly(3-hydroxy-3-alkylpropionic acid) as active ingredient are biodegradable [178, 179], [185, p. 14].

Manufacture. In the *Sierra Process* [187] the coating material is a copolymer of dicyclopentadiene with drying or semidrying oils in an organic solvent (glycerol ester of linseed oil). The granules are coated with at least two layers in a coating drum operating at 65 – 70 °C. Maleic acid, for example, is added to improve the drying of the oil. Coating weights vary from 10 to 20 wt %; the commercial products are mainly blends of different coating weights.

The *Chisso Asahi process* [188, 189] produces a particularly smooth coating. The incorporation of finely powdered inorganic materials such as talc and silica into the coating [185, pp. 15, 16] makes it possible to produce controlled-release fertilizers in which the rate of release of nutrients in the soil varies with temperature. A hot 5 wt % solution of the coating material in a hydrocarbon or chlorinated hydrocarbon solvent is sprayed onto the warm granules of fertilizer in a fluidized bed, and the solvents are immediately evaporated with hot air (60 – 70 °C).

Polyolefins, ethylene – vinyl acetate copolymers, poly(vinylidene chloride), and mixtures thereof are used as coating material. The moisture permeability is modified by means of the ratio of ethylene – vinyl acetate (high permeability) to polyethylene (low permeability) [185, pp. 12 – 16].

The release pattern is determined by a water-leach test at 25 °C; for example, T-180 indicates that the product releases 80 % of its nutrient over 180 d at 25 °C in water. Products are produced from T-40 to T-360 [185, pp. 19 – 21].

The *Pursell Technologies Reactive Layers Coating (RLC)* process [190, 191] produces attrition resistant controlled-release fertilizers by coating a plant nutrient with a coating material that chemically bonds to it. Solvent-free polyols and polyisocyanates are pumped to nozzles, located along the entire length of a horizontal, cylindrical rotating drum. The two reactive liquids are applied sequentially in ultrathin layers onto the surface of preheated urea granules, where they polymerize directly to form a continuous polyurethane encapsulating membrane. The first layer of polyisocyanate can also react with the urea granule, chemically bonding the polymer coating to the surface of the urea granule. The thickness of the layer depends on the number of reactive layers and allows controllable release durations of up to 6 months to be achieved.

The polyols used in the process are predominantly polyester polyols. The isocyanates used are also a major factor in influencing the properties of the polyurethane encapsulation. Preferred isocyanate raw materials include polymeric diphenylmethane diisocyanates. Though the process had been primarily defined for the use of urea, most other plant nutrients/fertilizers can also be utilized.

Commercial Products and Trade Names. The main polymer-coated substrates are urea (40–0-0 and 38–0-0), potassium chloride/potassium sulfate, and NP, NK, and ammonium nitrate containing NPK fertilizers. Various grades also contain secondary and minor elements.

Trade names: The Scotts Company, US: Osmocote, Osmocote Plus (NPKs + MgO + TEs), High-N, Sierra, and Sierrablen; Prokote, Scotkote. Chisso Corp., Japan: Meister (urea, KCl and K_2SO_4) Lp and Long, Nutricote (NP, NK, NPK). Pursell Technologies Inc., US: POLYON lines (PC-U, PC-SOP, PC-NPK, PC-MAP, PC-KNO_3). Agrium, Canada: Duration and ESN (clay-coated PCU). Aglukon Spezialdünger, Germany (subsidiary of AgrEvo): Plantacote Depot, Plantacote Control (NPK), and Plantacote Mix. BASF, Germany: Basacote (NPK + TE). Haifa Chemicals, Israel: Multicote 4 (PC-NPK, PC-U, PC-KNO_3). Asahi Chemical Ind., Japan: Nutricote. Mitsubishi Chemical, Japan: M cote (PCU).

4.4.6. Anti-Float Materials

Special controlled-release fertilizers which sink immediately on application have been developed for application to irrigated crops. Diatomaceous earth or wetting agents such as liquid surfactants are applied to the external surface of the coated fertilizer to achieve this antifloat effect by breaking the surface tension between the water and the coated fertilizer [192].

Commercial Products and Trade Names. Pursell Technologies Inc. POLYON PCU-AF/AntiFloat, marketed in Japan by Sumitomo; Haifa Chemicals resin-coated anti-floating urea MULTICOTE.

4.4.7. Controlled-Release Fertilizers on Carriers

Bayer manufactures controlled-release NPK fertilizers based on water-insoluble synthetic ion-exchange resins [199, 200]. The nutrients are released from the resin granules by reaction with salts in the ground water.

Commercial Products and Trade Names. Bayer AG Lewatit HD 5 NPK 18–7-15 and Lewaterr 80 NPK (31–12–33).

4.4.8. Supergranules

A slow release of nutrients can also be achieved by granulation or compaction of conventional fertilizers with a relatively small surface to volume ratio (supergranules, briquettes, tablets or sticks or stakes). Some of these formulations also contain urea – formaldehyde or IBDU.

4.4.9. Legislation

In the United States, 50 states regulate their own agricultural policies, including fertilizers. There are some guidelines and Federal EPA regulations which can be imposed on the individual states (mainly concerning registration of pesticides under RECRA — Resource Conservation And Recovery Act — in the EPA). However, fertilizers are excluded [201]. In Western Europe there are not as yet general regulations of the EU Commission on slow- and controlled-release fertilizers, and there are no coated controlled-release fertilizers in the EU type list. There are regulations concerning definitions and classification in the individual member states. These cover fertilizer types such as coated urea, coated NPK, and partly coated NPK.

In Germany, CDU, IBDU and urea – formaldehydes (UFs) are classified as individual fertilizers. Legislation also includes the group of N, NPK, NP, and NK fertilizers containing UF, CDU or IBDU; other legislation covers coated and encapsulated fertilizers [202, 203].

To achieve European standardization, a Task Force slow-release fertilizers (TFsrf) has been formed with the aim of defining the conditions under which type of fertilizer included in the EU fertilizer type list can be newly categorized as a slow- or controlled-release fertilizer [127, p. 11]: A fertilizer may be described as slow-release if the nutrients declared as slow-(controlled-) release meet, under defined conditions including that of a temperature of 25°C, each of the following three criteria:

1) No more than 15 % released in 24 h
2) No more than 75 % released in 28 d
3) At least about 75 % released in the stated release time

This European Task Force has close contacts to the Controlled Release Task Force formed in the United States by AAPFCO (Association of American Plant Food Control Officials) and TFI (The Fertilizer Institute). In Japan registration of slow- or controlled-release fertilizers requires a dissolution test in water under well defined conditions [204], [127, p. 105].

4.5. Nitrification and Urease Inhibitors

4.5.1. Introduction

Ammonium ions in the soil — whether from decomposition of organic material or from the application of ammonia-containing mineral fertilizers — are oxidized to nitrite and nitrate. Bacteria of the species *Nitrosomonas* spp. are responsible for the transformation into nitrite. The nitrite is relatively rapidly oxidized to nitrate by *Nitrobacter* and *Nitrosolobus* spp., so that there is normally no toxic accumulation of nitrite in the soil [205, pp. 156, 157], [206, pp. 287, 289]. The process is known as nitrification. The formation of the environmentally relevant gases N_2O and NO may be regarded as a side-reaction of the nitrification process [207].

Nitrate is readily soluble in water and in the aqueous soil medium, and so is completely mobile in the soil, in contrast to ammonia, which is strongly adsorbed in soil colloids and base-exchange complexes. Therefore, it can be leached readily from the soil [208 – 212]. Under unfavorable (anaerobic) conditions nitrate can be reduced by denitrification to N_2 [206, p. 289]. This can result in further considerable losses of nitrogen [213, pp. 90 – 95].

Addition of a nitrification inhibitor to ammonia containing fertilizers or urea retards nitrification and minimizes leaching of nitrogen as nitrate and losses of nitrogen due to denitrification. Furthermore, nitrification inhibitors also suppress methane emissions and lower nitrous oxide emissions [207, 212, 214 – 218].

On application to the soil, amide nitrogen, as in urea, UAN (urea – ammonium nitrate solution), and some NPK fertilizers, is transformed by the enzyme urease via the unstable ammonium carbamate ($H_2NCOONH_4$) to ammonia, and CO_2 [205, p. 156].

This transformation has two major drawbacks:

1) It results in sometimes very high volatilization losses of ammonia when urea is applied to the surface [219, 220] or under flooded conditions.
2) It can produce severe seedling damage by ammonia and nitrite [221].

Urease inhibitors inhibit or reduce the formation of urease, which is ubiquitous in surface soils.

This slows down the rate of urea hydrolysis in the soil and prevents or at least depresses the transformation of amide nitrogen into ammonia.

Definitions. *Nitrification inhibitors* are compounds that delay bacterial oxidation of the ammonium ion by depressing the activity of *Nitrosomonas* bacteria in the soil over a certain period of time. Thus, they control leaching of nitrate by keeping nitrogen in the ammonium form longer, and preventing denitrification of nitrate [222, p. 12]. *Urease inhibitors* prevent or depress transformation of the amide nitrogen of urea into ammonium hydroxide and ammonia over a certain period of time by inhibiting hydrolytic action on urea by urease; thus they avoid or reduce volatilization losses of ammonia.

There is considerable confusion concerning the terms nitrogen stabilizers, nitrification inhibitors, urease inhibitors, and stabilized fertilizers. The terms nitrogen stabilizers and nitrification inhibitors have been used interchangeably. Strictly speaking, stabilized fertilizers refers only to those which are modified during production with a nitrification inhibitor, such as ALZON and BASAMMON. In all other cases, fertilizers and nitrification and urease inhibitors are sold separately [222, p. 12].

Advantages and Disadvantages of Nitrification and Urease Inhibitors. Nitrification inhibitors significantly reduce leaching losses of nitrate by stabilization of ammonia [219, 220] and reduce emissions of the environmentally relevant gases N_2O and NO [207, 214 – 216, 223]. Nitrification inhibitors indirectly improve the mobilization and the uptake of phosphate in the rizosphere [224]. Urease inhibitors reduce ammonia volatilization losses, particularly from top-dressed agricultural fields and under reduced tillage conditions [225, p. 9, 10], [226 – 228]. Urease inhibitors furthermore reduce seedling damage where seed-placed levels of urea-containing fertilizers are too high [219, 221].

Possible disadvantages include the fact that fertilizers containing ammonia and a nitrification inhibitor may result in increased ammonia volatilization if they are not incorporated into the soil immediately after application. Depending on the type of nitrification inhibitor, the activity of soil bacteria may not only be interrupted for a certain time period, but the soil bacteria may actually be killed. This can be regarded an undesirable interference in a natural soil process [213, p. 219], [229, pp. 37 – 44].

4.5.2. Types of Nitrification and Urease Inhibitors

Extensive research on nitrification and urease inhibitors has been carried out mainly in Europe, Japan, Russia, and the United States. Various chemical fumigants and pesticides have also been tested to establish their possible effectiveness in inhibiting nitrification (nematicides; soil-insecticides and herbicides) [230, pp. 547 – 554].

Until the late 1960s research was carried out in the United States and Japan on N-Serve (2-chloro-6-trichloromethylpyridine; Dow Chemical Company), AM (2-amino-4-chloro-6-methylpyrimidine; Mitsui Toatsu Chemicals), Terrazole (5-ethylene oxide-3-trichloromethyl-1,2,4-thiodiazole; Olin Mathieson); ASU (1-amide-2-thiourea; Nitto Chemical Industry), and ATC (4-amino-1,2,4-triazole hydrochloride); substituted phenyl compounds (DCS), and compounds of the *s*-triazine line (MAST) [231, pp. 64 – 82]. In Eastern Europe and the former Soviet Union, CMP (1-carbamoyle-3-methylpyrazole) and its main metabolite MP (3-methylpyrazole) were tested extensively. However, only products based on pyridines, dicyandiamide, pyrazoles have gained practical agronomic importance as nitrification inhibitors. Terrazole, AM, and ASU (thiourea) had some regional importance, particularly in the United States and in Japan.

Reseach on urease inhibitors has concentrated on phosphoric triamides. Limited research has been carried out with PPD/PPDA (phenyl phosphorodiamidate) and ATS (ammonium thiosulfate) [222, p. 32].

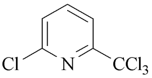
There are no reliable statistics publicly available on the use of nitrification inhibitors due to the unique production structure. Estimates of the acreage treated with fertilizers containing nitrification inhibitors for the United States are 1860 $\times 10^6$ ha (1995/96), 1660 $\times 10^6$ ha thereof with nitrapyrin and 200 000 ha with dicyandiamide. For Western Europe a very rough estimate is 200

000 ha of arable cropland treated with fertilizers containing dicyandiamide [222, p. 63, 64].

4.5.3. Pyridines

4.5.3.1. Nitrapyrin

Nitrapyrin consists of 2-chloro-6-trichloromethylpyridine [*1929-82-4*] and related chlorinated pyridines, such as 4,6-dichloro-2-trichloromethylpyridine [*1129-19-47*].



Manufacture. The (trichloromethyl)pyridine compounds are manufactured by photochlorination of methyl-substituted pyridines. The desired amount of chlorine gas is passed through the appropriate methyl-substituted pyridine, generally in the presence of its hydrochloride. The product is recovered by conventional procedures such as filtration or distillation [232]. A flow diagram for the production of chlorinated picolines from readily available raw materials such as α-picoline is given in [233].

Nitrapyrin is produced exclusively by DowElanco in the United States and distributed under the trade name N-Serve (NS) [234 – 236].

Properties. Nitrapyrin is a white crystalline solid with a mild sweetish odor, *mp* 62 – 63 °C; *bp* 101 °C at 133 Pa. For use in agriculture nitrapyrin is formulated as a liquid product.

N-Serve 24 nitrogen stabilizer consists of 22.2 wt % 2-chloro-6-trichloromethylpyridine, 2.5 wt % related chlorinated pyridines including 4,6-dichloro-2-trichloromethylpyridine, and 75.32 wt % Xylene-range aromatic solvent [*64742-96-6*].

N-Serve 24E nitrogen stabilizer consists of 21.9 wt % 2-chloro-6-trichloromethylpyridine, 2.4 wt % related chlorinated pyridines, 4,6-dichloro-2-trichloromethylpyridine, and 75.7 wt % Xylene-range aromatic solvent.

Both formulations contain 2 lb of active ingredients per gallon ($\approx$ 240 g/L); NS24 is recommended for use with anhydrous ammonia (82 % N) and impregnation onto urea; NS24E for use with liquid fertilizers (aqueous ammonia, solutions) and with manure (slurry).

Nitrapyrin has a very selective effect on *Nitrosomonas* bacteria. However, this effect is not only bacteriostatic but also bactericidal, so that part of the population in treated soil is killed [213, p. 219], [236, 237].

Toxicity. The single dose toxicity of nitrapyrin is low; the technical material has a LD_{50} of ca. 1000 mg/kg of body weight in laboratory animals. It is slightly irritating to the eyes and skin and has a low vapor toxicity. The equivalent LD_{50} (oral, female rat) for the two formulations is 2140 mg/kg (N-Serve 24) and 3300 mg/kg (N-Serve 24E). In soil and in plants, nitrapyrin is chemically and biologically rapidly degraded into 6-chloropicolinic acid, the only significant chemical residue from its use, and further to N_2, Cl^-, CO_2, and H_2O.

Application. The recommended application rate is 1.4 – 5.6 L/ha. In warm soils the nitrification inhibiting period is normally 6 – 8 weeks; it can be 30 weeks or more in cool soils.

However, in agronomic use this long-term standard nitrification inhibitor has two drawbacks:

1) Loss by volatilization from treated fertilizers during storage
2) The bactericidal effect, which may be regarded as an undesirable interference in a natural soil process

The loss by volatilization restricts it to simultaneous application with anhydrous or aqueous ammonia or fertilizer solutions which are injected directly into the soil at a depth of at least 5 – 10 cm. This limits acceptance in regions where nitrogen fertilizer is not commonly injected. Therefore, N-Serve is available commercially only in the United States.

4.5.3.2. Other pyridines

3,6-dichloro-2-trichloromethylpyridine is a proven nitrification inhibitor [238]. However, it is not readily obtained by ring chlorination of a 2-substituted pyridine because such chlorinations are not sufficiently selective to produce a preponderance of the desired isomer.

Hence, 3,6-dichloro-2-methylpyridine is prepared by the addition reaction 1,1-dichloro-2-propanone and acrylonitrile to give 4,4-dichloro-5-oxohexanenitrile. Subsequent cyclization in the presence of hydrogen chloride gives 3,6-dichloro-2-methylpyridine, which is chlorinated to obtain 3,6-dichloro-2-trichloromethylpyridine [239].

Commercial Products and Trade Names. N-Serve 24 Nitrogen Stabilizer, N-Serve 24E Nitrogen Stabilizer, DowElanco.

4.5.4. Dicyandiamide

Dicyandiamide [*461-58-5*] exists in two tautomeric forms (→ Cyanamides, Chap. 3). Its nitrification-inhibiting property was first reported in 1959 [240].

Manufacture. All large-scale production processes are based on calcium cyanamide. In the first step cyanamide is liberated from calcium cyanamide by carbonation in aqueous solution at pH 7 – 8. The cyanamide is then dimerized to dicyandiamide at pH 9 – 10.

$$\mathrm{CaNCN+H_2O+CO_2 \rightarrow H_2NCN+CaCO_3}$$

$$\mathrm{2\,H_2NCN \rightarrow H_2N-C{=}NCN}$$

The dicyandiamide is isolated by filtration or centrifugal crystallization.

The disadvantage of this production process is the high energy input for the production of calcium carbide, the raw material for the production of $CaCN_2$; this is reflected in the relatively high price for the product as a nitrification inhibitor. There are only three major producers worldwide: SKW Trostberg and SKW Stickstoffwerke Piesteritz in Germany; Odda Smelteverk in Norway; and Nippon Carbide in Japan. The former Canadian producer, Cyanamid Canada, has ceased production.

Properties. Dicyandiamide is generally supplied as white or colorless crystals in paper or jute bags. Under dry conditions it can be stored for an unlimited period. It has low water solubility (3.2 g/100 g water at 20 °C) and contains at least 65 % nitrogen. When applied to the soil it is decomposed (partly abiotically and partly biotically by specific enzymes) and converted via guanylurea and guanidine to urea, a conventional fertilizer [241 – 244].

Dicyandiamide has a bacteriostatic effect on the *Nitrosomonas* bacteria. Depending on the amount of nitrogen applied, soil moisture, and temperature, the nitrification-inhibiting effect of dicyandiamide lasts 6 – 8 weeks.

Toxicity. With an LD_{50} of 10 000 mg/kg oral (female rat), dicyandiamide is practically nontoxic. The Ames test did not reveal any mutagenic activity. Furthermore, long-term studies have shown that dicyandiamide has no cancerogenity. Therefore, any risks for human health can be excluded. This also refers to its residues [237, 245].

Processing. In Western Europe the majority of ammonium-containing fertilizers are applied in solid form. However, a satisfactory nitrification-inhibiting effect can not be obtained by simple mechanical mixing of dicyandiamide with the solid fertilizer. Dicyandiamide added to the fertilizer prior to granulation, it decomposes at the usual granulation temperatures of 100 – 140 °C. When dicyandiamide is spread onto the finished fertilizer granules it does not adhere firmly to the granule surface. The use of vegetable, animal, or mineral oils as adhesion promoters has drawbacks with regard to storage and spreading. BASF has developed a process for applying dicyandiamide to ammonium- and sulfate-containing fertilizers without decomposition and with good adherence to the surface of the granules [246]. The fertilizer granules at 60 – 130 °C are mixed in a rotary drum with 2 – 4 wt % of finely ground dicyandiamide with simultaneous addition of a 40 – 50 wt % aqueous solution of $Ca(NO_2)$. The surface of the fertilizer material is rapidly cooled, thus preventing a decomposition of the applied dicyandiamide, which adheres well to the fertilizer granules.

Freeport-McMoRan Resource Partners in the United States has developed two processes for incorporating dicyandiamide into urea in combination with other nitrification- or urease-inhibiting compounds. In the first, dicyandiamide is incorporated into urea in combination with ammonium thiosulfate and a phosphate. Controlled release of N is claimed [247]. In the second, dicyandiamide is incorporated into urea in combination with *N*-(*n*-butyl)thiophosphoric triamide (NBPT) [248].

Application. Dicyandiamide is applied directly with N or NPK fertilizers and fertilizer solution, in which it is incorporated in correct proportion for the ammonia content. These stabilized fertilizers are recommended for all agricultural crops, particularly when grown on light-textured soils where heavy precipitation is expected within 6 – 8 weeks after application or where crops have a relatively slow growth rate during the early growing stages (e.g., potatoes).

Commercial Products and Trade Names. Ensan (BASF technical product); Basammon stabil (27 % total N, of which 1.6 % is dicyandiamide N (Ensan) and 13 % S); Nitrophoska stabil 12–8-17 (12 % total N, of which 1.1 % is dicyandiamide N (Ensan), plus 2 % MgO and 7 % S). Didin (SKW technical product); Alzon 27 (27 % total of N, of which 1.6 % is dicyandiamide N (Didin) and 31 % S); Alzon 47 [47 % total N, of which 3 % is dicyandiamide N (Didin)]; Piadin (SKW Stickstoffwerke Piesteritz) liquid mixture of DCD and 3MP (3-methylpyrazole, the main metabolite of CMP) in a proportion of 15 : 1, contained in Piasin 28/Alzon-flüssig (a urea – ammonium nitrate solution).

4.5.5. Pyrazoles

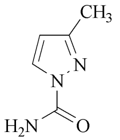
The group of pyrazole compounds has the largest number of compounds showing a nitrification-inhibiting effect [249, 250]. They include 3-methylpyrazole; 3,4-dimethylpyrazole; 4-chloro-3-methylpyrazole; 3-methylpyrazole phosphate; 3,4-dimethylpyrazole phosphate; 4-chloro-3-methylpyrazole phosphate; compounds resulting from the addition of polyacrylic acid to 3,4-dimethylpyrazole, 4-chloro-3-methylpyrazole, 3,4-dimethylpyrazole phosphate, 4-chloro-3-methylpyrazole phosphate; and from the addition of polyphosphoric acid to 3,4-dimethylpyrazole (1:20) and (1:1). In the 1980s and 1990s various compositions were patented [251 – 256, 324].

Properties. The nitrification-inhibiting effect of pyrazole compounds is better than that of dicyandiamide. However, they have one or more of the following disadvantages: they are liable to hydrolysis, which lowers the stability in storage and the activity period in the soil. They are too toxic and they are highly volatile. 3-Methylpyrazole is so volatile that significant amounts are lost when it is applied onto the surface of fertilizer granules or on fertilizer storages. Metal salts and metal complexes of 3-methylpyrazole [257] are also relatively volatile.

The most extensively tested pyrazole is 1-carbamoyl-3-methylpyrazole (CMP; in Russia: KMP). This compound is not as volatile as 3-methylpyrazole, but its manufacture is difficult and high evaporation losses may still occur when it is applied to fertilizers and on storage.

4.5.5.1. 1-Carbamoyl-3-methylpyrazole

1-Carbamoyl-3-methylpyrazole (and its metabolite 3-methylpyrazole, MP) has the molecular formula $C_5H_7N_3O$.



CMP was developed by VEB Agrochemie Piesteritz (now SKW Stickstoffwerke Piesteritz, Germany). Further research and practical use was mainly carried out in the former German Democratic Republic, in Central Eastern Europe, and in the former Soviet Union.

Manufacture. Carbamoyl-3-methylpyrazole (CMP) is produced from 3(5)-methylpyrazole (MP) by carbamoylation with sodium cyanate in aqueous HNO_3. After 1 h, the resulting CMP is removed by filtration, washed with water, and dried in a vacuum dryer. The yield is 90 %.

Properties. Bulk density 630 kg/m^3, solubility in water 0.56 g/100 g, *mp* 123 – 125 °C, evaporation pressure 4.41×10^{-2} Pa (20 °C). Therefore, the technical solid product has to be transported and stored in closed containers. When mixed with solid or liquid fertilizers, these have to be applied and incorporated into the soil immediately after preparation of the mixture. CMP has a bacteriostatic but not bactericidal effect on *Nitrosomonas* bacteria.

Toxicity. CMP has an LD_{50} of 1580 mg/kg (rat, oral) and its metabolite 3MP and LD_{50} of 1312 mg/kg (rat, oral).

Application. For use in field testing and agriculture CMP was formulated as a 50 % CMP-preparation for mixing with solid ammonium-containing fertilizers or solutions. However, because of its liability to hydrolysis and to prevent evaporation losses the CMP formulation could only be added at the time of applying the fertilizer and, like nitrapyrin, had to be incorporated into the soil immediately.

Commercial Products and Trade Names. At present (1998) there is no registration for 1-carbamoyl-3-methylpyrazole or any other pyrazole compound as a nitrification inhibitor in Europe. In accordance with German fertilizer law, Stickstoffwerke Piesteritz has registered a 15 : 1 mixture of dicyandiamide with 3MP under the name Piadin, recommended for use with UAN fertilizer solutions.

4.5.5.2. Outlook

In recent years research has concentrated on overcoming the high evaporation losses on adding pyrazole compounds to fertilizer granules and solutions, on storing such modified fertilizers, and on applying them onto the soil. BASF [258] has reported a process in which fertilizer granules are covered with salts of 3-methylpyrazole and made resistant against abraision and evaporation by addition of an inorganic or organic polyacid [259]. This treatment significantly lowers the volatility of the nitrification inhibitor and allows smaller amounts to be used. The storage stability of fertilizers treated by the BASF process is also improved. In a test for 4 weeks at 30 °C, 40 – 50 % R. H., and 1.2 m/s air velocity on 3,4-dimethylpyrazole/polyphosphoric acid 1/20 and 1/1 (DMPP), losses of the applied nitrification inhibitor were 0 and 12 %, respectively. Thus, DMPP is of future interest as a nitrification inhibitor.

4.5.6. Neem/Neem-Coated Urea

The extract from the press cake of the seed of the neem tree (*Azadirachta indica*) exerts a nitrification-inhibiting effect on *Nitrosomonas* spp. This effect is reversible.

The active compound in this biological nitrification inhibitor consists of various terpenes/triterpenes (epinimbin, nimbin, deacetylnimbin, salanin, azadirachtin, deacetylsalanin).

Toxicity. The formulated product is nontoxic.

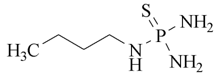
Application. For practical use, a product containing 5.0 % active ingredient is to be mixed with urea in a ration of 1 : 100 before application.

Commercial Products and Trade Names. Nimin (5 – 5.5 % active ingredient) produced by Godrej Agrovet, Pirojshanagar (India).

4.5.7. Urease Inhibitors

Although it has long been known that substantial evaporation losses in form of ammonia from urea may occur, it was only in the 1980s that the first chemical substances with effective urease-inhibiting properties in soils were disclosed, namely the phosphoric triamide compounds. Losses of between 3 and 40 % and more of applied nitrogen are possible when urea is not incorporated immediately after application and stays on dry soil (particularly on soil with a high pH and with high temperature). Also if it is applied with conservative tillage, particularly no-till, and on crops which are not tilled, such as bananas, sugar cane, oil palms, and rubber, as well as on flooded rice [206, p. 290], [213, p. 211], [218, 260 – 263], [264, pp. 52, 59]. Reference [265] lists 146 triamide compounds, of which *N*-(*n*-butyl)thiophosphoric triamide (NBPT) showed the best inhibition values.

***N*-(*n*-butyl)thiophosphoric triamide** [*94317-64-3*], NBPT urease inhibitor is the best developed of the *N*-alkyl thiophosphoric triamide for commercial applications.



Manufacture. NBPT is prepared by a two-step synthesis in THF:

$$PSCl_3 + n\text{-}BuNH_2 + NEt_3 \rightarrow n\text{-}BuNHPSCl_2 + HNEt_3Cl$$

$$n\text{-}BuNHPSCl_2 + 4\,NH_3 \rightarrow n\text{-}BuNHPS(NH_2)_2 + 2\,NH_4Cl$$

The approximate product composition from this manufacturing process is as follows [337]:

- *N*-*n*-butylthiophosphoric triamide (NBPT), min. 85 wt %
- *N*,*N*-di-*n*-butylthiophosphoric triamide (DNBPT) 0 – 3 wt %
- *N*,*N*,*N*-tri-(*n*-butyl)thiophosphoric triamide (TNBPT) 0 – 3 wt %
- Thiophosphoric triamide (TPT) 0 – 3 wt %
- Others 0 – 10 wt %
- THF 0 – 2 wt %
- Triethylamine 0 – 2 wt %

Properties. Pure NBPT is a white crystalline solid, industrial grade NBPT is a waxy, sticky, heat- and water-sensitive material, which render this material difficult to handle. This material is susceptible to decomposition during storage and distribution. The vapor pressure is 1.1 kPa at 40 °C. The compound is an excellent urease inhibitor that inhibits the activity of urease for 12 – 14 d on dry soil. When incorporated into the soil in combination with urea or urea-containing fertilizers, it significantly reduces seedling damage when seed-placed levels of such fertilizers are too high [219, 221]. For satisfactory use on flooded crops, further research is needed. *N*-methyl-pyrrolidone (NMP) is a good carrier for NBPT [268]. However, cheaper formulations with better long-term stability are obtained with glycols and glycols with a liquid amine cosolvent [269].

Toxicity. The acute oral LD_{50} of NBPT is 1000 – 4000 mg/kg. The Ames tests were negative [266, p. 23]. The compound poses a very low acute toxicity hazard to workers and has received EPA approval. Because it inhibits free urease in the soil without affecting bacterial growth, it is not classified as a pesticide and hence not regulated under TSCA. In the soil, the product degrades into the fertilizer elements nitrogen, phosphorus and sulfur.

Application. For practical use in agriculture NBPT (Agrotain) is formulated as a green clear liquid containing [267] 25 % *N*-(*n*-butyl)thiophosphoric triamide, as active ingredient, 10 % N-methylpyrrolidone, and 60 – 65 % other nonhazardous ingredients. The recommended rate of application depends exclusively on the quantity of amide-nitrogen applied as urea, UAN, or in the form of NPK-fertilizers (1.4 kg per tonne of urea).

Agrotain is primarily recommended for preplanting surface application of urea and urea-containing fertilizers, but may be used in preemergence, side-dress, top-dress, or other post-planting applications. It is not recommended for use if rain is imminent [222, pp. 38, 39].

Commercial Products and Trade Names. The only commercial product for use in agriculture is Agrotain (IMC-Agrico).

4.5.8. Environmental Aspects

In assessing the value of nitrification and of urease inhibitors not only must the better utilization of the applied nitrogen be taken into account, but also the possibility of maintaining clean ground water, as well as reduced emissions of ammonia and other environmentally relevant gases [222]. In Germany, where, in water catchment areas with restrictions or for other reasons, a reduction in applied nitrogen is required, the recommendation is that nitrogen application can be reduced by approximately 20 kg/ha without loss of yield.

Of equal importance are the positive environmental properties of nitrification inhibitors in significantly reducing emissions of climatically relevant gases such as N_2O and methane [207].

The application of urea or UAN-solution modified with a urease inhibitor such as NBPT would permit a substantial reduction in nitrogen losses to the atmosphere, and consequently also in the application rates, without affecting growth and yield of fertilized crops.

4.5.9. Legal Requirements

In Western Europe, there is no uniform regulation for DCD, the leading nitrification inhibitor (urease inhibitors are not yet in use). As in the case of slow- and controlled release fertilizers, individual countries [270, 271] have established national classification and legislation [272]. The pyrazole compound CMP (in combination with DCD) also comes under fertilizer legislation.

In the United States only fertilizers, but not additives to fertilizers, are excluded from RECRA (Resource Conservation And Recovery Act) regulations of the EPA. Therefore nitrapyrin — the active ingredient in N-Serve, the leading nitrification inhibitor in the United States — is classified as a pesticide in the EPA registration. In 1996 it was decided that all nitrification inhibitors have to be EPA registered as pesticides in the United States [222]. However, in spite of the new regulation, DCD will not require registration as a pesticide. NBPT, which does not affect soil organisms, is not classified as a biocide, but is regulated under the TSCA.

4.6. Organic Fertilizers (Secondary Raw Material Fertilizers)

At present an EC catalogue of commercial organic fertilizers is not available. Since these fertilizers mainly contain exploitable plant and animal wastes and in future will contain more waste of organic origin (with or without pretreatment such as composting, anaerobic fermentation, etc.), comprehensive legal provisions are in preparation. In Germany these organic fertilizers are designated secondary raw material fertilizers (*Sekundärrohstoffdünger*). According to the German Fertilizer Law their main components are organic waste materials for agricultural and horticultural utilization (secondary raw materials). These fertilizers are also subject to the German Waste Law (analysis of pollutant content, description of subsequent utilization) and the German Fertilizer Law (control of nutrient content) [273 – 275]. Depending on the quality standard, monitoring systems varying in analytic sophistication are specified. The main argument for the application of these fertilizers is the preservation of natural (and therefore limited) nutrient resources (e.g., P) by means of systematic recycling. The applied amount of these fertilizers is mainly limited by their nutrient content. In the case of low quality, the pollutant load can also determine the applied quantity. In Germany the permitted pollutant load conforms to the threshold values fixed in the decrees for the utilization ofsewage sludge (AbfKlärV), which are likely to be lowered substantially for reasons of soil protection [276]. According to the pollutant content or the ratio of nutrients to pollutants, organic wastes can be ranked as to their applicability as secondary raw material fertilizers (Fig. 23). For fertilizers containing several organic waste materials, each component must meet the legal requirements for secondary raw material fertilizers. Blending of unapproved material with compounds of low pollutant content is prohibited.

Another group of organic – mineral fertilizers are mixtures of fertilizer salts (N, P, K) with peat, composted bark, lignite dust, or, occasionally, dried slurry. The difference between these fertilizers and secondary raw material fertilizers is that the primary product of organic origin is not classified as waste. Nevertheless, threshold values for heavy metal concentrations have been set [e.g., 3 mg Cd/kg dry weight (dw); 750 mg Zn/kg dw]. In the case of peat, different combinations of fertilizer salts (N, NP, NPK, PK) are added. In the case of composted bark, lignite, or slurry, only mixtures with NPK fertilizers are supplied [274].

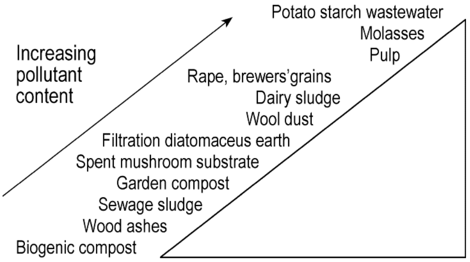


Figure 23. Applicability of wastes for agricultural use [277]

Organic fertilizers are also classified according to their effects:

- Fertilizers with an improving effect on soil condition have a stable organic substance as well as a slow effect on N supply (low concentration of readily available nitrogen)
- Fertilizers with short-term effects on nutrient supply, especially of nitrogen, have high contents of mineral nitrogen and/or readily available organic N compounds

Examples for the first category are composts (i.e. biogenic composts, garden composts) and fertilizers based on peat. The second category includes sewage sludge (high NH_4 concentration), blood meal, and potato starch wastewater (readily degradable organic N compounds).

Organic fertilizers with or without the addition of mineral fertilizer salts are classified as follows:

1) Fertilizers based on peat (or materials of similar stability): peat, composted bark, lignite
2) Fertilizers based on waste materials of animal origin: horns, bone meal, blood meal, hide meal, feather meal, guano
3) Fertilizers based on waste materials of plant origin (selected examples of waste materials from the food- and feedstuff industries): castor cake, cacao waste, brewer's grains, rape (marc), vinasse, spent mash, potato starch wastewater, filtration diatomaceus earth
4) Fertilizers based on municipal waste: sewage sludge, biogenic and garden composts

4.6.1. Fertilizers Based on Peat or Materials of Similar Stability

Peat is an organic material of stable structure and low nutrient content that has no effect on nutrient supply without the addition of mineral fertilizers, but improves soil condition (e.g., aeration, water-retention capacity). The raw material for peat fertilizers is mainly highly decomposed upland moor peat (black peat) or acidic low moor peat (pH < 6). These peats (pH 3 – 5, volume weight 50 – 200 g/L, salt content 50 – 1500 mg/L, ash 2 – 15 %, organic matter 85 – 98 %) have high sorption capacity (cation sorption capacity 300 – 600 mval/L).

Depending on the kind of application, the crop, and the nutrient status of the soil, several mixtures of peat with mineral fertilizers (N, NP, NPK, and PK salts) are available. The following minimum requirements for nutrient content are specified: 1 % N, 0.5 % P, 0.8 % K, 30 % organic substance [274].

Similar mixtures of organic and mineral fertilizers are based on composted bark or lignite (partial substitute for peat) and other organic materials such as dried slurry or spent mushroom substrate (SMS). The minimum fraction of organic substance is set at 15 %. The organic substance of composted bark is highly stable against biological degradation and resembles the organic substance of peat. After complete decomposition, composted bark shows no N immobilization and is therefore suitable for replacing peat in mixtures with other fertilizers (pH 5 – 7, volume weight 150 – 300 g/L, salt content 100 – 1500 mg/L, ash 12 – 45 %, organic substance 55 – 88 %). Threshold values for heavy metal concentrations are specified for these fertilizers [274, 278].

4.6.2. Fertilizers Based on Waste Materials of Animal Origin

Only waste materials that pose no health risk may be converted into fertilizers. The raw materials arise as byproducts at butchers' shops, slaughterhouses, and carcass-disposal plants. Horn, bone meal, and blood meal are the most widely used in agriculture. In some cases, the primary products, containing mainly N and P, are upgraded by the addition of K salts [279 – 282].

Horns. Horn materials (e.g., horns, hoofs, claws) consist mainly of the filament protein keratin. Since keratin decomposes slowly, horns represent a slow N source (22 % of the protein is in the form of cystein). The rate of N release increases with the extent of grinding (chips < grit < meal). Nutrient concentrations are listed in Table 24.

Bone Meal. Bones are ground, partly degreased, and cleaned. The main constituent of bone protein is the filament protein collagen (90 % of bone N is bound in collagen). By treatment with hot water and steam, collagen is converted into glutine and is removed. Therefore, steamed bone meal contains only 0.8 % N (untreated bones 4 – 6 % N). Due to the high P content (7 – 12 % P), bone meals are mainly applied as P fertilizers (Table 24). Occasionally, tricalcium phosphate is converted into monocalcium phosphate by acid treatment.

Blood Meal. Besides blood, blood meals often contain other slaughterhouse wastes such as intestine contents. These mixtures are dried and ground (N content 9 – 13 %; Table 24). Sometimes, mixtures of fresh blood (3 % N, 0.1 – 0.2 % P, 0.1 % K, 80 % water content) with solid wastes are used. Like meat meal, blood meal has a short-term effect on N supply.

Table 24. Nutrient concentrations in fertilizers based on animal wastes (% in dry matter)

Fertilizer	N	P	K	Ca	Mg	C/N
Horn	10 – 14	0.4 – 4.0	0.2 – 0.8	1.5 – 7.5	0.5 – 1.0	3 – 4
Blood meal	9 – 13	0.2 – 1.0	0.2 – 1.5	1.5 – 3.0	0.4	2.4
Feather meal	12	0.3	0.2			4
Bone meal	4 – 6 (0.8)	7 – 12	0.2	18 – 25	0.6	4.5
Carcass meal	6 – 11	2.4 – 7.0	0.3 – 0.5	4 – 10	0.2	3.5
Guano	8 – 16	2 – 7	1 – 3	18	3 – 5	3 – 4

Hide Meal. The main constituents of hide meal, a waste material from leather production, are skins and hair. The effect on N supply is quite slow (8 – 11 % N dw, C/N 5). In Germany, the threshold value for Cr^{3+} is set at 0.3 % in dry matter (for agricultural utilization, Cr^{6+} is prohibited in hide meal).

Feather Meals. These fertilizers show slow N release, comparable to that of horns. The N content of 13 – 14 % (Table 24) is mainly bound as keratin.

Meat and Carcass Meal. Occasionally, meat meal and carcass meal are converted into organic fertilizers. These slaughterhouse wastes have a high proportion of protein and hence a short-term effect on N supply (meat meal: 11 % N, 2.4 % P; meat-and-bone meal: 10 % N, 2.5 – 7 % P; carcass meal 6 – 10 % N; Table 24).

Guano consists of partially mineralized excrements of seabirds and can also contain feathers and carcasses. It is obtained from deposits in arid coastal regions of South America. Guano is converted to guano fertilizers by acid treatment. Guano fertilizers consist mainly of inorganic substances and contain 8 – 16 % N, 2 – 7 % P (ammonium and calcium phosphates) and 1 – 3 % K (Table 24). Since up to 50 % is in the form of ammonium, guano has a short-term effect on N supply.

4.6.3. Fertilizers Based on Wastes of Plant Origin

Provided the waste materials do not pose any health risk, conversion into fertilizers can be performed without special pretreatment. Both aerobic (composting) and anaerobic methods (fermentation, generation of biogas) are suitable for the treatment of plant wastes. The pretreatment and conditioning of some wastes are regulated. All substances described have low pollutant contents. Therefore, the applied quantities are only limited by nutrient contents [274, 281, 282]. The nutrient concentrations in these fertilizers are summarized in Table 25.

Castor cake is the residue of castor beans after oil has been pressed. Owing to its high protein concentration, castor cake contains 5 – 6 % N, which is ammonified in soil quite rapidly and thus becomes plant-available. The fertilizers are only traded in sealed packages due to their allergenic properties. Furthermore, the toxic substances ricin and ricinin must be destroyed by steam treatment at 120 °C for several hours, and dust has to be absorbed by treating the castor cake with linseed oil.

Cacao waste is a residue of cocoa production and has a lower N and P content and higher K content than castor cake.

Brewers' grains (water content 75 %) and *rape* (water content 40 – 60 %) result as waste from brewing and from production of fruit juices and wine. They are used as fertilizers in fresh and composted form and have only a minor short-term effect on N supply.

Vinasse. Sugar-containing molasses is a waste material of sugar production from sugar beet. It is used for alcohol, yeast, and glutamate-production. The remaining sugar-free molasses is concentrated to 60 – 70 % and is then used as sugar-beet vinasse, an organic N and especially K fertilizer. Vinasse has a medium-term effect on N supply.

Pulp remains after alcohol production (distillery) from corn or potatoes (5 – 7 % dry matter). Potato pulp contains more K than corn pulp.

Table 25. Nutrient concentrations (% dw) in fertilizers based on wastes of plant origin

Fertilizer	N	P	K	Ca	Mg	org. S	C/N
Castor cake	5.5	0.8	0.8 – 1.6	0.4	0.3	80	8
Cacao waste	2.3 – 3	0.4 – 0.5	2.5 – 3.0	0.6	0.5	90	17 – 24
Brewers grains	4	0.4 – 0.7	0.5 – 1.0	0.3	0.2	65 – 75	10 – 12
Fruit pulp	1.0	0.3	1.3	0.8	0.1	85 – 95	40 – 50
Rape	1.5 – 2.5	0.4 – 0.8	3 – 3.5	1.0 – 1.8	0.2	75	20 – 30
Vinasse	3 – 4	0.15	6 – 7	0.6 – 1.2	0.3	50	8
Pulp	5 – 6	0.7 – 1.0	0.8 – 6.0			75 – 85	8 – 10
Potato starch wastewater	4 – 8 *	0.7 – 0.9 *	10 * – 12				5 * – 7
Filtration diatomaceus earth	0.7	< 0.1	< 0.1	0.2	< 0.1	6	4 – 8

* In fresh potato starch wastewater.

Pulp has a medium-term effect on N supply, because potato and corn protein must first be decomposed by microorganisms. Ten cubic meters of pulp is equivalent to 30 – 40 kg N, 4 – 6 kg P, 5 – 40 kg K, and 200 – 300 kg C. Pulp is applied for fertilization as fresh material. Storage without addition of preservatives leads to unpleasant odors [283].

Potato Starch Wastewater. The production of potato starch generates large quantities of potato starch wastewater, which is used as a fertilizer. Depending on the production technique, 3 – 50 % of the total N is present in the ammonium form. Furthermore, the protein N is mineralized rapidly. Therefore, potato starch wastewater has a short-term effect on N supply. It also has a high K concentration. Potato starch wastewater is classified as follows:

- Fresh potato starch wastewater (ca. 6 % dry matter; 1 L is equivalent to 60 g dry matter, 5 g N, 025 g P, 6 g K)
- Treated potato starch wastewater (e.g., protein precipitation, evaporation, partly mixed with wastewater), 1 – 5 % dry matter (in the case of storable syrup, up to 55 % dry matter [284, 285])

Filtration diatomaceous earth is the filtration residue in breweries (75 % water content). Yeast proteins are the main N-containing substances. Owing to the narrow C/N ratio, this waste material has a short-term effect on N supply.

4.6.4. Fertilizers Based on Municipal Waste

This group is represented by biogenic and garden composts as well as by sewage sludge. In Germany the produced nutrient quantity of secondary raw material fertilizers is estimated at 270 000 t N per annum and 90 000 t P per annum, of which sewage sludge accounted for 60 % of N and 75 % of P. Composts accounted for 20 – 25 % of N and P. This demonstrates the importance of nutrient recycling by utilizing these waste materials as fertilizers. The precondition for recycling these wastes in agriculture and horticulture is a high quality standard, which strongly depends on the content of pollutants, especially heavy metals, dioxines, and furans. In Germany legal provisions for the utilization of sewage sludge and biocomposts have already been set or are in preparation (Waste Law, Fertilizer Law). These rules are likely to reduce environmental risks to a tolerable minimum and to promote the acceptance of the secondary raw material fertilizers [275, 281, 282]. Lately, sewage sludge and biocomposts have been classified as organic NPK fertilizers in the group of secondary raw material fertilizers [274].

Sewage sludge is mainly produced in municipal purification plants. Sewage sludge is classified into primary (residue after mechanical purification, deposits in settling tanks) and into secondary sludge (residue after biological purification by biomass and chemical purification by precipitation). Generally, the two kinds of sewage sludge are mixed and are subjected to various treatments. A precondition for the utilization of sewage sludge as fertilizer is an acceptable health standard. In Germany pollutant concentrations of sewage sludge have been considerably reduced over the last 20 years (e.g., Cd, Figure 24). At present, the average Cd concentration is 80 % lower than the threshold value specified in the decrees (AbfKlärV) for the utilization of sewage sludge (10 mg Cd/ kg dry matter) [276]. In 1993 dioxin and furan concentrations averaged 27 ng/kg, well below the threshold value of 100 ng/kg dry matter. Adjustment of the threshold values to the present quality standard is in preparation. In 1994 the average concentrations of heavy metals in sewage sludge applied in agriculture (in mg/kg dry matter) were Pb 84, Cd 1.8, Cr 56, Cu 251, Ni 32, Hg 1.6, Zn 977, all well below the permitted maximum loads set in the decrees for the utilization of sewage sludge (AbfKlärV) [276, 286].

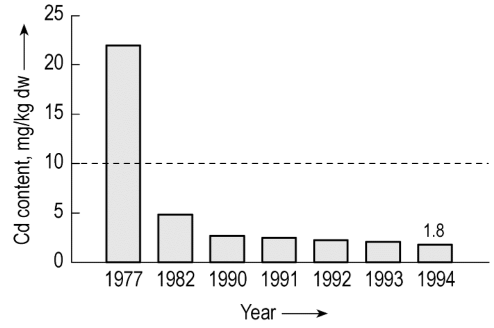


Figure 24. Cadmium concentration in sewage sludge from 1977 to 1994 [286] (the dashed line marks the threshold value for agricultural use [276])

Depending on the pretreatment (dewatering; precipitation of P with Ca, Fe, Al salts; lime addition) nutrient concentrations in sewage sludge vary considerably (Table 26). Therefore, the nutrient contents of these fertilizers must be routinely monitored and adjusted if necessary. The short-term effect on N supply depends on the NH_4 content (fraction of total N). The effect on P supply depends mainly on prior precipitation and pretreatment (lime addition, drying). The applied amount of these fertilizers is determined by nutrient concentrations. For example, the input of P should correspond to the P removed by harvest. Thus the applied quantity remains under the maximum amount of 5 t dry weight of sewage sludge per hectare in three years.

Biogenic and Garden Composts. Biogenic compost originates from biologically degradable waste, separated and collected in households. The portion of biologically usable waste in total domestic waste is 30 – 40 wt %. Garden compost consists of waste materials of plant origin such as litter or remains from pruning, collected in gardens, parks, and embankments and in National Parks. Composts represent the final product of a controlled rotting process in piles or bioreactors. According to the extent of rotting, composts are characterized as fresh or mature composts. Biogenic wastes are subjected to biogas production and subsequent composting.

As a result of the separate collection of the organic wastes, biogenic composts have lower pollutant concentrations than composts based on total domestic wastes (Table 27). Heavy metal concentrations of biogenic and especially garden composts remain under the threshold values set in the decrees for the utilization of biogenic composts (BioAbfV, in preparation). Average concentrations of organic pollutants (e.g., dioxins, furans) of 10 – 15 ng TE/kg dry weight lie within the range of the unavoidable natural background load from the atmosphere. Nutrient concentrations of composts vary less than those of sewage sludge but still have to be routinely monitored (Table 28). Garden composts have lower nutrient contents than biogenic composts. Compared to sewage sludge (high N and P levels) composts have high K contents and mainly a soil-meliorating effect. The short-term effect on N supply is quite low (only 10 % of total N is represented by mineral N). An effect on N supply is barely detectable after applications for several years. The maximum quantity of compost application is likely to be restricted to 20 t (30 t in case of high quality , i.e., minor contents of heavy metals) dry weight over three years per hectare [i.e., 100 (150) kg ha^{-1} a^{-1} of N) [275, 287, 289].

4.7. Manure

There are four types of animal manures: solid manure, liquid manure, slurry, and dry manure from poultry. Solid manure consists of feces, urine, and bedding. Usually, *solid manure* contains 100 % of the feces; the fraction of the urine retained depends on amount and kind of bedding material, animal type, and the way of housing. The most widely used bedding material is straw, but it can also be peat litter or sawdust. *Liquid manure* contains the urine of the animal to-

Table 26. Dry matter and nutrient contents of sewage sludge (in wt %) [275]

	Dry matter	N	P	K	Mg	CaO
Range	6 – 23	2 – 6	1.5 – 7.0	0.2 – 0.5	0.4 – 0.7	0 – 15
Maximum	75	25	15			40
Average	12	3.8	1.6	0.3	0.6	

Table 27. Heavy metal concentrations in composts originated from domestic, biogenic and garden wastes (mg/kg dry matter) [287, 288]

Element	Domestic waste	Biogenic waste	Garden waste	Maximum concentration (BioabfV *)
Pb	286	55	59	100 (150) **
Cd	3.9	0.4	0.4	1 (1.5)
Cr	60	27	28	70 (100)
Cu	261	50	36	70 (100)
Ni	40	15	14	35 (50)
Hg	2.6	0.3	0.2	0.7 (1)
Zn	1020	201	133	300 (400)

* BioabfV: Bioabfallverordnung (German Biowaste Regulations), August 1998.
** Maximum quantity of compost application: 30 (20) t dry weight over three years per hectare.

Table 28. Nutrient concentrations in composts (% dry matter) [275]

Compost from	N	P	K	Mg	CaO	Salts (g/L)
Biogenic wastes	1 – 1.8	0.2 – 0.5	0.5 – 1.3	0.3 – 1.6	1.7 – 9.5	3 – 9
Garden wastes	1.0	0.2	0.6	0.5	8.5	(1 – 6)

gether with some rain water and cleaning water and small amounts of feces and bedding material. *Slurry* is a mixture of feces and urine with some additional water and some bedding and feed material. *Layer dry manure* consists of the excrement layers from battery farming.

Solid manure production is the most frequent animal manure handling system for raising young layers, broilers, turkeys, and cattle, the latter especially on smaller farms. For fattening pigs and cattle on larger farms, slurry systems have been favored in the last 30 years because production costs, especially labor costs, are lower.

4.7.1. Composition [290 – 296]

A major fraction of the nutrients consumed by animals is excreted with the feces and urine. For nitrogen, this is ca. 70 – 80 % of the intake, for phosphorus ca. 80 %, and for potassium 90 – 95 %. Table 29 lists the nutrient amounts produced per year by various animals.

The nutrient contents of manures are affected by type of feed, kind and amount of bedding material, amount of water supply, and kind and length of storage. Even for the same type of manure, the nutrient content can therefore show a wide range; deviations of more than ± 50 % from the average contents are possible. Table 30 lists the average content of organic matter, nitrogen, phosphorus, and potassium in various types of manures.

4.7.2. Manure Nutrient Efficiency [291, 294, 297 – 303]

Availability of Nutrients. In animal manures, phosphorus, potassium, magnesium, calcium, and the micronutrients are predominantly present as inorganic compounds. Their plant availability is comparable to that of mineral fertilizers. The fraction of inorganic nitrogen depends on the type of manure (Table 31). The organic nitrogen becomes partly available to the crop after mineralization in the soil. In the long run and under optimal conditions, liquid manure reaches a nitrogen fertilizer equivalent of up to 100 %, slurry 70 – 90 %, poultry excrement 60 – 70 %, and solid manure 50 – 60 %.

As for all fertilizers, especially with regard to nitrogen, the nutrient efficiency of manures is highly dependent on the application conditions. Especially for slurry and liquid manure, spring application usually results in a much better nitrogen efficiency than autumn or winter application, especially in areas where nitrate leaching

Table 29. Nutrient amounts excreted per year from various animals

Animal	Nutrient amount, kg		
	N *	P_2O_5	K_2O
Milking cow (6000 kg/a milk yield)	110	38	140
Fattening cattle (125 – 600 kg live weight)	42	18	44
Sow with piglets	36	19	16
Fattening pig	13	6	6
Laying hens (100)	74	41	33
Fryers (100)	29	16	16
Turkeys (100)	164	81	71

* Excluding gaseous losses from storage or application.

Table 30. Contents of organic matter and nutrients in various manures

Manure type and amount	Organic matter, t	Nutrient amount, kg		
		N	P_2O_5	K_2O
Solid manure, cattle, 10 t	2	54	32	70
Solid manure, pig, 10 t	2	80	80	60
Solid manure, fryer, 1 t	0.2	28	21	23
Solid manure, turkey, 1 t	0.2	23	17	16
Dry poultry manure, 1 t (50 wt % solids)	0.4	28	21	15
Slurry, cattle, 10 m^3 (10 wt % solids)	0.7	47	19	62
Slurry, pig, 10 m^3 (6 wt % solids)	0.5	56	31	30
Slurry, poultry, 10 m^3 (14 wt % solids)	0.9	98	83	48

Table 31. Percentage of ammonium N and organic N in various manures

Type of animal	Type of manure	Percentage nitrogen as	
		Ammonium	Organic
Various animals	solid manure	15	85
Poultry	dried feces	30	70
Poultry	fresh feces	45	55
Cattle	slurry	55	45
Poultry	slurry	60	40
Pigs	slurry	70	30

occurs over winter. Ammonia losses can be kept low if slurry is incorporated into the soil as soon as possible after application.

Humus Effect. As shown in Table 30, animal manures contain an considerable amount of organic matter. This organic matter may increase the organic matter content of the soil, depending on the application rate and the cropping system. Application of solid organic manures usually leads to a larger increase in organic matter content than slurry due to the bedding material, which is low in N and hence less readily decomposable. The application of organic matter improves soil quality in terms of water-retention capacity, turnover nutrient availability, and nutrient pore volume, and resistance to soil erosion.

4.7.3. Environmental Aspects [294, 295, 298, 304 – 307]

Environmental problems may result from inappropriate application of animal manures, especially at times when the crop does not require nutrients, at rates which exceed the nutrient demand, or if animal manures are not incorporated into the soil immediately after application. The consequences can be:

- Nitrate losses due to leaching after nitrification of ammonium N or mineralization of organic N
- Ammonia losses from the soil or crop surface
- Potassium losses due to leaching on light soils
- Phosphorous accumulation in the top soil and in the subsoil; phosphorus leaching from peat soils

With the aim of decreasing nitrate leaching into ground water, some countries have established legal regulations that restrict the amount of manure and/or timing of application (see Chap. 9). A regulation to reduce ammonia losses from manure application and storage has been implemented in the Netherlands.

5. Fertilizer Granulation

5.1. Introduction

The granulation of fertilizers was one of the most significant advances in fertilizer technology, affording considerable advantages to both manufacturer and user. Today, a well-defined grain size distribution is specified just as nutrient contents and good application properties are. Although the first granular fertilizers came on the market between 1920 and 1930, a stronger trend toward granulation developed — especially in the United States — only after the end of World War II.

In 1976, both granular fertilizers and bulk blends enjoyed shares of somewhat more than 40 % in the U.S. mixed-fertilizer market. Granular fertilizers were losing ground against bulk-blend products and liquid fertilizers [313]. In 1990, the corresponding figures are about 63 % for bulk blends, 22 % for liquid fertilizers and 15 % for granular fertilizers. In Europe, Africa, and Asia, granular fertilizers are the most frequently used form, far ahead of bulk blends and fluids.

Advantages of Granular Fertilizers. Forming and subsequent conditioning are indispensable for the production of fertilizers suitable for use. It was recognized at an early stage that fertilizers in powdered or finely divided form readily cake during storage. This is less of a problem with low-surface-area granules. Only free-flowing materials allow mechanized handling and distribution. Granules often require less storage space because of their greater bulk density: they are stored and transported more economically. A further advantage of granular fertilizers over powdered and crystalline products is that they tend to produce less dust, so that product losses are reduced. A granular product with a definite grain-size spectrum is a prerequisite for uniform mechanical application with field equipment (see Section 8.2): granules with diameters between 1 and 5 mm are most suitable. At the same time, losses caused by the wind, and the accompanying environmental problems, are dramatically reduced. Moreover, granules produced from various feedstocks (solids, slurries, melts) by granulation do not segregate, in contrast to bulk-blended products (Section 5.5).

The use of granular instead of powdered fertilizers delays nutrient delivery to the plant until the granules have disintegrated completely (controlled delivery to the plant, diminished leaching losses). In the case of some controlled-release fertilizers, larger granules release nitrogen more slowly (see Section 4.4). Field studies in Swedish soils have shown that granular superphosphate with a grain diameter of 1 – 3.5 mm was twice as effective as finely-divided fertilizers [314], since the granular form retards phosphate fixation in the soil [315]. This reported effect varies with the soil type, the pH, the proportion of water-soluble P_2O_5 and the type of plant [316]. In the case of mineral fertilizers not containing P_2O_5 (N, NK, and NMg fertilizers), however, the grain size has only a slight effect.

Definitions [312, Chap. 1].

- Straight fertilizer: a fertilizer containing only one nutrient.
- Compound fertilizer: a fertilizer containing two or more nutrients.
- Complex fertilizer: a compound fertilizer formed by mixing ingredients that react chemically.
- Granular fertilizer: a fertilizer in the form of particles between two screen sizes usually within the range of 1 – 4 mm.
- Prilled fertilizer: a granular fertilizer of near-spherical form made by solidification of free-falling droplets in air or other fluid medium (e.g., oil).
- Coated fertilizer: a granular fertilizer that has been coated with a thin layer of some substance to prevent caking or to control dissolution rate.
- Conditioned fertilizer: a fertilizer treated with an additive to improve physical condition or prevent caking. The conditioning agent may be applied as a coating or incorporated in the granule.

- Bulk-blend fertilizer: two or more granular fertilizers of similar size mixed together to form a compound fertilizer.

Granulation Loop Granulation may be coupled with a production step, such as the manufacture of ammoniated triple superphosphate, or on the other hand it may be only a forming step in a production process, for example, granulation in the nitrophosphate process [317]. But other production operations also come under the heading of granulation: the preparation of feed materials and, after forming, the steps of drying (Fig. 26), cooling, screening, comminution of material with too large a grain diameter (oversize), recycling of this comminuted material and of material with too small a grain diameter (undersize) to the granulator, and finally conditioning of the particles with the desired grain size (product fraction). The processing steps, linked into a loop by the recycle, are called the granulation loop (Fig. 25).

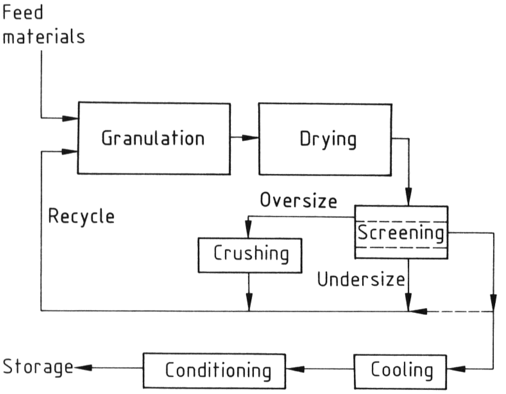


Figure 25. Granulation loop

Recycling is carried out for the following reasons:

1) The size distribution leaving the granulator differs from the required distribution
2) The ratio of liquids to solids in the available feed is in excess of the requirements for the desired size enlargement
3) Granulated material is recycled to provide nuclei for the granulation process

Processes which correspond to (1) may be described as granulation efficiency limited; an example is the agglomeration of low-solubility fertilizers. Condition (2) is generally encountered where readily soluble or high water content feeds are agglomerated and can be described as liquid phase balance limited. Liquid phase balance frequently leads to high recycle rates with consequently high processing costs (Chap. 5.4). For the control of granulation see [318, p. 280]

The *granulation efficiency* often is defined as the mass fraction of particulate material that leaves the granulator as finished product, that is, with grain sizes in the desired range (assuming 100 % sieve efficiency) [317]. It is also possible, however, to state the granulation efficiency as the mass fraction of finished product at the dryer outlet [319]. This definition allows for some regranulation in the dryer. The mass ratio of material not withdrawn (recycled material) to product is often referred to as the recycle ratio. For example, a 20 % granulation efficiency implies a recycle ratio of 4 : 1 if other losses are disregarded.

The *recycle ratio* is important to the process of granulation. Recycle is necessary because, after the product has passed once through the granulator, a certain quantity of particles lies outside the desired region of the grain-size spectrum (off-size material) and must be run through again. For a given mixture and a given temperature, optimal granulation takes place only within a narrow range of the solid-to-liquid ratio. The quantity of recycled fines depends not only on the chemical properties of the materials but also on the water content of the slurry and on the granulation device [320]. Recycle is also needed to generate nuclei for agglomeration and to stabilize the granulation conditions in the granulator.

The quality of the granules is influenced by the following factors:

- Type and fineness of the feedstock
- Moisture content of the granules
- Surface tension of the wetting liquid and wettability of the particles
- Mode of motion in the granulator
- Inclination and speed of the granulator
- Type and properties of the binder

Granulation Processes. Granulation processes can be classified by the nature of the feed materials to be granulated (i.e., granulation

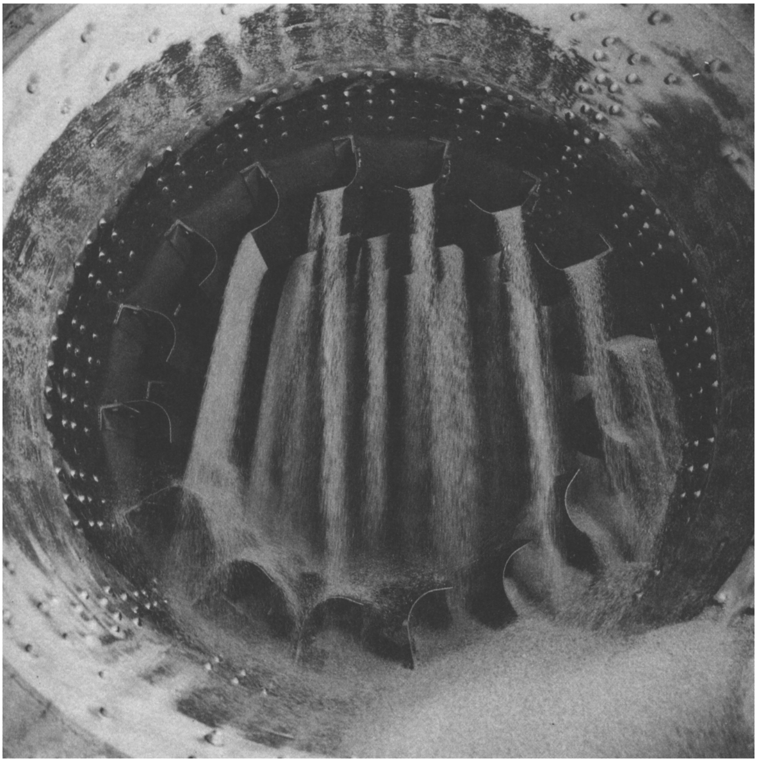


Figure 26. Drying drum, showing granulated product
Courtesy of BASF Aktiengesellschaft

of solids, slurries, melts [308, pp. 250 – 260], [313]) and by the type of granulation equipment used. The most important types of equipment for granulating fertilizers are shown schematically in Figure 27. For the most important fertilizer materials, both straight and multinutrient, Table 32 offers an overview of the main commercial granulation processes, along with further possibilities.

5.2. Granulator Feedstocks

Granulation of Solids with Water or Aqueous Solutions. A solid phase (dry mixed nongranular or powdered material) and a liquid phase or steam (granulation aid) are required. Steam is discharged under the bed of material at the feed end, and water is sprayed on the bed through spray nozzles. For each mixture there is a percentage of liquid phase at which granulator efficiency is optimum. The higher the temperature, the less water and hence less drying is required [308, p. 251]. The system is granulation-efficiency controlled. Granulation takes place by agglomeration of the particles. The granulation efficiency is high and the recycle ratio is low (roughly 1 : 1). Examples are the granulation of superphosphate (with and without simultaneous ammoniation), the granulation of superphosphate in the presence of $(NH_4)_2SO_4$ and K_2SO_4, and the granulation of monoammonium phosphate together with other nutrients [313] to yield high-analysis formulations. While the granulation of solids has proved to be a flexible and economical process, it has the drawbacks of diminished quality as to physical properties and appearance. What is more, the P_2O_5 component (monoammonium phosphate or superphosphate) has to be prepared in a separate plant [313]. For an example of granulation with a solid P_2O_5 component, see [358, 359]; for granulation of NPK fertilizers containing urea, see [360].

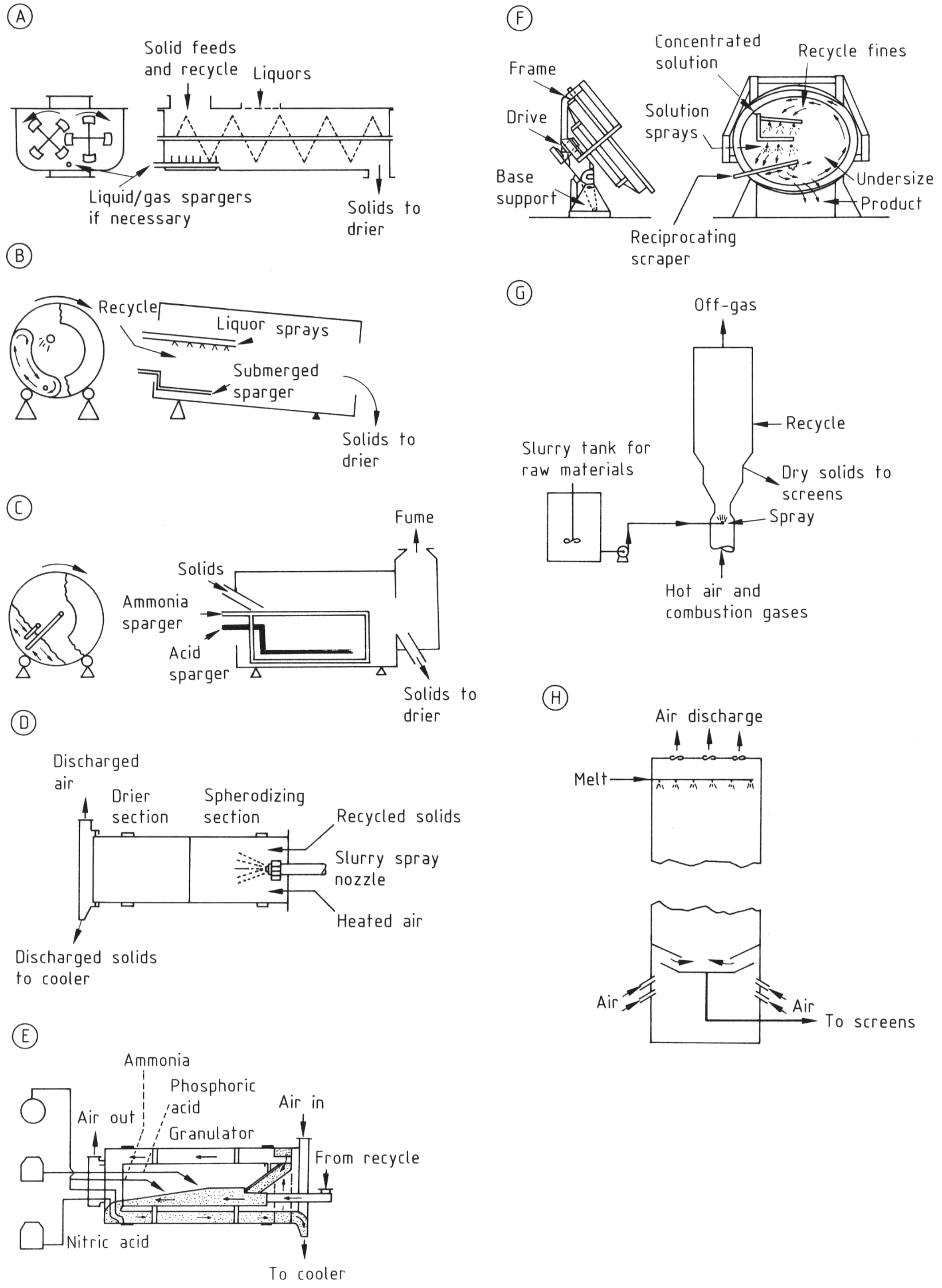


Figure 27. Granulation equipment [321]
A) Pugmill (blunger); B) Rotary drum; C) TVA ammoniator – granulator drum; D) Spherodizer process; E) SAI-R drum granulator; F) Inclined pan granulator; G) Fluidized-bed granulator/drier; H) Air-cooled prilling tower

Table 32. Equipment for granulation of fertilizer materials * [317]

Fertilizer material	Granulation equipment: main commercial techniques are in boldface, while possibilities are in normal typeface
Calcium nitrate	prilling, flaking, pan granulator [322], drum granulator, compaction, pugmill/blunger [320]
Ammonium nitrate	prilling [308, p. 103], [323], cold spherodizer [323, 324], pan granulator [322, 323, 325, 326], drum granulator, fluidized-bed granulation [327, 328], spouted-bed granulation, TVA falling-curtain drum granulation
Calcium ammonium nitrate	prilling [309, p. 195], pugmill/blunger [308, p. 104], [309, p. 196], drum granulator, pan granulator [322, 329], hot spherodizer, cold spherodizer, fluidized-bed granulation [327, 330], spouted-bed granulation, TVA falling-curtain drum granulation
Ammonium sulfate nitrate	pugmill/blunger [309, p. 205], drum granulator [331], prilling [309, p. 205], pan granulator [332]
Ammonium sulfate	crystallization, hot spherodizer, compaction, pipe reactor-drum [333]
Urea	prilling [323, 328, 334] cold spherodizer [323, 324], pan granulator [322, 323, 325, 326, 335], crystallization, drum granulator [336, 337], compaction [338], fluidized-bed granulation [328], spouted-bed granulation [339], TVA falling-curtain drum granulation
Urea with ammonium sulfate	prilling [341, pp. 71 – 73], cold spherodizer, pan granulator [342], fluidized-bed granulation [340], spouted-bed granulation, TVA falling-curtain drum granulation
Superphosphate	drum granulator [343], pan granulator [309, p. 234], pugmill/blunger
Triple superphosphate	drum granulator [308, p. 191], [344], pan granulator [309, p. 348], pugmill/blunger [308, p. 191], [344], compaction
Monoammonium phosphate	drum/ammoniator-granulator [311, pp. 6 – 8], [345, 346], pugmill/blunger [311, p. 30], [347], prilling [311, p. 8], [347], crystallization, compaction
Diammonium phosphate	ammoniator-granulator [311, pp. 6 – 8], [345, 346, 348], crystallization, pugmill/blunger [346 – 348], compaction
Ammonium polyphosphate	ammoniator-granulator[311, p. 217], pugmill/blunger [311, p. 217]
Nitrophosphate (NP)	hot spherodizer, prilling [349, 350], pugmill/blunger [320, 351], pan granulator [332, 351], drum granulator [351, 352], fluidized-bed granulation
Potash	compaction [353], crystallization
PK	drum granulator [343], pan granulator, pugmill/blunger, fluidized-bed granulation [354]
Nitrophosphate (NPK)	hot spherodizer [324, 355, 356], prilling [349, 350], pugmill/blunger [320, 346, 355, 356], pan granulator [357], drum granulator [345, 346, 351, 355, 356], fluidized-bed granulation, compaction [317]
Compounds on ammoniacal base	drum/ammoniator-granulator, pugmill/blunger, hot spherodizer, prilling
Compounds with ammonium nitrate	ammoniator-granulator, pugmill/blunger, hot spherodizer, drum granulator, prilling
Compounds with urea	drum/ammoniator-granulator, pugmill/blunger, hot spherodizer, compaction, prilling
Compounds with micronutrients	ammoniator-granulator, pugmill/blunger, hot spherodizer, drum granulator, compaction

* Compaction is illustrated in Figure 34. The equipment for the other processes is illustrated in Figure 27.

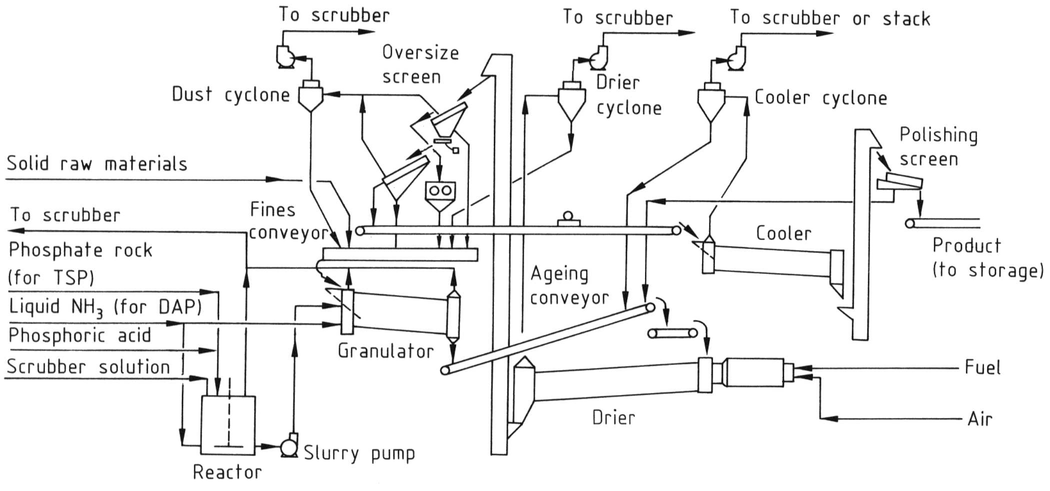


Figure 28. Slurry granulation process [317, p. 23]

Slurry Granulation. The materials to be granulated are in the form of a slurry, usually derived from reaction of sulfuric, nitric, or phosphoric acid with ammonia, phosphate rock, or a combination thereof. In some process modifications, solid materials may be added to the slurry before or during granulation (Fig. 28). Slurry granulation is liquid-phase controlled. Usually a thin film of a slurry having the fertilizer composition is sprayed onto small solid particles. The granules are built up in layers (layering process). The process is mainly controlled through the recycle and the slurry water content (the recycle ratio may be 5 : 1 or more [313]). Granulation is aided by various impurities (Al/Fe compounds, organic substances); see [320]. Drying can be combined with granulation into one processing step. A modification of the slurry process is the Spherodizer process developed by C & I Girdler (Section 5.3.2). Slurry granulation is widely practiced in Europe for the production of N, NP, and NPK fertilizers. In the United States, the process has been modified so that acids, phosphoric and/or sulfuric, or partly neutralized acids are completely ammoniated in the granulator (ammoniator – granulator, Section 5.3.2) [361]. For example, $(NH_4)_2SO_4$ can be granulated in a drum by this method [414].

Granulation with solutions or slurries includes fluid-bed spray granulation (mechanism of agglomeration [362, 363]) and spray drying. In the continuous fluid-bed spray granulation process, solutions, suspensions, or melts can be converted to a granular product in a single step [364]. In contrast to spray (flash) drying, this process can be made to yield granules with a particle size of up to 5 mm [365]. The liquid for granulation is sprayed through nozzles located in or above the fluid bed onto the particles, which comprise comminuted oversize or undersize from the cyclone separator. Warm air in the fluid bed promotes the drying of the particles, and the sprayed particles increase in size. If melts are sprayed into the bed, cold fluidizing air carries off the heat of solidification. Fluidization is accomplished by blowing air through a plenum with a grid. Agglomeration with urea, NH_4NO_3, and K_3PO_4 has been reported [362].

Spray or flash drying represents a direct path from the liquid product to granules. The end product ranges from a powder to a fine grit. The feed liquid is atomized hydraulically, through feed nozzles, or pneumatically, with two-fluid nozzles or atomizer disks. The solution is sprayed into a tower-like vessel with a hot air stream and thus solidified into the fine granules. The dry product is removed pneumatically and collected in a cyclone system, or it can be removed with a bucket wheel at the bottom of the tower [366]. A few special fertilizer products are made by spray drying.

Fluidized-bed methods include the NSM process (Fig. 29) [327, 328], [370, pp. 277 – 288]. The granulator is a rectangular vessel with a perforated plate at the bottom to provide a uniform distribution of air. The fluid bed, which is initially made up of fines, has a height of 0.5 – 2 m and an area of several square meters. It is subdivided into chambers to obtain a narrow gradation in the end product. The granulation liquid or melt is sprayed into the fluid bed in each section by air. Heavier particles, which remain in the bottom portion of the fluid bed, can pass into the next section or to the outlet. In this way, the granular product migrates through the fluid bed from the first to the last section. The NSM plant has a capacity of 800 t/d for urea, and the production costs are less than those for prilling. For the properties of slurry granulation processes, see [367, 368]; for studies on the layering process, [369]. For fluid-bed granulation, see [363].

A modification combining granulation and drying in a variant of the fluid-bed process is the “spouting-bed granulator” [313, 371, 372]. The conical vessel stands on end, with a Venturi tube at the bottom, the narrowest section; into this section, either hot air propels a hot saturated solution or cold air propels a melt. The fluid bed is set up in the cone. The fast-moving particles require no perforated distributor plate. Drying or cooling takes place rapidly, and the material builds up in onion fashion. The dust collected in the cyclone is recycled (2 : 1 recycle ratio) [313]. Granulation tests on ammonium sulfate in the spouted bed have been reported [373]. Despite successful pilot tests, no full-scale unit has yet been built [371].

Melt Granulation. Spherical agglomerates produced from the melt (e.g., urea and ammonium nitrate) are called prills. These are usually obtained by spraying a salt melt or a highly concentrated solution into the top of a tower. The melt should have a very low viscosity (< 5 cP)

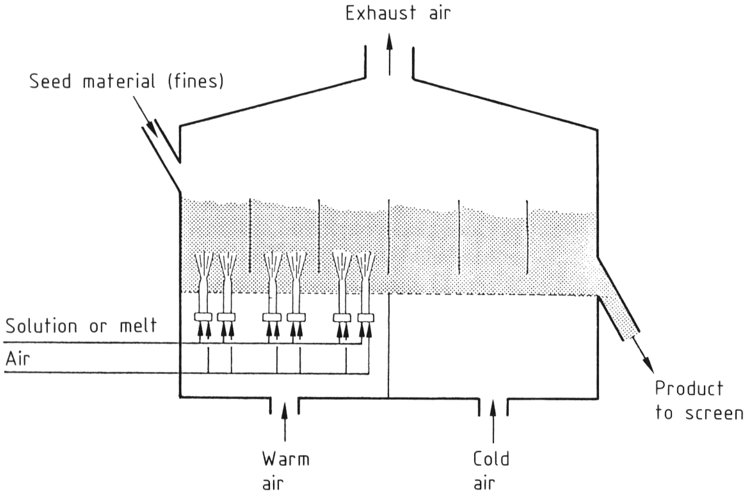


Figure 29. NSM fluidized-bed granulator [327, p. 7]

but a high surface tension at temperatures just a few degrees above the melting point [374]. The liquid jet breaks up into droplets in the free air space. As they fall in contact with counter-flowing cool air, the droplets solidify. The tower height (and thus the falling distance) and the velocity of the cool air are adjusted so that the prills are sufficiently hard when they strike the bottom of the tower [329]; tower heights are typically 45 – 55 m for ammonium nitrate [396]. The prills can be removed with scrapers or belt conveyers, or they can be cooled in a fluid-bed cooler located at the bottom end of the prilling tower [375]. Alternatively, the heat of crystallization can be carried away by spraying the droplets of melt into an oil bath. This is done, for example, with calcium nitrate [376], which is subsequently centrifuged and screened [377].

The recycle ratio in prilling is ca. 0.1 – 0.2 [315]. The prill, with a diameter of 1 – 3 mm, is usually smaller and rounder than the particle obtained by granulation. Because of the high air throughputs in the prilling space and the resulting off-gas problems, and also because of the smaller particle size, prilling has lost importance [315]. For small capacities, such as 250 t/d, granulation is economically superior to prilling; for high capacities, from 1000 t/d up, conditions determine which process is more economical [315, 378]. Schoemaker and Smit present a comparison between granulation and prilling in the manufacture of fertilizers [379].

For the prilling of NPK mixtures consisting of NH_4NO_3, $NH_4H_2PO_4$, and KCl, see [374].

For tests of oil prilling of a urea – ammonium sulfate mixture (34–0–0–9S), see [341, pp. 71 – 73], [342]; for tests of oil prilling of urea – ammonium polyphosphate mixtures, see [382]. Monoammonium phosphate can be obtained in melt form with a pipe reactor and sprayed into a prilling tower (Swift process) [347].

Multinutrient fertilizers mostly have high melting points and are very viscous [313]. One exception is a mixture of monoammonium phosphate and ammonium nitrate, which melts at a low temperature and has a low viscosity. The melt is granulated in a drum (recycle ratio 1 : 1). Depending on whether KCl is added in the granulator, formulations such as 24–24–0 and 17–17–17 are obtained. In a TVA process [380], phosphoric acid and NH_3 are reacted in a T reactor to yield an anhydrous melt; this can be granulated by itself to an ammonium phosphate/ammonium polyphosphate mixture (from 11–55–0 to 12–57–0) [313], or urea can be added to obtain a 35–17–0 or 28–28–0 granular product. If KCl is added, 19–19–19 can be produced [313, 381]. Granulation takes place in a drum or a pug mill (cf. Sections 5.3.1 and 5.3.2).

Melt-granulation processes have the advantage that a dryer, which is otherwise the largest and most expensive unit in granulation plant, can be dispensed with [308, p. 256]

5.3. Granulation Equipment

The condition for granulation is that a bed of solid particles moves, with simultaneous intensive mixing, in the presence of a liquid phase. This motion provides the particle collisions and bonding needed for granule growth. There are many types and models of granulating equipment, most of which use one of three basic intensive mixing mechanisms [321]:

1) Rotation of one or more shafts carrying staggered paddles in a fixed trough (pug mill, blunger).
2) Rotation of the whole device, such as drum or pan.
3) Movement of particles by a third phase, as by blown air in a fluid-bed granulator. In slurry granulation the third phase is usually hot air or hot combustion off-gases, which can serve as a drying medium at the same time. In this way, two processing steps in the granulation loop can be carried out in a single apparatus [365].

In order to improve pelleting conditions or pellet qualities, binding agents can be added along with the granulation liquid. The binding agents may be solid or liquid, may form films, crusts, or crystals, and may harden at standard temperature or at higher temperature [383].

Because granules can also be obtained by dry compaction, the compactor should be considered as a granulator here.

Various authors have reported data on granulators [309, 317, 321, 352, 384 – 388]. Ries has attempted to classify granulating equipment and processes [366, 389 – 391].

The granulating devices used most often in the fertilizer industry are drums, pans, and pug mills. While fluid-bed granulation has come into use in the fertilizer field, mixer – granulators and compactors are more frequently employed to form fertilizer granules. Spray drying and extrusion processes are used only for special fertilizer products.

5.3.1. Pug Mill

A pug mill (Fig. 27 A) consists of a U-shaped trough and, inside it, one or two shafts bearing strong paddles staggered in a screw-thread fashion. In frequency of use, two-shaft pug mills are dominant [317]. The shafts rotate at equal speeds in opposite directions in the horizontal or slightly inclined trough. The solid particles (fresh feed plus recycle) are fed in at one end of the trough and are thrown up in the middle of the trough, where they are wetted with the granulation liquid. In the trough, the paddles move, knead, and transport the moistened particles toward the discharge end. The particles can be given a better-rounded external shape either in a downstream tumbling drum or in the feed zone of the drying drum. Placement of a perforated NH_3 inlet pipe (sparger) at the bottom of the trough makes it possible to ammoniate and agglomerate the fertilizer at the same time. The pug mill is sturdy and can adapt to variable service conditions; it produces hard granules of uniform composition [321]. If the angle between the paddles and the shafts is optimized, the energy consumption can be reduced. The paddles are usually provided with a wear-resistant coating to prevent abrasion [320]. Processes have been described for granulating in a pug mill an ammonium polyphosphate melt (12–57–0), and the same melt with urea (28–28–0) [380], and the same with KCl (19–19–19) [341]. For tests on 35–17–0, see [392]. The combination of a pipe reactor with a pug mill for the granulation of NPK has been reported [393].

5.3.2. Drum Granulator

The drum granulator (Fig. 27 B and Fig. 30), which is the type of granulator in widest use for fertilizers, is an inclined rotating cylinder. The rotation speed is usually adjustable. For a given drum and a given granular product, there is an optimal peripheral speed that gives the highest yield of granules.

An inclination of up to 10° from the horizontal ensures adequate movement of product toward the discharge end. Because, however, this inclination is not enough to effect classification, the discharged product has a fairly broad grain-size distribution, in contrast to the pan-granulator product (Fig. 31A).

Drums in which the lengthwise axis is inclined upward from the feed end to the discharge [395] give a narrower particle-size spectrum. Such an upward inclination also increases the drum fillage.

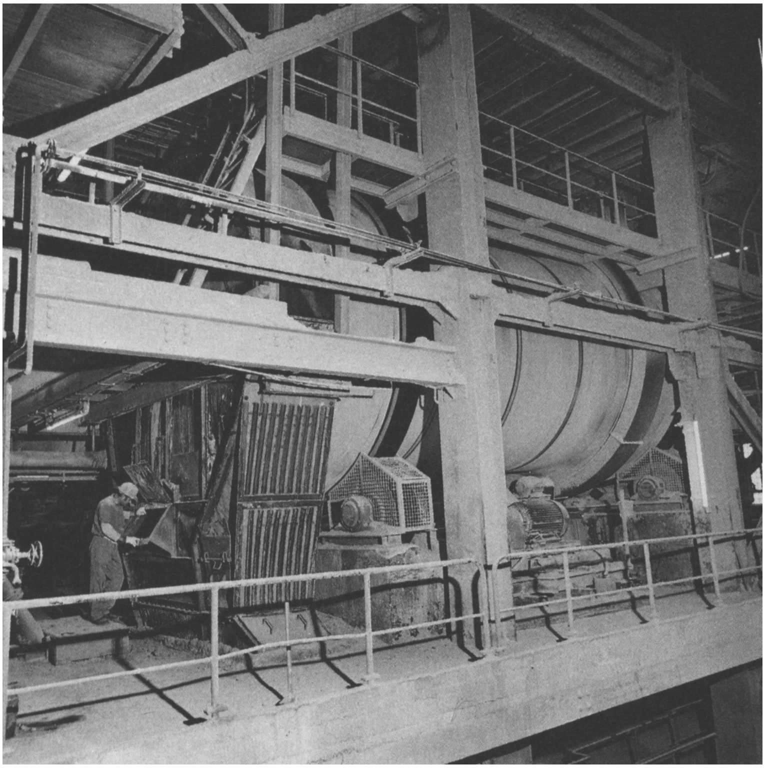


Figure 30. Drum granulator
Courtesy of BASF Aktiengesellschaft

In drums currently used in the fertilizer industry, the length-to-diameter ratio is ≥1 and may reach 6 : 1. The feed end may have empirically designed distributing elements on the inside wall to spread the feed material. In the adjacent part of the drum, where the granulation liquid is fed in, a good tumbling motion should be ensured. This can be achieved with light lifting flights, but they must not lift the granulate too high. In the remainder of the drum, the pregranulated material should be tumbled to a round shape and further compacted. This is also achieved with light flights on the wall and an appropriate fillage. The fillage in the spray and tumbling areas can be controlled by means of internal ring dams. The cylinder may be either open ended or fitted with ring dams at the ends [396] to prevent overflowing at the feed end and to control the bed depth and thus residence time. Fixed or movable scrapers inside the drum or hammers or other rapping devices outside on the drum can be used to remove or reduce excessive product caking inside the drum. Some material buildup on the drum wall may promote granulation [397]. Cylindrical drums are used for continuous granulation with and without internals.

As in the case of the pug mill, recycled product (undersize) generates a moving bed of material in the drum; a slurry containing, say, 3 – 8 % water can be sprayed onto the bed [309].

Powdered feed materials (mixed and wetted in an upstream mixer if necessary to provide granule nuclei) can be granulated in the drum through spraying with water, solutions, suspensions, and highly concentrated slurries, or through blowing with steam. The bed volume should be 20 – 30 % of the cylinder capacity [398]. The recycle ratios for drum granulation are generally between 1 : 3 and 1 : 6. Optimization of these plant parameters for each product class is done by trial and error.

The drum granules are better rounded but less dense than the pug-mill granules [321]. Drums 4.5 m in diameter and 16 m long are in use in the fertilizer industry.

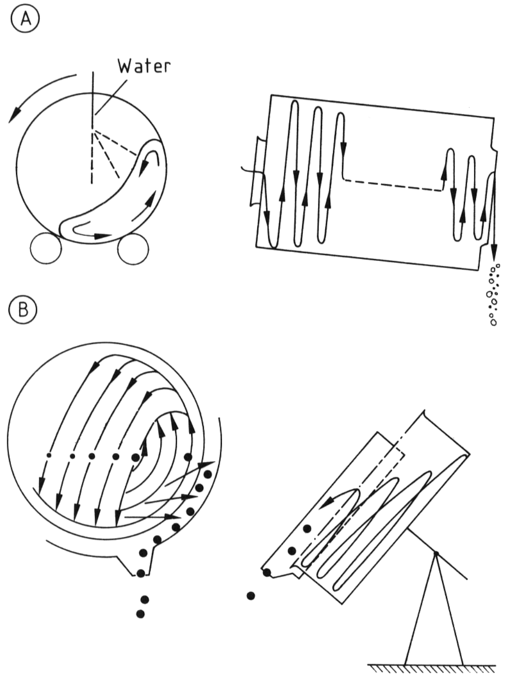


Figure 31. Schematic representation of granule development in the drum granulator (A) and pan granulator (B) [394]

An important modification of drum granulation is the TVA ammoniator – granulator (Fig. 27C and Fig. 32) [308, pp. 250 –260], [399 – 401]. This is a drum roughly equal in length and diameter, with ring dams at the ends but no lifting flights. Ammonia reacts with phosphoric and sulfuric acids below the surface of the tumbling bed of fresh feed and recycle. The reaction generates heat, which vaporizes the water at the same time that granulation takes place. The heat is removed by injected air. The ammonia and the acids are supplied to the bed through perforated distribution pipes mounted parallel to the drum axis. The requisite bed depth is ensured by the ring dam at the drum discharge. In a modern process, a mixture of phosphoric and sulfuric acids and ammonia is neutralized in a pipe-cross reactor situated upstream of the granulating drum (Fig. 33). The slurry is then fed to the drum along with recycle. While more phosphoric acid is sprayed onto the tumbling bed, ammonia is fed into the bed [313]. In this way, NPK fertilizers can also be produced [335, pp. 44 – 48]. In the SA CROS process for monoammonium phosphate production, phosphoric acid and ammonia are mixed and reacted in a pipe reactor. The slurry is distributed over the tumbling bed together with the steam generated; no subsequent ammoniation takes place in the bed [402]. For granule improvement with an interstage pan, see [403]. The use of the pipe reactor in combination with the granulating drum for the manufacture of granular ammonium phosphates was introduced by TVA in 1973 [311, p. 45] and was later incorporated in many plants [404]. A possible improvement in the drum granulator is represented by the double-pipe granulator, which is especially well-suited to fertilizer mixtures with a high proportion of recycle (Scottish Agricultural Industries system, Fig. 27 E) [309, 405]. For example, by virtue of the high recycle ratio with corresponding residence times, a hard ammonium nitrate – ammonium phosphate mixture can be granulated.

Another modification of the drum granulation process described is the spray-drum process (Spherodizer, Fig. 27D). In a rotating drum, preneutralized slurry is sprayed onto a dense curtain of granules cascading from baffles inside the drum. The water content of the slurry must be, say, 12 – 18 % to allow good spray dispersion [309]. During granulation, hot combustion gases flow through the drum in cocurrent [406], so that drying takes place at the same time. The dried particles are then sprayed again, redried, and so forth. The grains grow in shell fashion with an onion structure and are very hard. Spherodizer units are built in capacities of up to 650 t/d. Such an apparatus has a diameter of 4.5 m and a length of 12 m [309]. The Spherodizer, developed by C & I Girdler [407, 408], was first used on an industrial scale in 1959. The *cold* and *hot* used for the versions of the Spherodizer describe the condition of the air that flows through the drum. The cold version is used with melt feeds, especially ammonium nitrate and urea, while the hot version serves for granulation and spraying with slurries (NPK fertilizers, nitrophosphates, ammonium phosphate – nitrate, urea – ammonium phosphate) [317]. Granulation and drying thus take place in the same device. Under optimal service conditions, the recycle ratio is approximately 1 : 1.

A combination of drum granulation and fluid-bed technology is embodied in the Kaltenbach-Thuring Fluidized Drum Granulation (FDG) process [325, p. 39], [409, 410]. The technique

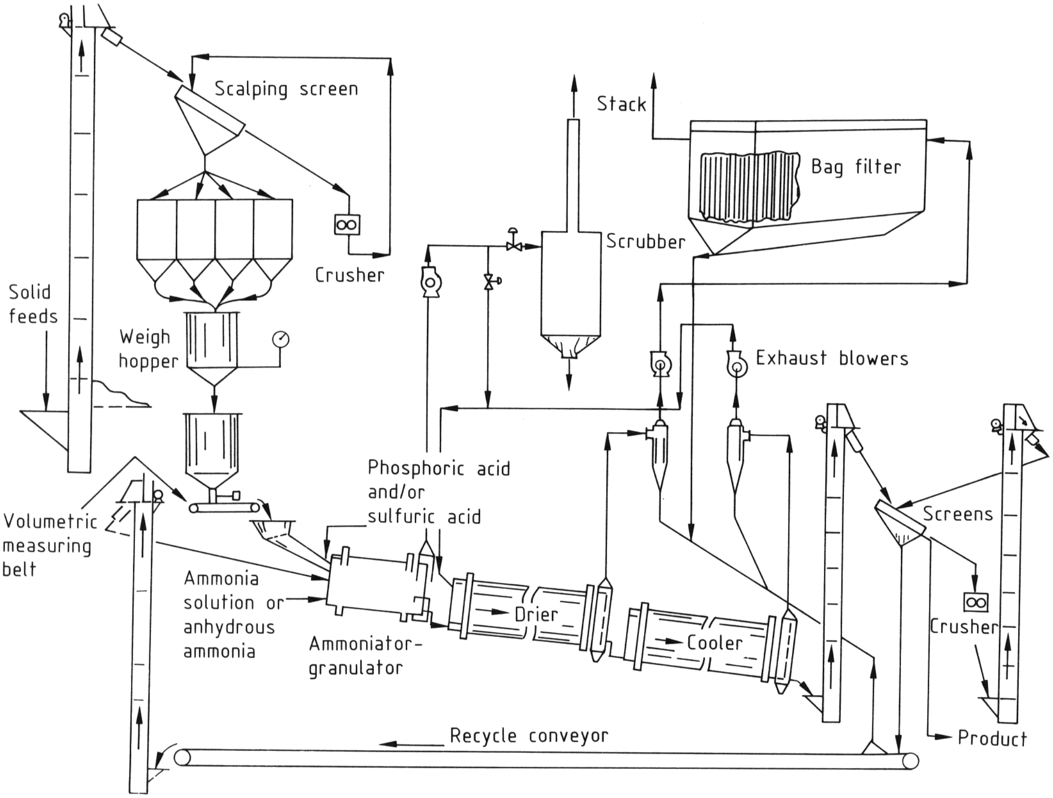


Figure 32. Ammoniator – granulator plant for NPK mixtures [317, p. 23]

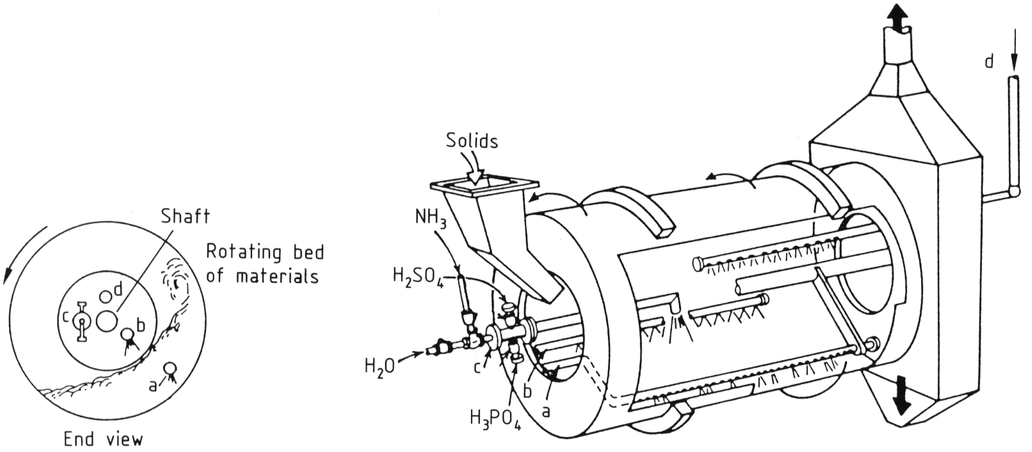


Figure 33. Location of pipe-cross reactor and spargers in ammoniator – granulator [313, p. 87]
a) Ammonia sparger; b) Phosphoric acid sparger; c) Pipe-cross reactor; d) Scrubber liquor
Reprinted by permission of John Wiley & Sons, Inc.

is suitable for both melt and slurry granulation (e.g., size enlargement for urea and ammonium nitrate prills).

In a drum, the best granulation takes place at 25 – 45 % of the critical rotation speed [361], which is the rotation speed at which the weight of the granules and the centrifugal forces are in balance [386], [318, p. 204]:

$$N_{\text{crit}} = 42.3\sqrt{\frac{\sin\beta}{D}}$$

D = drum diameter, m
β = drum inclination
N_{crit} = critical rotation speed, rpm

5.3.3. Pan Granulator

The tumbling motion of granules during agglomeration can also take place on a rotating inclined pan (Figs. 27 and 31 B).

For a given pan size, if the inclination of the pan axis to the horizontal is increased, the granules roll upward less steeply but have a longer residence time in the pan. The granulation nuclei and the small granules initially move in the vicinity of the pan bottom. During granulation, the rotation of the pan and the force of gravity cause them to take up a spiral path. The particles grow and eventually reach the bed surface. The spiral diameter decreases continuously until the granules, finally becoming large enough, run over the rim of the pan (Fig. 31 B). Melts or slurries are often sprayed onto the bed, but water or solutions can also be used as granulation aids, and steam can be injected into the bed. If water is employed, it should be applied in the region of the largest spiral diameter [320]. Experience has shown that the spray liquid must be dispersed more finely, the finer the solids for granulation [413]. Because the overflow product has a rather uniform grain size, downstream classification can often be dispensed with. By means of an advancing and retreating scraper blade, the pan bottom can be kept fairly clean and the formation of crusts can be avoided. Here, as in the drum, some material coating the pan prevents wear and promotes the correct tumbling action [396]. The pan can also be made in the shape of a truncated cone or can have at its periphery a tumbling ring, onto which the granules fall from the pan rim; surface coating agents can be applied. Pan granulators are manufactured with diameters of up to 7.5 m [317]. Typically, the height of the rim is one-fifth of the diameter.

Concentrated salt melts of urea, ammonium nitrate, or calcium nitrate can be processed in the pan granulator; the products are easily applied fertilizer pellets, and an alternative to prills [322, 323, 383, 415].

For the production of granular triple superphosphate, phosphoric acid is added to digest finely milled crude phosphate in a granulator – mixer; this step yields a moist, crumbly product, which is directly processed in a subsequent pan to the required pellet size with the injection of steam and the addition of hot phosphoric acid [383]. For the pan granulation of urea – ammonium sulfate mixtures, see [342].

The relationship between the critical rotation speed and the pan diameter and inclination is the same as for the drum granulator [396].

In general, pan rotation speeds are $n \approx 0.6 - 0.75 n_{\text{crit}}$, where n_{crit} is the critical rotation speed; the pan axis is usually inclined at 45 – 55 ° to the horizontal [411]. According to the TVA [412], the optimal angle is ca. 65 °. The throughput of a pan granulator can be calculated roughly as follows [386]:

$$\dot{m} = k \cdot 1.5\, D^3$$

$\dot{m}$ = throughput, t/h
k = factor ca. 0.95 – 1.1 for mixed fertilizers
D = pan diameter, m

5.3.4. The Granulator – Mixer

While the pan granulator must be fed with powdered or pre-pelleted material, the granulator – mixer can accept friable, plastic, pasty, or crumbly feeds. If the mixing elements move at the proper speed, the material is comminuted to the desired grain sizes [383]. The disintegration of hard agglomerates is made possible by cutter rotors mounted at the sides of the mixing space [416]. Granulator – mixers are often used in batch operation, while pan granulators are run continuously. Process engineers in the fertilizer industry have also combined the two kinds of apparatus with the mixer upstream to improve product quality. The mixing vessel itself either has a fixed position or may rotate, while the movable mixing elements (e.g., mixing stars, spirals, shafts with attached vanes, plowshare mixing elements) effect intimate mixing and thus granulation by virtue of their rotation. The shape and rotation speed of the mixing elements are usually variable and can be adapted to a range of mixing and granulation jobs. Wear of the mixing elements must be expected. The mixing vessel proper can have a variety of shapes: smooth pipe, zigzag rotary pipe, pan, cone, Y, tub, and so forth. The mixer is often provided with external auxiliary heating. The liquid used for granulation can be fed to the mixing space and distributed by means of a hollow shaft [385], but suitable openings and feed pipes on the vessel can also feed in the liquid. For granulation – mixing of fertilizers, the device has a specific energy consumption of 2 – 6 kW per 100 kg of product [417]. The granulation time can be taken as 5 – 10 min. Grain sizes between 0.1 and 5 mm are achievable. The capacity is up to 30 000 kg/h per mixer [366]. Ries compares the grain-size distribution curves of fertilizer granules from granulator – mixers with those of the starting fineness [418].

5.3.5. Roll Presses

The size enlargement of a finely dispersed charge material by external compression is implemented in press agglomeration (Fig. 34). The charge is gripped by two counterrotating rolls, nipped in the gap, and compressed. As the void volume decreases, the material generally undergoes a two- to threefold compaction. While a charge hopper is adequate for a free-flowing material, a material that is not sufficiently free-flowing can be transported to the nip by screw feeders, with some precompaction. If the rolls are smooth, the material exiting from the nip ("shell") has a smooth surface. If the rolls have mating depressions, briquetts are produced. The shells are next reduced to the desired grain size (in a crusher or mill) and screened. The fines and oversize are recycled (Fig. 35). Rolls are manufactured in diameters up to 1.4 m and widths up to 1.5 m [390]. They may be mounted side-by-side or over-and-under.

For the specific compressive forces for urea, KCl, and $(NH_4)_2SO_4$, see [353]; for data on the compaction of special fertilizers, [420, 421]; of K_2SO_4, [320]; of calcium cyanamide, [422]. For a general description of fertilizer compaction, see [423, 424]; for a monograph on roll pressing, [425]; for the principles of pressure agglomeration, [419].

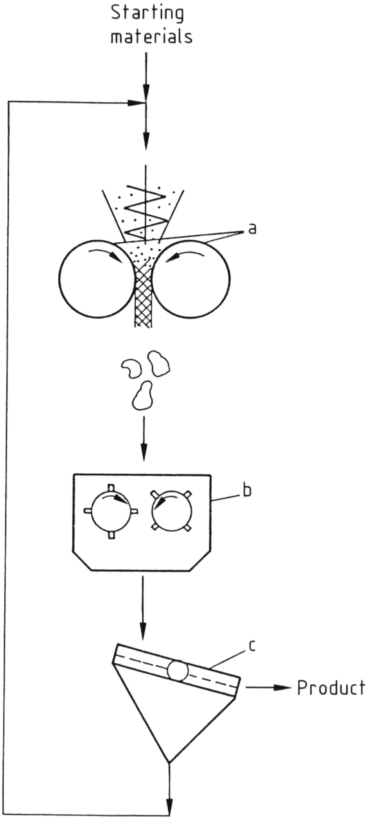


Figure 34. Press agglomeration with smooth rolls [386, p. 215]
a) Rolls; b) Crusher; c) Screen

5.4. Costs of Agglomeration

The costs incurred for granulation depend not just on the agglomeration properties, but — for equal or nearly equal agglomeration properties — on the size and type of equipment used in the process. For equipment and investment costs for pan granulators, drums, mixers, and roll-compaction equipment, and on hourly operating costs versus equipment size, see [426]. With regard to personnel, mixers and roll presses are

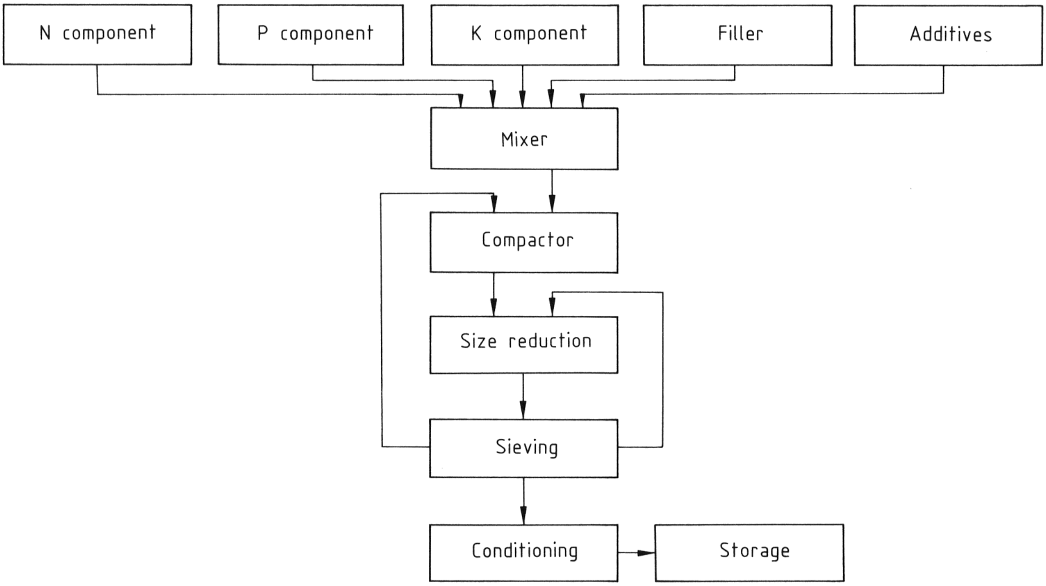


Figure 35. Compacting of a multinutrient fertilizer [419, p. 34]

considered to require one-half man (year-round, rotating shifts), while pans and drums are figured at one man each. In contrast to dry compaction (roll presses), drying costs have to be added in for mixer granulation. Up to a certain moisture content, mixer granulation with drying is quite competitive with dry compaction. For processes and costs of agglomeration, see also [427]. In comparing the granulation of solids and slurries, the investment costs are one-third higher for slurry granulation, and the operating and utility costs are likewise greater [313].

For production costs with various granulating equipment, see [428, 429]. For a cost and process comparison between prilling and granulating, see [378, 430]; for the costs of granulating monoammonium phosphate and diammonium phosphate, [311]; for the costs of NPK granulation in the Norsk Hydro nitrophosphate process, [349]; for the costs of fertilizer compaction, [431]. For economic aspects and comparative estimates of manufacturing costs, see [308, pp. 138, 266].

5.5. Bulk Blending

The mechanical mixing of single components in granular form, called bulk blending, is a special way of producing multinutrient fertilizers. Bulk blending was introduced in the USA at the beginning of the fertilizer industry [447]; it is not nearly so widespread in Europe. In the process, several of the usual starting components, such as superphosphate, triple superphosphate, monoammonium phosphate, diammonium phosphate, urea, and potassium chloride, are combined in an uncomplicated device such as a rotating drum. The nutrient ratio can be adjusted as desired. The components are briefly mixed (up to 15 t/h) and made available to the farmer in batches that are usually loaded directly into the distributor.

The precondition for this process is that the components in the mixture be physically and chemically compatible [317, 448]. For example, urea and ammonium nitrate must not be present together, since a mixture of these is very hygroscopic and tends to deliquesce. Further, stoichiometric mixtures of urea and ammonium nitrate are sensitive to impact, and even a solution of the two can form an explosive mixture [449]. Mixtures of urea or diammonium phosphate with normal or triple superphosphate have only limited compatibility. If an aqueous salt mixture has a somewhat elevated pH and simultaneously contains NH_4^+ ion, NH_3 may be liberated.

Bulk blending has the drawback that segregation can occur during silo filling, packaging, transportation, and application. A uniform grain size or grain-size distribution is essential for reducing segregation, even if the particles differ in density. Design measures at the silo inlets and inside the silos can prevent segregation [335, pp. 37 – 39]. Drum mixing generates dust, which may necessitate cleanup measures depending on the amount of dust and the size of the mixing equipment.

The process has the advantages that the $N : P_2O_5 : K_2O$ ratio desired by the farmer can easily be obtained; micronutrients, insecticides, and herbicides can easily be metered in, and the dealer requires less storage space.

For the production of bulk-blended urea with an appropriate gradation, see [370, pp. 277 – 288]. For the bulk-blending system in the United States, see [447, 450 – 452]; for the use of mechanical fertilizer mixing in Germany, see [453].

5.6. Quality Inspection

For successful handling and application, certain ranges of physical properties must be specified for the fertilizer particles. Quality control, which includes chemical analysis as well, is performed by the fertilizer manufacturer. For the determination of the physical properties of mineral fertilizers, see [308, 432 – 434].

Grain Shape. Fertilizer particles should have the least possible surface area, since irregular shapes lead to increased abrasion and a tendency to cake.

Grain-Size Spectrum. The diameter of ordinary commercial fertilizer grains is in the range of 0.5 – 6 mm. U.S. products generally have a somewhat finer size spectrum (primarily 1 – 3.35 mm) [317] than European products (primarily 2 – 5 mm). In exceptional cases, the product grains may be coarser, as in the case of a woodland fertilizer applied from the air (6 – 12 mm), or finer, as in the case of ammonium sulfate and crystalline mixed-salt fertilizers (< 2 mm) and other special fertilizers. The grain-size distribution is important for the intended application, for example to ensure uniform distribution of fertilizer nutrients by field equipment. The grain-size spectrum is determined by screen analysis (ISO 8397 standard screening). For the grading curves of granular fertilizers in comparison to the starting fineness, see [418].

Settled Density. The settled density is important for the sizing of packaging equipment and storage areas. For a given fertilizer grade, it should fluctuate as little as possible. The settled densities of granular fertilizers can be determined in accordance with ISO 3944; those of finely divided fertilizers (with a high content of <0.5 mm), in accordance with ISO 7837.

Compacted Density. The compacted density is generally as much as 10 % higher than the settled density. It represents the maximum bulk density that can be achieved through vigorous shaking. The compacted density can be measured in accordance with ISO 5311.

Dumping Angle. The dumping angle (angle of slope) of a fertilizer is important for the design of storage areas and for transportation. The dumping angle should be as large as possible and can be measured in accordance with ISO 8398.

Grain Hardness. The grain hardness is a measure of the fracture strength of fertilizer grains and their mechanical stability in storage. As a rule it is measured by placing grains of a definite size between two parallel plates and compressing [435].

Abrasion Resistance. The abrasion resistance is a measure of the mechanical stability of fertilizer grains moving against one another and of their stability in free fall (wear due to tumbling and dropping). Abrasion causes dusting of the fertilizers during storage operations, transportation, and application. The abrasion resistance should be as great as possible and can be determined with, for example, the TVA method [308].

Caking Tendency. One of the most important properties of a fertilizer is its storability, which can be determined through measurement of its tendency to cake. By careful drying and effective surface treatment (see Section 5.7), the caking tendency can be significantly reduced and thus the storage qualities improved. This property is measured by, for example, a shear test on caked fertilizer.

Hygroscopicity. The hygroscopicity of a fertilizer characterizes its sensitivity to atmospheric humidity. Grains of a highly hygroscopic fertilizer exposed to sufficiently high air humidity take up moisture, which impairs their initial grain hardness and abrasion resistance. The hygroscopicity of a fertilizer is assessed from the water-vapor adsorption isotherm. The rate of water uptake and the critical relative humidity of the salt system can also be determined [434, 436]. Critical humidities are listed in [437]. Corresponding to the critical relative humidity is the partial pressure of water vapor over a saturated salt solution forming a very thin skin of liquid over the salt surface. If the humidity of the ambient air is less than critical, the liquid skin gives up water; if greater, the product gains moisture.

5.7. Fertilizer Conditioning

A conditioner is a material added to a fertilizer to promote the maintenance of good physical condition (flowability) during storage and handling. The use of conditioners is essential with many products, but is not required with all fertilizers. It is preferable to use other means, such as good drying, to avoid caking. Even if the fertilizer grains are dried adequately from an economic standpoint, caking may occur and impede storage, transportation, and field application.

Hardening and caking result from the crystallization of water-soluble salts and the formation of bridges between the grain surfaces during storage. The surfaces also suffer plastic deformation under pressure, and the reduction of the water vapor pressure in the joint between the new contact surfaces causes the particles to adhere to one another [438]. The reaction

$$NH_4NO_3 + KCl \rightarrow NH_4Cl + KNO_3$$

during storage may also be indirectly important in poor storage qualities [315, p. 370], [439].

The internal conditioning of fertilizers means incorporating additives in the granules before or during granulation to improve the physical properties and the anticaking qualities. Internal conditioners usually act as hardeners or crystal modifiers, for example to improve the storage properties of ammonium nitrate fertilizers. Internal conditioners inhibit or modify the effects of crystal phase inversions due to temperature changes during storage. The inversion at 32 °C can cause uninhibited ammonium nitrate granules and prills to shatter and cake. In the case of urea prills and granules, 0.2 – 0.5 % of formaldehyde or urea – formaldehyde is added to the urea melt as a hardener and anticaking additive [308, p. 301]. The addition of 1.8 % $Mg(NO_3)_2$ protects ammonium nitrate from caking. The destructure effect of the phase change at about 32 °C is avoided [440, p. 200].

External conditioning, also called coating and surface treatment, means applying to the granule surface a thin layer of powders or surfactants to reduce the caking tendency. The addition of wax and/or oil enhances the action by suppressing dust formation. This process step is carried out in a rotating drum or a fluid bed. Although coating with a fine, inert powder (kieselguhr, talcum, lime, kaolin) has long been practiced as an external form of inorganic conditioning, surface treatment with nonionic organic sealants (polyethylene waxes, paraffins, urea – aldehyde resins) and coating with surfactants to make the grain surface hydrophobic came into use later. The surfactants employed are, above all, fatty amines and sulfonates. These are also used [315] in combination with powders and waxes and/or oils [370, pp. 289 – 303]. For the use of special oils as anticaking agents, see [441]; for an example of a surfactant, [442]. For special coatings to prevent caking, see [443]. Because of the many anticaking agents and fertilizers in production, no overall recommendation can be made as to special additives for general use [438].

Intentional aging of fertilizer in a storage pile prior to bagging or bulk shipment is referred to as curing. In products that benefit from curing, chemical reactions that cause caking bonds apparently proceed to near completion during the curing period. The heat of reaction retained in the curing pile speeds the completion of the reactions. After curing there is reduced tendency for additional bonds to develop [308, p. 302]. In the manufacture of superphosphates, pile curing for about 30 d frequently is employed to improve physical properties.

5.8. Environmental Aspects

In fertilizer plants, the gaseous effluents from all equipment handling solid materials, including screens, have to be cleaned owing to their content of fine dust (and harmful gases). Although the most serious dusting occurs during the drying of granular fertilizers, dust is also formed in the granulators. These units are therefore operated under a partial vacuum. The dust in the off-gas is usually collected in cyclones and recycled. When dry dust collection is inadequate, wet separation in scrubbers, which also absorb gases like NH_3, is employed. Recycling of the scrub waters is implemented in the AZF process [444]. For NPK fertilizers, experience has shown that a soft granular product has a stronger dusting tendency than a hard one. For certain fertilizer formulations, less dust is produced from the drum than from the pug mill [445].

Gaseous effluents like ammonia, nitrogen oxides, and fluorine compounds are evolved in the production of NPK fertilizers and feedstocks. Normally these exhaust gases are scrubbed, and the resulting scrubber liquors are recycled to the process.

Liquid or aqueous effluents from fertilizer plants are usually of smaller volume compared to those vented to the atmosphere [308, p. 322]. They generally result from scrubbing equipment and can be concentrated and recycled. Spills and washings are usually collected in floor sumps and also concentrated and recycled.

For the removal of emissions from fluid-bed granulators, see [370, pp. 277 – 288]; for fluorine emission in triple superphosphate production, [446]; for a summary of environmental practices in the fertilizer industry, [308, pp. 319 – 328].

6. Analysis

The point and purpose of fertilizer analysis is to check the declared fertilizer grade and confirm that the contents of grade-determining components, nutrients, nutrient forms, nutrient solubilities, and incidental components are as printed on the bag. In the Western countries, all fertilizers are subject to official inspection, and the laws permit only small deviations within given limits.

In nearly every country, only products with established compositions and analyses are allowed in trade; therefore, inspections must be performed during production, and factory laboratories must use testing methods in compliance with the established official techniques of analysis (Table 33)

6.1. Sampling and Sample Preparation

Sampling must produce a sample that corresponds to an exact, representative average of a large product batch. The most appropriate time for fertilizer sampling is during bagging or when the bulk product is being loaded into conveyances. Only when sampling at this time is impossible should samples be taken from closed bags or from a bulk product stockpile. As a rule, the sample taken should make up at least 0.1 % by weight of a batch for delivery. Fertilizer regulations also contain provisions for sampling methods. A minimum requirement is given in EN 1482.

A suitable sample divider is next used to reduce the sample quantity to some 1 – 2 kg. The final sample must be prepared for analysis by comminution, screening, and homogenizing. The smallest portion called for by the analytical technique must still be representative of the whole final sample. At the same time, this preparation must not alter the gradation of the fertilizer in such a way as to have a marked effect on typical properties such as the solubility in extractants.

6.2. Determination of Nitrogen

The most important nitrogen compounds are nitrates, ammonium salts, urea, urea – aldehyde condensates, and cyanamide. Farm-produced fertilizers (e.g., liquid manure) have most of their nitrogen in organic form (protein).

Total Nitrogen. The analytical method for determining total nitrogen is dictated by the components present in the fertilizer. For straight N fertilizers that contain only ammonia nitrogen, e.g., ammonium sulfate, it is sufficient to alkalize the sample solution and distill the liberated

Table 33. National and international standards for fertilizer analysis

Method	European Economic Community [454]	Federal Republic of Germany [455]	International Organization for Standardization [456]	United States (AOAC) [457]
Sampling and sample preparation (see Section 6.1)	No. L 213 on pp. 2 – 4 EN 1482	No. 1.1, 1.2, 1.3 DIN/EN 1482	ISO 3963; ISO 5306; ISO 7410; ISO/DIS 7742	No. 2.1.01 – 2.1.05
Nitrogen analysis (see Section 6.2)				
Total nitrogen	No. 2.3; § 7.1 in No. 2.6.1; § 7.2 in No. 2.6.2	No. 3.5 (3.5.1 – 3.5.5)	ISO 5315	No. 2.4.02 – 2.4.06
Ammonia and nitrate N	2.2 (2.2.1 – 2.2.3)	No. 3.3 (3.3.2 – 3.3.4)	ISO 11 742	No. 2.4.09 and 2.4.10
Ammonia N	No. 2.1; § 7.2.5 in No. 2.6.1 and § 7.5 in No. 2.6.2	No. 3.2.1 – 3.2.6	ISO 5314, ISO 7408	No. 2.4.07 and 2.4.08
Nitrate N	§ 7.2.4 in No. 2.6.1 and § 7.4 in No. 2.6.2	No. 3.4.1 and 3.4.2	ISO 4176	No. 2.4.11 and 2.4.12
Urea N	§ 7.2.6 in No. 2.6.1, § 7.6 in No. 2.6.2	No. 3.8 (3.8.1 – 3.8.5)	ISO 8603	No. 2.4.20
Controlled-release N	EN 13 266	No. 3.10	in preparation	
Phosphate analysis (see Section 6.3)				
Extraction	No. 3.1.1 – 3.1.6	No. 4.1.1 – 4.1.7	ISO 5316, ISO/DIS 7497	No. 2.3.01, 2.3.06, 2.3.11, 2.3.14,
Dissolved phosphate	No. 3.2	No. 4.2, 4.3	ISO/DIS 6598	No. 2.3.02 – 2.3.05, 2.3.07 – 2.3.09, 2.3.12 – 2.3.14
Potassium analyses (see Section 6.4)	No. 4.1	No. 5.1, 5.2	ISO 5317, ISO 7407, ISO 5310	No. 2.5.01 – 2.5.08
Other analyses (see Section 6.5)				
Calcium		No. 6.1 and 6.2	ISO/CD 10 151	No. 2.6.01, 2.6.05 – 2.6.07
Magnesium	No. 8.1, 8.3, 8.6, 8.7	No. 7.1 and 7.2	ISO/CD 10 152	No. 2.6.01, 2.6.17 – 2.6.21
Sulfur	No. 8.1, 8.2, 8.4, 8.5, 8.9		ISO 10 084	No. 2.6.28
Micronutrients	No. 9.1 – 9.11	Chap. 8 (8.1.1 – 8.9.2)		No. 2.6.01 – 2.6.04, 2.6.10 – 2.6.16, 2.6.22 – 2.6.25, 2.6.29 – 2.6.32

ammonia into an acid of known concentration in the receiving flask. For samples containing nitrate, on the other hand, the nitrate content must be reduced first. Examples of ways to reduce the nitrate are with iron or chromium powder in an acid solution, with ARND alloy in a neutral solution, or with DEVARDA alloy in an alkaline solution. Nascent hydrogen reacts with the nitrate to give ammonia in quantitative yield. Distillation from the alkalized reaction solution gives the sum of ammonia N and nitrate N.

For fertilizers that contain other forms of N besides ammonia and nitrate, the reduction step must be followed by the conversion of the other N forms (urea, cyanamide, protein) to ammonia by Kjeldahl digestion.

The final determination of total N in every case is by distillation of ammonia from the alkalized pretreated solution into a receiving flask with an acid standard solution and backtitration of the residual acid excess.

Ammonia Nitrogen Apart from Other N Compounds. In theory, the ammonia component is easily isolated from commercial mixed-salt fertilizers by distillation from sample solutions alkalized with NaOH or KOH. Urea and other organic N forms readily give additional ammonia in alkaline solution. If such compounds are present, the distillation conditions must be kept as mild as possible. The solutions are alkalized with soda, calcined magnesium oxide, or freshly precipitated calcium carbonate, and the ammonia liberated is distilled under reduced pressure at room temperature or with the help of a strong air purge.

For pure ammonium salts of strong acids, the formaldehyde method offers a quick procedure for ammonia determination. The reaction of ammonium ion with formaldehyde

$$4\,NH_4^+ + 6\,CH_2O \rightarrow (CH_2)_6N_4 + 6\,H_2O + 4\,H^+$$

liberates protons equivalent to the ammonium ions present; these can be directly titrated with sodium hydroxide standard solution.

Nitrate Nitrogen Apart from Other N Compounds. In many cases, nitrate N is determined as total N minus ammonia and urea N. The most versatile direct method is precipitation of the nitrate with nitron and final determination by gravimetry. Another sensitive method, recommended for specially formulated mixed fertilizers with low nitrate contents, is a colorimetric technique based on the nitration reactions with 2,4- or 3,4-xylenol. The nitration products give intensely colored compounds in alkaline solution.

Urea Apart from Other N Compounds. Three different methods are available for the selective determination of urea:

1) Separation of urea by precipitation with xanthydrol(9-hydroxyxanthene), yielding dixanthylurea; gravimetric final determination
2) Enzymatic hydrolysis of urea, controlled by ureases; distillation of produced ammonia into a receiving flask with acid standard solution, where it is absorbed
3) Colorimetric method (for low urea contents) based on the reaction of urea with *p*-dimethylaminobenzaldehyde

Nitrogen Fertilizers with Controlled-Release Urea – Aldehyde Condensates. Ureaform, Isodur, and Crotodur are nitrogen compounds that are only slightly soluble in cold water but are nonetheless effective as fertilizers. The delayed water solubility provides a basis for the analytical characterization of these compounds: extraction with cold water isolates the readily available N components (ammonium, nitrate, free urea). Only when the extraction residue is treated with hot water do isobutylidene diurea, crotonylidene diurea, and the short-chain components of the urea – formaldehyde condensates go into solution.

In an acid medium, especially at high temperature, condensates of urea with formaldehyde and with isobutyraldehyde tend to hydrolyze to urea and the aldehyde. In mixed fertilizers with an inherent acid tendency, there is thus a danger of altering the solubility characteristics in the course of the analysis. For this reason, the separations are carried out in buffered solutions of pH 7.5 [455].

To calculate the percent N contents, either the total N is determined in the extraction solutions or else the AOAC procedures for urea – formaldehyde condensates are carried out and a nitrogen activity index is determined.

$$\frac{\%\mathrm{CWIN}-\%\mathrm{HWIN}}{\%\mathrm{CWIN}}\times 100 = \mathrm{AI\ in}\%,$$

where CWIN is cold-water-insoluble nitrogen and HWIN is hot-water-insoluble nitrogen.

The nitrogen activity index for urea – formaldehyde condensates is around 50; crotonylidene diurea and isobutylidene diurea have values of more than 90.

6.3. Determination of Phosphate

Because phosphorus fertilizers are rated by their contents of phosphate available to plants, various extraction methods have been devised.

Extraction with Water. Most countries define *water-soluble phosphates* as those components that go into solution at room temperature when an aqueous suspension is made with 1 g of sample to 50 mL of suspension volume (in the USA, 1 g of sample to 250 mL).

Extraction with Citrate Solution. The technique of citrate extraction determines phosphates, such as $CaHPO_4$, that are insoluble in water but soluble in complex-forming salt solutions.

The most common methods in Europe use ammonium citrate solutions with a prescribed citrate concentration. The officially approved extraction processes differ in the choice of pH. Extraction is performed in a strong alkaline medium with an ammoniacal ammonium citrate solution, or in a neutral ammonium citrate solution. Most often, extraction is carried on for 30 min at room temperature and is followed by a treatment at 40 °C; for the EEC process with neutral ammonium citrate solution, 65 °C is prescribed.

Extraction with Citric Acid Solution. Originally, the citric acid solubility was stated only for Thomas phosphate, but the lack of agreement between the plant availability of P_2O_5 and the solubility in ammoniacal citrate solution led to other straight and mixed phosphate fertilizers being rated by citric acid solubility. Treatment with 2 wt % citric acid solution (5 g of sample is agitated in 500 mL of citric acid solution for 30 min at 20 °C) dissolves phosphorus – silicon heteropolyacids, which are hardly soluble in complex-forming salt solutions.

Extraction with Formic Acid Solution. Soft and hard phosphate rock can be distinguished by their behavior in 2 % formic acid. A 5-g ground rock sample is shaken at 20 °C for 30 min with 500 mL of the formic acid solution. In the case of soft phosphate rock, 50 – 70 % of the total phosphate dissolves; in the case of hard phosphate rock, only ca. 25 % dissolves.

Extraction for Total Phosphate Determination. A technique applicable to all fertilizers as well as crude phosphates is digestion with sulfuric acid, nitric acid, and copper sulfate. Mixtures of hydrochloric and nitric acids or nitric and perchloric acids have also been proposed for quantitative extraction.

Determination of Phosphate. After hydrolysis of polyphosphates in acid solution, if necessary, phosphate is precipitated as quinolinium molybdatophosphate and weighed. Possible substitutes for the gravimetric final determination are methods in which the precipitate, washed acid-free, is dissolved with an excess of sodium hydroxide standard solution and back-titrated with nitric acid standard solution. Reaction of the dissolved phosphate with a molybdate – vanadate solution yields a soluble, colored heteropolyacid complex, which can be determined by colorimetry.

6.4. Determination of Potassium

For almost all fertilizers that contain potassium, this component is dissolved in water. In complete fertilizers, it is advisable to perform the extraction in acid solution so that, if gypsum is present, none of the potassium will take part in double salt formation and remain undissolved as syngenite. For the determination, the potassium is precipitated with sodium tetraphenylborate from a weakly alkaline or acidic solution; the product, slightly soluble potassium tetraphenylborate, is weighed. Another proposal, mainly in the USA, is to precipitate the potassium as the chloroplatinate (AOAC). Flame photometry is also recognized as an official test method.

6.5. Analysis of Calcium, Magnesium, and Trace Elements

Complexometric methods with EDTA have come into widespread use for determining calcium and magnesium. Photometric techniques for the determination of other metal ions effective in growth (Cu, Fe, Mn, Zn, Co, Mo) have been described. To an increasing extent, however, atomic absorption spectrophotometry has gained in importance. Emission spectral analysis with plasma excitation is also used in fertilizer analysis. But this procedure is new, and as yet no official analytical specifications exist for it.

Boron must be isolated by distillation in the form of methyl borate before it can be determined. The boric acid is reacted with 1,1-dianthrimide or azomethine H, and the colored product is determined by photometry. For boron contents of 0.1 % and higher, boric acid and polyhydric alcohol (usually mannitol) are reacted to give didiolboric acid, which is determined volumetrically.

7. Synthetic Soil Conditioners

Soil conditioners are substances with which the soil and substrate properties, seldom ideal for the growth of plants, can be optimized and stabilized. Their purpose is to exert biotic, chemical, or physical influences on soils in such way as to improve the soil structure and water regime [462]. Synthetic soil conditioners have well-defined composition, stable quality, and properties suited to the requirements they must meet. They may, for example, supplement or replace natural substances that are unsuitable from an environmental and ecological standpoint, are in scant supply, or must be conserved.

7.1. Foams

Foamed polystyrene and foamed urea – formaldehyde resin are used as soil conditioners; foamed phenolic and polyurethane resins are used as florists' mounting media or plant growth media [458].

7.1.1. Closed-Cell Expandable Polystyrene Foam

Expandable polystyrene (PS) foams consist of polystyrene pre-expanded by blowing agents at temperatures of about 100 °C and, after holding, expanded with steam. The forms used for soil conditioners are flakes, beads, or raspings [458 – 460, 463, 464].

Physical and Chemical Properties. Expandable PS foams have closed cells. They contain 98 % air by volume and can hold 1 – 2 % water on their surface [465, 466]. They do not, however, absorb water. Air exchange does take place [467]. Styromull foam flakes are 4 – 16 mm in diameter with a loose density of 12 – 20 kg/m^3 [459]. The permeability to water between expandable PS flakes without compression is roughly the same as that of fine gravel; under 25 % compression, it matches that of coarse sand; at 75 % compression, that of fine sand.

Expandable PS foams are largely resistant to attack by acids and alkalies; they are odorless, chemically neutral, and unobjectionable to plants. These foams have been considered resistant to degradation by soil bacteria. Physical degradation takes place under the action of ultraviolet radiation, and biodegradation, especially by soil fungi, yields carbon dioxide and water [467]. This process is slow, however, so that the foams are effective soil conditioners with a relatively long lifetime.

Use. Expandable PS foams in comminuted form for soil application have been described [468, 469]. Uses range from incorporation into soils and garden substrates to the conditioning of weak-structured peat [470].

Incorporated, they have soil-loosening, aerating, and draining actions. Foams are also employed as soil conditioners in crop farming and landscaping, and they have proved useful as drainage aids in slit drainage and as filter materials for covering drain pipes [458, 471, 472].

For soil aeration and structural stabilization around the roots of urban trees, expandable PS foam beads (1 – 2 mm diameter) are recommended for use with soil aeration equipment (e.g., Terralift) [473, 474].

Trade Names. Hygropor, Styromull (BASF, Ludwigshafen, Germany); Styrofoam (Dow Chemical, Midland, Mich.).

7.1.2. Primarily Open-Cell Urea – Formaldehyde Resin Foams

Urea – formaldehyde foams consist of condensates of urea with formaldehyde in a well-defined molar ratio. They are solid foams with rigid walls and little flexibility. The materials used as soil conditioners are mainly urea – formaldehyde foams modified for plant compatibility.

Physical Properties. Urea – formaldehyde foams can be produced with densities of 2 – 50 kg/m^3 (as water-free uncomminuted material); foams with a density of 22 kg/m^3 are used for mixing into soils and substrates. Packed moist from processing, urea – formaldehyde flakes (trade name Hygromull) weigh approximately 35 – 40 kg/m^3.

The cell walls are partly open. They are thicker, and the cell volumes smaller, the higher the density. Cell diameters lie between 100 and 300 µm [460, 475, 476]. The capillarity is low (1 – 2.5 %); the capillary elevation is 300 – 400 mm [460]. The capillary elevation for a garden substrate treated with foam is described as advantageous [477].

The grades used as soil conditioners are made water-absorbing by modification of the condensate resin and comminution to flakes measuring 4 – 20 mm. Under vacuum, the water capacity is more than 90 vol % [478]; for Hygromull flakes having a density of 22 kg/m^3, this corresponds to 4100 wt %. The water capacity can be determined appropriately by the method of DIN 11542 (1967). At atmospheric pressure, the initial water uptake is slow but rewetting is very fast [478].

Water release is uniform and goes to completion without losses due to evaporation, so that the water stored in the foam flakes can be economically utilized by plants. The water is held in place by suction forces of pF 1.2 – 2.54 (cf. Section 2.2.4). Urea – formaldehyde foams in a loose bed have the permeability of moderately fine sand; under 25 – 35 % compression, that of fine sand [479].

Chemical Properties. As the condensation product of urea and formaldehyde, the foams are synthetic organic substances. Incorporated into moist soils and substrates in flake form, they are known to be biodegradable. At pH 6 – 7, the process goes at 3 – 5 % per year [480]; at pH 3.9 – 4.1, degradation is speeded up (15 – 20 %), especially at temperatures over 40 °C. The stability falls off rapidly above 80 °C. In horticultural substrates, steam sterilization is tolerated up to a maximum of 1 h.

The components of the urea – formaldehyde foams are readily biodegradable: The urea component mineralizes to ammonium and is then converted microbially to nitrate. The formaldehyde component is liberated upon mineralization; it undergoes microbial degradation in 48 – 72 h in soil or water, even more quickly in air. Bioaccumulation does not occur [481].

A theoretical effective lifetime of some 20 – 30 years is desirable for soil conditioning [462, 482].

Raw Materials and Manufacture. A process, part of which has been patented, is used to produce foams from modified urea – formaldehyde condensation products with compressed air, foaming agents, and hardeners in fixed or mobile equipment [483].

In Germany, the maximum allowable workplace concentration (MAK) in production is 1 ppm formaldehyde; this level may be exceeded only for short periods and within limits. In the United States, the absolute MAK is 3 ppm.

Use. The use of urea – formaldehyde foams as soil conditioners has been described by DOEHLER [484]. BAUMANN advanced their use (1953 – 1968) and developed the Plastopanik technique [459]. Foams were brought into reproducible use through extensive research [458, 460, 462, 470, 485, 486].

For reasons of cost, applications cluster in the areas of garden crops, such as pot and container plants, cut flowers (e.g., carnations, chrysanthemums), flower bulbs, fruits (including strawberries), vegetables, and eucalyptus, and in landscaping, where foams are used in newly seeded lawns and woods, in the transplanting of large trees, and in sports areas and golf courses.

In terms of soil physics, urea – formaldehyde foams optimize the air and water regimes in soils and substrates. They enhance the pore volumes, the maximum, minimum, and plant-available water capacity, and the aeration, and they lower the soil density. Plants respond with improved shoot and root growth, better early growth and development rates, and increased crop yields and qualities [462].

Trade Names. Hygromull, Hygropor (mixtures of Hygromull with Styromull) (BASF Aktiengesellschaft, Ludwigshafen); Agricon (Intrinco, Vaduz, Liechtenstein).

Official licenses have been issued for Hygromull and Hygropor in Austria, Belgium, France, Luxembourg, the Netherlands, Norway, Spain, and Switzerland and also for Agricon in Saudi Arabia and other Middle Eastern countries.

7.2. Colloidal Silicates

Colloidal silicates include compounds of polysilicic acid, produced and stabilized mainly by synthetic means, with a high content of reversibly soluble silicic acid and added flocculating electrolytes [460, 462, 487 – 489].

Agrosil colloidal silicate consists of (1) partly dehydrated sodium silicate, precipitated (neutralized) with acids, (2) electrolytes (phosphate, sulfate), and (3) an organic additive to retard aging. Official licenses have been issued for it in Austria, Belgium, Denmark, France, Luxembourg, the Netherlands, Norway, Spain, Sweden, Switzerland, and some Middle Eastern countries.

Physical and Chemical Properties. Colloidal silicates are solid, fine-grained, and thus easily distributed substances that can be dispersed with water to form silica gels and silica sols. Silica gels, examined under the electron microscope, are described as porous; they exhibit surface activity for the addition and inclusion of water and nutrients [490, 491]. Incorporated into soils, they fill the voids between soil particles [492] and bind these together with organic and inorganic complexing agents to form water-stable crumbs [462, 493 – 496]. Pore redistribution takes place in this process [490, 497]. Sorptive salt buffering has been described in soil mixtures [488, 491, 498].

The chemical activity is ascribed in particular to the low-molecular-mass silica sols. In the soil, they enable the holding of phosphate in solution or its activation by desorption [490]; depending on the pH, they can irreversibly fix heavy metals [461, 462, 499 – 504].

Raw Materials and Manufacture. Raw materials for the production of Agrosil colloidal silicate are spray-dried and liquid sodium silicate, phosphoric and sulfuric acids, and an organic aging retardant such as urea, humic substances, pectins, or proteins. The manufacturing process is patented [505, 506].

Use. Colloidal silicates are conceived as soil supplements or soil conditioners [462, 488, 493]. To a certain extent, they make it possible to return soils affected by salts and heavy metals to agricultural use [462].

Their action as soil conditioners depends on their incorporation in the soil and their ability to take up water (precipitation, irrigation). Quantities used per are (= 10^2 m^2) are 7 – 20 kg, preferably 10 – 15 kg. In gardening and landscaping, they have an effective lifetime of 3 – 5 years; aftereffects in unworked soils have been seen for 10 and 14 years.

Direct effects due to soil conditioning include improved water and sorption capacities, the activation of plant nutrients in the soil, physical improvement of soil structure through pore redistribution and crumb formation; and the fixing of heavy metals (such as Cd, Cu, Pb, and Zn) in the presence of alkaline earths. Indirect effects include improved soil life (respiratory activity and nodule bacteria), the release of excess water (a consequence of crumb formation), and enhanced phosphate mobility. The growth of new shoots and roots is encouraged, both organic and inorganic substances are accumulated in the vegetation in greater quantities, less water is needed, wilting of grass is reduced, and fungus and bacteria resistance is increased [462, 507].

In the Swiss classification, the product is not classed as toxic.

Trade Names. Agrosil (Guano-Werke AG, BASF).

7.3. Polymer Dispersions and Polymer Emulsions

Poly(vinyl acetate), poly(vinyl propionate), butadiene – styrene copolymer, *cis*-butadiene, and various acrylic acid polymers have been described and employed as soil conditioners with actions in and on the soil [460].

Physical and Chemical Properties. The products are mainly applied to the soil surface in aqueous solutions. They cross-link the particles of the uppermost soil layer and, depending on the concentration of the active agent, form a closed film or networklike coatings. These are permeable to precipitation but diminish evaporation. Incorporated into the soil, they promote crumb formation [494].

As organic substances with a relatively high dilution, polymer dispersions are degraded relatively quickly by UV radiation when on the surface of the soil and by microbial action when in the soil. Their action is therefore limited in time, and their stability depends on ambient conditions such as cold and heat.

Use. Polymer dispersions are employed chiefly for seed protection in landscaping, and also in vegetable and flower-bulb growing. They are applied at planting time by spraying, usually along with fertilizers and soil conditioners (e.g., Agrosil) or mulches (cellulose, straw). They can also be applied after planting by area spraying or, in the case of vegetables planted in rows, by stripe spraying [508].

The quantities used depend on the product and vary between 10 and 50 g/m^2; the dilution with water depends on the purpose and varies between 1 : 1 and 1 : 60 (product : water).

The duration of the structure-stabilizing or protective action depends on the quantity used [509] and on environmental conditions such as weathering and insolation.

Polyacrylates and polyacrylamides are recommended for use alone or with, e.g., starch to promote water storage in soils [460, 510 – 515]. The waterholding effect is, however, greatly diminished by pH values higher or lower than 7.0, water hardness, and dissolved substances such as urine or soil nutrients. No satisfactory practical solution has been found for these limitations [516], but more recent generations of these so called superabsorbers are claimed to be more tolerant towards dissolved salts. Various applications to gardening substrates and flower-growing soils have been described [517].

Polymer formulations are used for protection against erosion, especially in conjunction with the sprouting of seeds. They perform an environmental function by offering limited protection to the seeds or small plants against wind and rain erosion until the plants are large enough to protect themselves. They are of increasing importance in furrow irrigation systems in North America for preventing soil erosion and increasing water infiltration into the soil. A concentration of 10 ppm in the irrigation water is necessary to achieve the desired effects [518]. Biodegradability is a prerequisite for the soil and plant application of selected polymers. Biodegradability is not assured in the case of some polyacrylates.

Trade Names. Curasol for poly(vinyl acetate) (Hoechst Aktiengesellschaft, Frankfurt); Hüls 801 for *cis*-butadiene (Chemische Werke Hüls, Marl); Aqua-Gel for polyacrylate plus starch (Miller Chemical and Fertilizer Corp.); Hydrogel Viterra for poly(ethylene oxide) (Union Carbide Corp., New York); SGP Absorbent for sodium polyacrylate plus starch (General Mills Chemicals, Inc., Minneapolis, Minn.); Soiltex G1 for polyacrylamides (Allied Colloids).

7.4. Tensides

Many tensides have been tested as soil conditioners, including ammonium laureth sulfate, ethoxylated alkyl phenols, polyoxyethylene esters of alkylated phenols, polyoxyalkylene glycols and their polymers, polyoxyethylene, polypropoxypropanol glycol butylesters, alkyl polyglycosides, sulfosuccinates, and poly(propylene oxide)s. The hydrophobic ends of the molecules of the these so-called wetting agents are adsorbed by water-repellent organic matter, and the hydrophil ends link the soil particles with water.

Use. In turfgrass culture thatch accumulation may occur due to reduced decay of the organic matter of the grass sward. Under dry conditions, this material becomes hydrophobic, and irrigation results in water losses because of poor infiltration rates and run-off [519, 520]. Spraying of wetting agents onto the affected areas at a rate of 10 – 20 L/ha increases water absorption and efficiency. Solid formulations are also available.

Trade Names. Primer (Aquatrols, USA); wetx'tra (Rhône Poulenc, France); Turf Ex (Service Chemicals, UK), Saturaid (Debco, Australia).

8. Storage, Transportation, and Application

Fertilizers are produced continuously, year-round, in large capital-intensive plants, but they are sold only in a few months at the beginning of and during the vegetation period. Large quantities must therefore be stored for long times. The logistic of delivering the product to the user at the proper time leads to a subdivision of storage into plant storage, dealer storage, and user storage. In this way, loading and transport are spread evenly through the year, with additional control by seasonally varied sales rebates.

The construction and operation of storage facilities depend on the size, the location, the type of fertilizer, and the danger level, all of which are dictated by the product.

8.1. General Storage Requirements

Fertilizers are classified as follows by danger level:

- Group A. Explosive fertilizers, such as those with a high ammonium nitrate content or with a low ammonium nitrate content and > 0.4 wt % organic matter.
- Group B. Fertilizers in which self-sustaining, progressive thermal decomposition (low-temperature decomposition) is possible. In the past this group comprised mainly multinutrient fertilizers which contain ammonium nitrate. Today, the ammonium nitrate based multinutrient fertilizers which are marketed are almost exclusively rated Group C.
- Groups C and D. Fertilizers that do not explode and are not susceptible to self-sustaining, progressive thermal decomposition.

The precise classification is set forth by law [521]. With its technical regulations, the German regulation concerning hazardous substances (*Gefahrstoffverordnung*) prescribes in detail how to construct and to operate storage facilities for ammonium nitrate based fertilizers. How many regulations have to be observed depends on the classification of the fertilizer. The strictest standards apply for Group A, followed by Group B. For nonflammable fertilizers (Groups C and D), the normal storage conditions for bulk materials apply.

Most fertilizers come in granular form and readily absorb moisture. As a result, they experience caking or granule disintegration; either effect makes application more difficult. The storage areas must therefore be dry. Not only the roof and walls must be tight, but the floor must be safe against rising moisture. Care must also be taken that moisture does not get into the storage building because of too much air circulation. Doors and windows must be kept closed when the relative humidity is over 65 %. The surface : volume ratio in storage should be as small as possible.

Fertilizers containing ammonium nitrate, especially calcium ammonium nitrate, must be protected from direct sunlight and from repeated temperature changes at 32 °C, because otherwise repeated recrystallization leads to granule disintegration.

When ammonium nitrate fertilizers are heated above 130 °C, low-temperature decomposition sets in, generating gases that may be toxic, depending on concentration. Practices must therefore be employed that safely prevent the action of fire or external heating. Such practices include general fire-protection measures such as no smoking, no use of fire or open light, and no unauthorized entry. Ammonium nitrate fertilizers must not be mixed with flammable materials (sawdust, coal dust, sulfur, petroleum, etc.) or with acidic or basic substances (lime, basic slag phosphate, acid salts, etc.). Welding and burning work may be carried out only with the most stringent safety precautions. Electrical equipment must be located outside the fertilizer pile. Cables and wiring must be located at least 0.5 m above the highest possible pile level. Special care should be taken that the pile does not cover up lights, especially portable lights connected by cable to the power supply.

With regard to moving mechanical parts (belt, screw, and bucket conveyors, etc.), care must be taken that these devices cannot run hot or experience fertilizer buildup at critical points. Diesel and gasoline trucks that go directly into the storage area represent a danger due to hot exhaust gases and hot mufflers. Hardened fertilizers must be loosened mechanically, not with explosives.

Low-temperature decomposition can be detected by white or brown smoke or a piercing smell. If this process develops and is recognized promptly, the sintered reaction zone can be separated from the unreacted fertilizer. Good access is needed, and precautions are needed to keep the sizable amounts of gas evolved from being a health hazard. If safe access is not possible, the decomposition must be brought to a stop by cooling with water. If any low-temperature decomposition takes place, an alarm must immediately be sent to the fire-fighting service.

Fertilizers affect most of the conventional building materials, especially when wet. Steel, aluminum, and zinc suffer more rapid corrosion and must be protected by several coats of paint (total thickness > 180 μm). Fertilizer dust can cause brittle fracture at welds in steel. Subsequent welding must be carried out with special care.

Mineral fertilizers attack concrete more or less severely, causing scaling and corrosion of the steel reinforcement. For this reason, concrete floors contacted by fertilizer should be protected by filled coal-tar pitch or epoxy-based plastic.

Wood, especially in the new form of glued lamellae, is a suitable material. Care should be taken to use corrosion-resistant fasteners.

Plant Storage. Storage at the fertilizer plant is almost always in bulk form. Large warehouses, with capacities of up to and beyond 50 000 t for one or more grades, are employed. The total storage capacity is usually several months' production. The size, shape, and outfitting of the warehouses depend on the frequency of shipping, the number of grades, the required loading capacity, and the area available. In order to reduce the risk, some grades are limited as to amount stored in a single warehouse, which may be accomplished by dividing the building. Large quantities are stored in elevators (tower silos) only under some restrictions, because of the risk of caking and the resulting high reclaiming cost.

If enough space is available and shipments are not frequent, a flat-floor warehouse in which material can be piled more or less high against the walls is the most economical design. Trough-shaped or basin-shaped storage structures with appropriate reclaiming equipment are used when space is limited and intervals between shipments are short.

The material used for the foundation and walls is usually reinforced concrete; the roof is most often made of wood. Glued lamellar wood construction makes it possible to span wide buildings without posts. Fertilizer can be piled against the walls to a height of 10 m or more. However, if the pile is too high, the material can segregate during placement. Slides during reclaiming are also a problem if material is piled too deep. The plant warehouses generally need not be heated, since the fertilizer leaves the production facility at a temperature of 35 – 45 °C (not over 50 °C). On the other hand, overhead conveyors and loading apparatus spanning moderate distances should be heated to keep them dry.

Piling is done mainly with overhead belts at the center or side, with transverse distribution by belts, chutes, or discharge pipes. Newer facilities have a distribution control room with closed-circuit television units.

Reclaiming capacity must be several times piling capacity. Because requirements vary, several methods have been devised. For high capacity and short shipment intervals, track-borne scrapers capable of automation are used. Bridge cranes are also employed. Many wheeled tractor loaders are in service; these can be shifted from one location to another, easily replaced if damaged, and reinforced if necessary. All warehouse equipment moves material by way of transfer hoppers to conveyor belts, troughs, or bucket conveyors, which carry the material to the loading point. Crucial factors in the choice of equipment are the loading capacity required, the storage qualities of the fertilizer, the cost of structures and equipment, the safety of the operation, and the expected operating costs.

Warehouses are not usually operated on the first in, first out principle. For practical reasons, however, the warehouse should be emptied completely from time to time, since varying raw materials may result in slight color variations, while going to zero aids precise inventorying, and for other reasons.

Shipping from the Plant. Fertilizers at present are usually shipped in bulk, in self-discharging railroad cars, trucks, silo cars with pneumatic loading of elevators, and canal boats and barges.

Before shipping, many plants screen the fertilizer again to remove dust, lumps, and impurities.

Shipment of fertilizers in bags is declining. The product is usually put in 50-kg open bags (pillow bags), which are then sewed or welded shut, or in valve bags. Valve bags are better suited to stacking on pallets because of their boxlike shape. Most bags are made of plastic — extruded polyethylene tubing or woven polypropylene strips coated or lined with polyethylene. Paper and jute bags are now rarely used. The machinery industry has developed largely automated equipment for bagging and loading or palleting, and much work is still under way to improve these devices and adapt them to various requirements. Because of the associated high investment costs, bagging takes place mostly at the fertilizer plant. Palleting, which simplifies subsequent transfer of the bagged product, has gained in importance. In many countries, fertilizers are shipped in large 500 – 1000-kg bags, likewise made of woven polyethylene or polypropylene.

Dealer Storage. Fertilizer is stored chiefly in buildings, which are usually divided boxwise. Because of the caking tendency and the resulting problems with reclaiming, especially in the case of ammonium nitrate fertilizers, elevators find use only for free-flowing grades, for a limited span of time, and for quantities up to 30 t.

In building storage, special care should be taken to protect against moisture, since the fertilizer no longer has its heat from production, and it often sits for several months under cool, moist conditions. Before receiving material, the warehouse must be completely dry. Fertilizer should be placed continuously, without long breaks. The pile height should not exceed 5 m. Immediately after placement, the fertilizer surface must be carefully covered with film not less than 25 µm thick, because of the mechanical stress. Joints in the film must have an ample overlap, usually 1 m. A tight seal should be made at the walls (e.g., with wood lath). Air circulation should be minimized (closed windows and doors, airtight roof). If product is reclaimed in stages, the cover must be restored each time.

A belt conveyor is suitable for placement of fertilizer. Mechanical abrasion restricts the use of screw conveyors (not over 5 – 6 m, 100 rpm).

User Storage. The interim storage of mineral fertilizers by the consumer is declining to the same extent that the dealers become more willing to undertake this kind of storage. Bulk fertilizer is kept mainly in flat storage boxes, just as in the trade, and the boxes are similar to those used for dealer storage. Elevator storage is practiced on a very limited basis.

Bagged product can be stored by the user without major precautions. To simplify transfer operations, between 20 and 30 50-kg bags are assembled on a pallet, with or without shrink-wrap; in some countries, large bags (0.5 – 1.0 t) are also employed. Bagged fertilizer can be stored outdoors for a limited time under certain conditions (no temperatures over 32 °C, white UV-stabilized covers).

Transportation. Group B fertilizers can generally be transported without special precautions. Only in exceptional cases are they considered hazardous goods as defined in the transportation regulations. Specific provisions for Group B, as well as Group A fertilizers, are set forth in international regulations for various kinds of carriers. The most important rules are recognized by nearly every industrial nation and have been incorporated into the national regulations.

Sea transport: IMDG (International Maritime Dangerous Goods Code)
Rail transport: CIM (International Convention on the Transport of Merchandise by Rail)
Road: ADR (European agreement concerning the international transportation of dangerous goods by road)
Air: IATA-RAR (IATA Restricted Articles Regulations)

The CFR contains rules for all modes of transportation in the USA.

8.2. Application

Solid mineral fertilizers are generally applied to agricultural sites in the form of granules, coarse or fine crystals, and powders. Fine crystals and powders are becoming less and less important, with the exception of lime which is used almost exclusively in powdered form.

To achieve a good nutrient efficiency and to avoid environmental pollution, the equipment used for the application of mineral fertilizers has to meet the following requirements:

1) Exact calibration of the amount of fertilizer applied and uniform distribution, both in the direction of travel and in the transverse direction, and independent of traveling speed and application rate.
2) In order to attain a high area of application, the effective band must be wide and the distributor design must permit a high rate of operation. The rate must be variable between 50 and 1000 kg/ha. Special distributors for liming must offer rates of up to 5000 kg/ha.

The uniformity of fertilizer application can be determined exactly on a test stand. Boxes with areas of 0.25 m^2 catch the fertilizer over the whole application width, and the product is then weighed. The mean is calculated from the individual values. The smaller the mean deviation from the average value, the more uniform the fertilizer distribution. Internationally, the test method is largely unified, so that the results are also easily comparable from country to country.

Application Equipment. Mineral fertilizers in the form of granules or coarse crystals are generally applied by broadcasting-type fertilizer distributors. Spreader rigs with pneumatic transverse distribution are also utilized, but their use is of declining importance. Powdered fertilizers such as lime are preferably applied by fixed-width fertilizer spreaders with mechanical transverse distribution to avoid dust formation during operation.

Broadcasting fertilizer spreaders, also called spinner spreaders, operate with working widths of 6 – 36 m. They are characterized by simple construction and easy handling, together with a high area performance. They constitute the absolute majority of all fertilizer distributors.

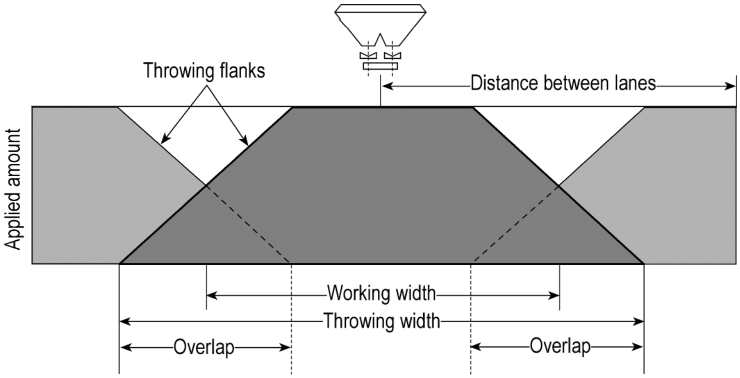


Figure 36. Broadcasting pattern for spinner spreaders

Broadcasting fertilizer spreaders distribute the fertilizer over a semicircular to semi-elliptical area around the spreading device. The spreading width is greater than the effective working width. As the amount of fertilizer which is applied per unit area decreases towards the borders of the spreading swath, overlapping of adjacent swaths is necessary for uniform transverse distribution of the fertilizer (Fig. 36). Modern broadcasting spreaders have broadcasting patterns with extremely flat sides, so that the risk of distribution errors in the overlap zone is minimized.

Three types of broadcasting spreaders with different spreading devices exist: single-disk, twin-disk, and oscillating spout (pendulum) spreaders (Fig. 37). The twin-disk spreader is gaining importance over the single-disk and oscillating-spout spreaders, since its basic concept is better suited for further technical development. Consequently, the spreading quality of twin-disk spreaders has been raised to a level almost matching that of pneumatic spreaders.

The spreading device in oscillating-spout spreaders is a pendulum tube that moves to and fro. Since this spreading technique allows working widths of only 6 – 15 m, whereas the large fields of modern agriculture require increasingly greater swath widths, the importance of oscillating spout spreaders is also diminishing.

Fixed-Width Fertilizer Spreaders. With fixed-width spreaders the transverse distribution of the fertilizer is achieved by means of booms, either pneumatically or mechanically. Unlike spinner spreaders, only one working width is possible.

In pneumatic fertilizer spreaders, the fertilizer is metered at the hopper by cam wheels, fed into distributor tubes, and transported by blast air to discharge outlets along the spreader booms, which are provided with deflectors (Fig. 38). Depending on the boom length, working widths of up to 24 m are possible. When working with a pneumatic spreader, overlapping of adjacent swaths is required, as with a spinner spreader. However, due to the steep flanks of the broadcasting pattern, the required overlap is much smaller (Fig. 39). Pneumatic spreaders can be used for the application of granulated and

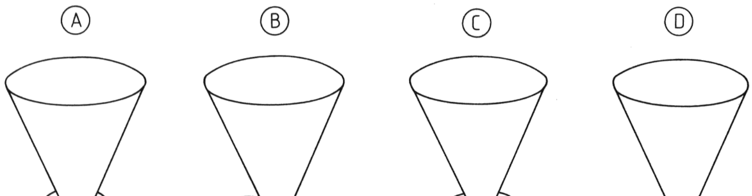


Figure 37. Broadcasting spreaders: single-disk centrifugal distributor (A), twin-disk centrifugal distributors with side-by-side (B) and over-and-under spinners (C), oscillating-spout distributor (D)

crystalline mineral fertilizers, if possible free of dust.

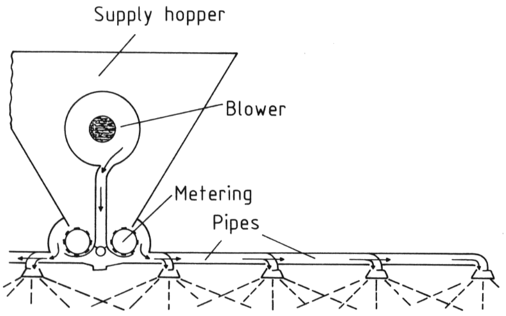


Figure 38. Schematic of a pneumatic fertilizer spreader

Spreaders with mechanical transverse distribution are generally equipped with a screw or auger (auger-type spreaders) Fertilizer flowing from the hopper is conveyed to the driven auger by various means and is then transported to the spreader tubes with adjustable discharge spouts (Fig. 40). Depending on the boom length, working widths of 6 – 8 m are possible. Auger-type spreaders are preferably used for the application of powdered fertilizers. Boom length and working width are identical. For uniform fertilizer distribution, exact driving in parallel runs is indispensable (Fig. 41).

Electronically Controlled Spreading Equipment. Electronic control units are increasingly being used to monitor and to improve the metering and distribution of mineral fertilizers. Thus, the correct amount of fertilizer can be automatically discharged when the traveling speed of the spreader is changed, and the amount of applied fertilizer can be displayed, based on permanent monitoring of the fertilizer discharge.

Site-Specific Fertilizer Application Guided by GPS. Until now farmers' fields generally received a uniform fertilizer rate. With the steadily increasing size of individual fields this practice is bound to change, as increasing field size also implies increasing heterogeneity of the soil and thus of the crop yield. For economical and environmental reasons, a future development towards the site-specific management of large-sized fields is imminent. Under this aspect, the global positioning system (GPS) is currently being tested under practical conditions for its suitability for crop management, including fertilizer application. GPS allows the exact position in the field to be determined and relocated, regardless of weather, location, and time. On this basis, it should be possible to apply fertilizers site-specifically in accordance with the existing soil and crop variations within a field. The complete technology, from yield recording by the harvester to nutrient application with the fertilizer spreader, has yet to be further developed. This will probably take another 5 to 10 years.

9. Environmental Aspects of Fertilizer Application

Fertilizers are used to enhance soil productivity or fertility (amelioration fertilization) or to maintain it at an economically and ecologically acceptable level (maintenance fertilization). The task of fertilizers is to replace the nutrients lost through the harvest and by other causes: irreversible fixation in the soil, leaching, escape in gas form, etc. Along with the positive effect of fertilizer application, there are also negative effects, especially with improper use.

Up to the beginning and middle of the 1970s, environmental problems triggered by fertilization practices were subject to local discussion only; examples were the buildup of heavy metals in soils and crops when sewage sludge was applied, the buildup of nitrates in the groundwater where vegetables were raised in the catchment areas, and the eutrophication of surface waters due to phosphates. Only later was the partly regional character of local environmental problems acknowledged.

From the early 1990s onwards, increasing emphasis was also placed on global aspects of the impact of fertilization on the environment, i.e., the influence of agricultural production in general and fertilization in particular on the increased emission of greenhouse gases. The awareness of the mutual relationship between surplus production of agricultural products and environmental problems within the EU has continuously grown over recent decades. In particular the interest in mineral emissions from agriculture has increased substantially, both in policy making and research and in practical farming.

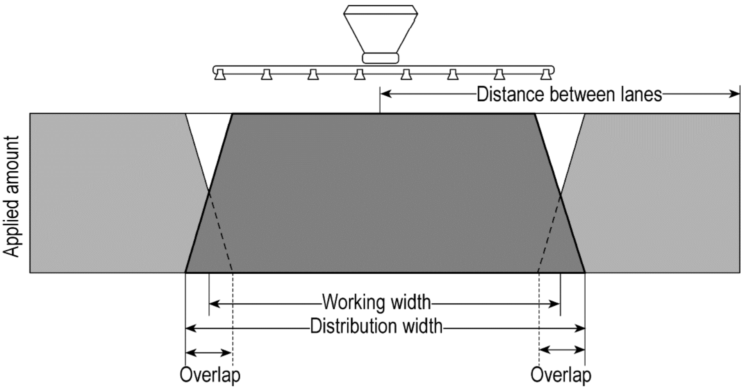


Figure 39. Broadcasting pattern for pneumatic spreaders

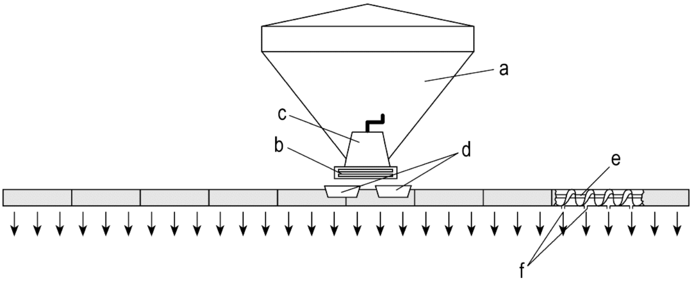


Figure 40. Schematic of a spreader with mechanical transverse distribution
a) Supply hopper; b) Elevator belt; c) Slide valve; d) Feed auger; r) Outlet

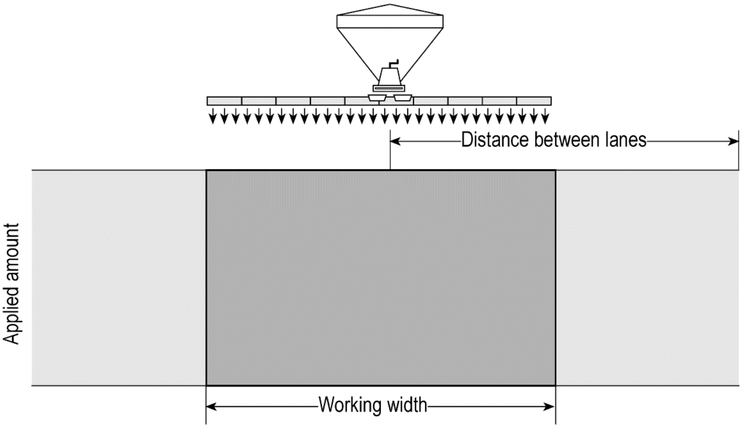


Figure 41. Broadcasting pattern of a spreader with mechanical transverse distribution

9.1. Nitrogen

Of all plant nutrients, nitrogen is the most effective in economic terms, but in ecological terms the most problematic. The plant absorbs nitrogen mainly as nitrate $\left(\mathrm{NO}_3^-\right)$ but partly as ammonium $\left(\mathrm{NH}_4^+\right)$. The plant's ability to assimilate larger molecules with organically bound nitrogen is limited.

Problems with nitrogen arise from a local or regional excess of nitrogen, regardless of its origin. Several cases, which are mostly of a regional character, are described first, then solutions are

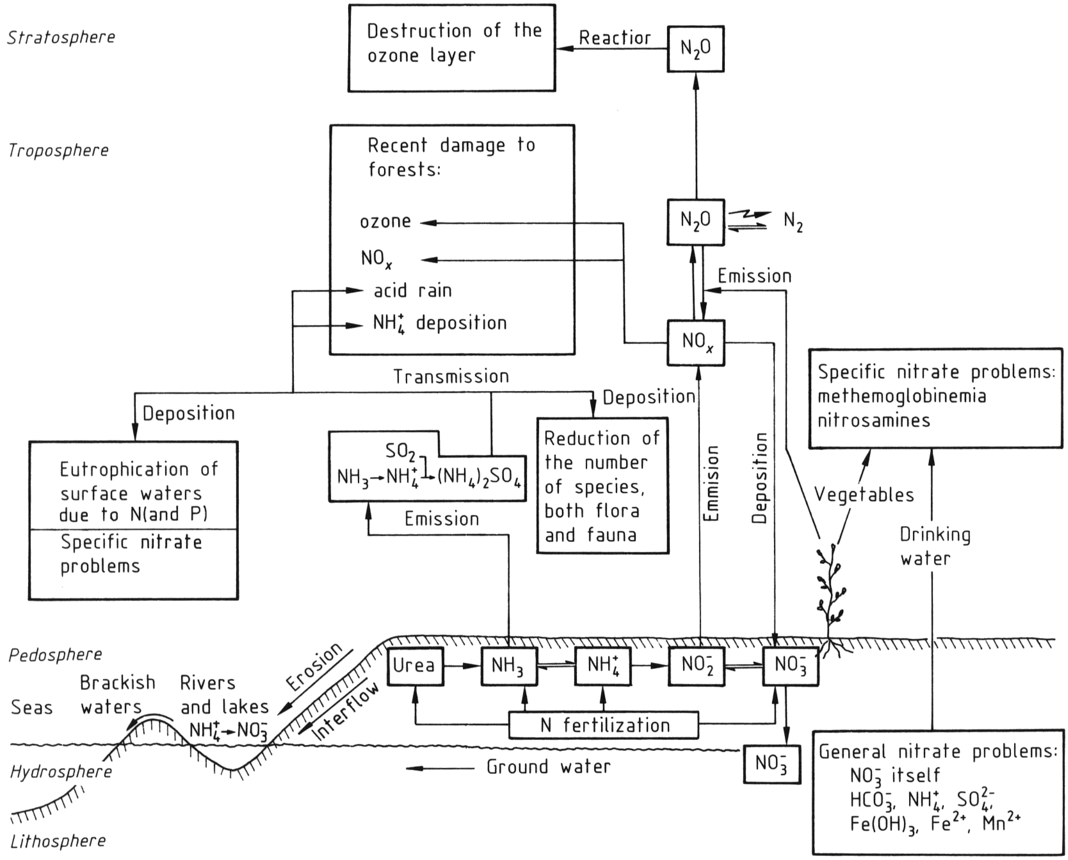


Figure 42. Agricultural nitrogen as an environmental factor

listed. Figure 42 summarizes the environmental aspects of nitrogen.

9.1.1. Ground Water

Various sectors of the economy — agriculture, forestry, water resources and wastewater management, transport, energy, and industry — are involved in ground water and surface water problems having to do with nitrogen. With regard to ground water, the quality of drinking water is the prime concern. A reduction in the maximum allowable nitrate content in drinking water within the EU, from 90 mg/L to 50 mg/L, has made the nitrogen problem more acute.

Until 1970 – 1975, virtually the only negative aspects considered with respect to nitrate were methemoglobinemia and the nitrate – nitrite – nitrosamine problem. Later, a number of other reactions triggered by nitrate and sulfate in the aquifer or during transport to it have come under discussion. Depending on the presence of aerobic or anaerobic conditions, the intensity of NO_3^- (and SO_4^{2-}) application, and the reserves of microbially available carbon sources, the reactions listed in Table 34 can yield the following compounds:

HCO_3^- or $Ca(HCO_3)_2$	water hardness
N_2O	stratospheric ozone breakdown
NH_4^+; H_2S; Fe^{2+}, Mn^{2+}	undesirable, toxic, or foul-smelling
$Fe(OH)_3$	ferric incrustation of wells

If available carbon sources are not present, or exhausted, nitrate (or sulfate) can break through into the ground water.

From around 1980 up to now increasing emphasis was placed on ground water as prime

Table 34. Sequence of environmental problems in the presence of excessive nitrate and sulfate in the pedosphere and hydrosphere

Oxygen and glucose in soil and ground water	Reduction processes	Energy released per mole of glucose, kJ	Problematic parameter	
			Input	Output*
Decreasing O_2 supply Decreasing supply of available organic carbon	*Catabolic reduction of O_2, NO_3^-, and SO_4^{2-}*			
	Respiration			
	$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$	2876		
	Denitrification			
	$5C_6H_{12}O_6 + 24NO_3^- + 24H^+ \longrightarrow 30CO_2 + 42H_2O + 12N_2$	2712		
	$C_6H_{12}O_6 + 6NO_3^- + 6H^+ \longrightarrow 6CO_2 + 9H_2O + 3N_2O$	2578	NO_3^-	N_2O
	Nitrate respiration			
	$C_6H_{12}O_6 + 12NO_3^- \longrightarrow 6CO_2 + 6H_2O + 12NO_2^-, NO_2^- \xrightarrow{H^+} NO_x$	1946	NO_3^-	NO_x
	Ammonification			
	$C_6H_{12}O_6 + 3NO_3^- + 6H^+ \longrightarrow 6CO_2 + 3H_2O + 3NH_4^+$	1817	NO_3^-	NH_4^+
	Sulfate respiration (in the absence of NO_3^-)			
	$C_6H_{12}O_6 + 3SO_4^{2-} + 6H^+ \longrightarrow 6CO_2 + 6H_2O + 3H_2S$	486	SO_4^{2-}	H_2S
	Inorganic reduction of NO_3^-			
Supply of available organic carbon exhausted	Dentrification with pyrite			
	$5FeS_2 + 14NO_3^- + 4H^+ \longrightarrow 7N_2 + 10SO_4^{2-} + 5Fe^{2+} + 2H_2O$		NO_3^-	SO_4^{2-}, Fe^{2+}
	Dentrification with soluble iron			
	$10Fe^{2+} + 2NO_3^- + 24H_2O \longrightarrow N_2 + 10Fe(OH)_3 + 18H^+ + N_2$		NO_3^-	$Fe(OH)_3$
	Dentrification with elemental or organic sulfur			
	$5S + 6NO_3^- + 4H^+ \longrightarrow 3N_2 + 5SO_4^{2-} + 4CO_2 + 2H_2O$		NO_3^-	SO_4^{2-}

* Any reaction producing CO_2 is able to increase the concentration of $CaHCO_3$.

source of diffuse nitrogen pollution of surface waters [525, 526].

Causes of Nitrate (and Sulfate) Damage. The following cases have been described in the Federal Republic of Germany:

1) Ground water lowering, plowing of pastureland, intensive cropping with N fertilization [527]
2) Intensive cropping with vegetables and/or intensive stockbreeding with appropriate N fertilization (Fig. 44) [528 – 532]
3) Intensive agricultural land use — commercial gardening, animal husbandry — with appropriate N fertilization [533]
4) Commercial gardening, intensive white asparagus cultivation, overuse of mineral fertilizers (Fig. 45) [534, 535]
5) In the Netherlands, the ground water in regions with intensive stockbreeding (the provinces of Geldern and Brabant) displays not only elevated nitrate levels but often high ammonium values at depths between 10 and 25 m [536].

Recent surveys on the nitrate concentration of the ground water in Germany resulted in quite different frequency distributions for a representative overall set of measurement points and a special set of measurement points restricted to agricultural "loading areas" according to EU Directive 91/676. In the representative survey, only 10 % of the samples exceeded the EU threshold concentration for drinking water, whereas in the near-surface groundwater of so-called agricultural-loading areas this was the case in more than 60 % of the samples (Fig. 43).

A distinction should be made between acute and chronic nitrate problems. Extreme overfertilization or pastureland plowing can cause sudden, acute nitrate damage in soils threatened by leaching (sandy soils, high water table, low or declining denitrification capacity). For example, years of overapplication of N (mainly for asparagus, with more then ten times the N depletion by

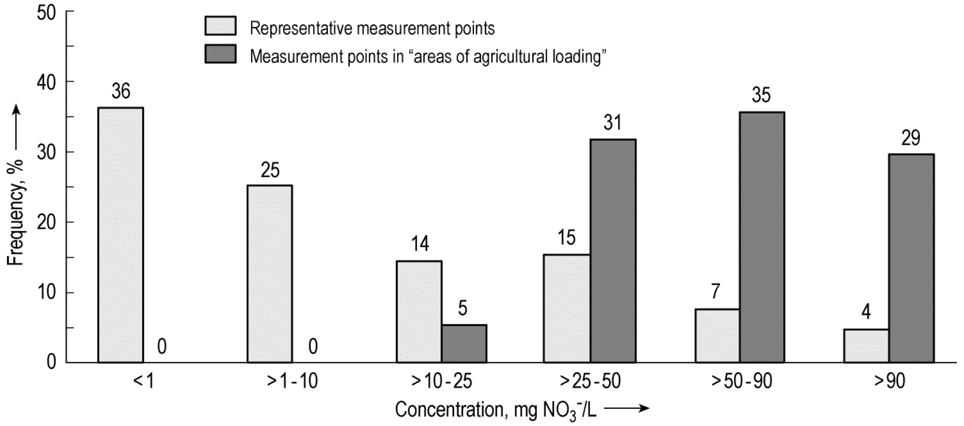


Figure 43. Frequency distribution of NO_3^- concentration in ground water in Germany [537, 538]

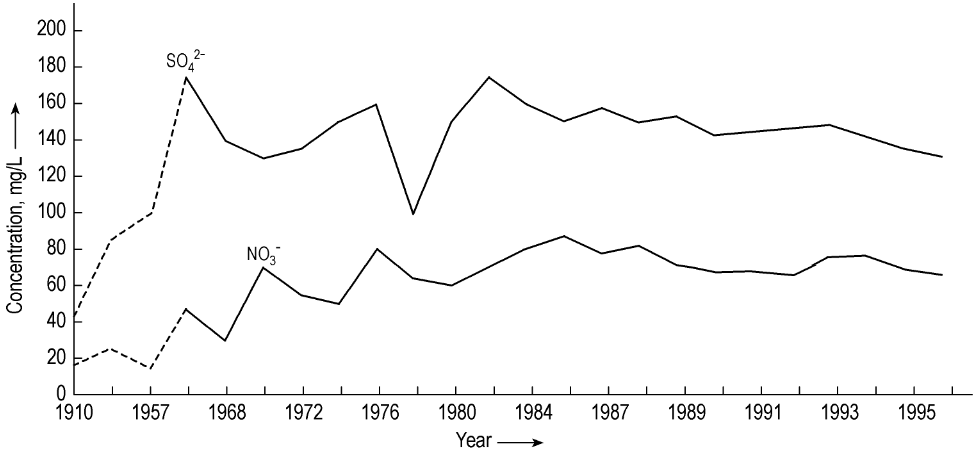


Figure 44. Nitrate and sulfate in the raw drinking water of Mussum, North Rhine-Westphalia, Federal Republic of Germany, 1910 – 1996 [532, 539].

the crop) in the drinking-water catchment area of the Bruchsal (Federal Republic of Germany) waterworks overloaded the denitrification capacity and caused a jump in nitrate in well waters (Table 35, Fig. 45) [535, 540].

Over a long period, an acute nitrate problem may become chronic. Even under economically optimal fertilization matched to base outputs, elevated ground water nitrate levels can come about [535, 541, 542]. The base outputs arise through leaching of water-soluble nitrogen-bearing substances. The unavoidable nitrogen base outputs, primarily in winter, are between 20 and 40 kg ha^{-1} a^{-1} [543 – 545]. A chronic nitrate problem is much more severe than an acute one with respect to detection and propagation, as well as the cost and the success of rehabilitation measures.

The causes of damage can be classified as follows:

1) Plowing of pastureland, forced in part by prior ground water lowering. In three to four years, this process robs light soils of 6 – 7 t of organic nitrogen through mineralization and leaching out of the root zone [546, 547]. In heavy soils, the process takes much longer. The nitrate formed by mineralization is first denitrified by microorganisms, with the simultaneous degradation of the microbially available carbohydrates. The denitrification of 6 – 7 t of nitrate N requires 16 – 19 t of such carbohydrates. In this way, the available

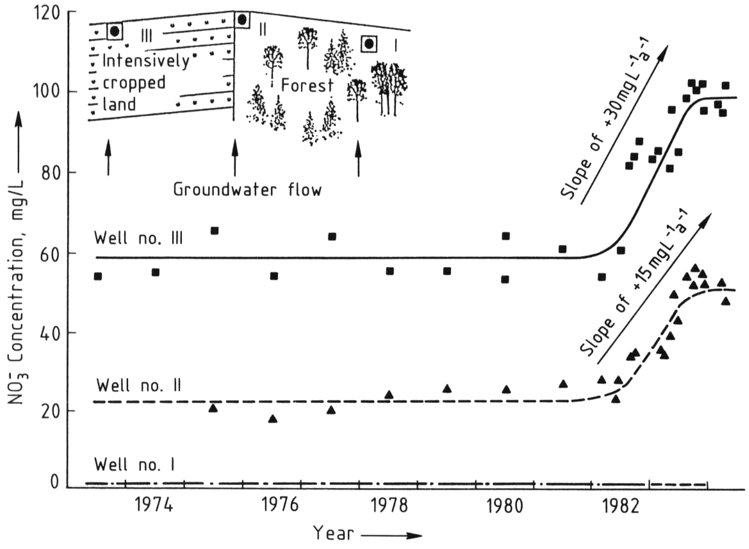


Figure 45. Nitrate concentration in water from three wells of Bruchsal Waterworks, 1973 – 1983 [540]
The insert shows the location of wells no. I – III.

Table 35. Denitrification potential and nitrate nitrogen concentration 2 – 3 m and 3 – 4 m under the surface of forest (pine or alder) and farmed land (cereals or asparagus) at Bruchsal (Federal Republic of Germany) in February, 1986

	Forest near well number I		Intensively cropped land near well number III	
	Pine	Alder	Cereals	Asparagus
	2 – 3 m under the surface			
Denitrification potential * , kg/ha	427	583	67	21
Nitrate nitrogen, kg/ha	6	18	23	56
	3 – 4 m under the surface			
Denitrification potential * , kg/ha	238	258	50	17
Nitrate nitrogen, kg/ha	4	3	50	60

* The denitrification potential is the concentration of water-soluble carbon, as glucose, multiplied by 10/27, which corresponds to the stoichiometry $5\,C_6H_{12}O_6 + 24\,NO_3^-$ (see Table 34).

organic matter soon becomes the limiting factor, and the denitrification capacity of the soil is exhausted. In soils with shallow foundation, there is thus a danger that the N output of a nearby intensive farming operation will appear almost quantitatively in the ground water. Depending on how close the wells are, the raw water may show elevated nitrate levels for decades [548].

2) Inappropriate crop rotation. Examples of poor crop rotation include high fractions of fallow or semifallow land (e.g., corn [maize] or sunflowers), summer grains without or with inadequate (winter) intercrops, and large fractions of legumes, especially if they are plowed in too soon [545, 549]. These practices usually result in high leaching losses, chiefly in winter.
3) Corn rotation with excessive liquid manure. In regions of large-scale stockbreeding, for example, in parts of the Netherlands, Belgium, Germany, and France, excessive amounts of liquid manure were formerly — and in many forms are still — applied.
4) Incorrect nitrogen fertilization. The problem is usually excessive fertilization, poor timing, and unsuitable fertilizer form, usually not an inappropriate application method.

The danger of overfertilization with mineral fertilizers is especially great in commercial gardening and in single crops with low N depletion (orchards, vineyards). Vegetables are usually harvested in the principal growth period of the vegetative phase. Leafy vegetables, above all, offer good market quality only if a good nitrogen supply is available at the time of harvesting. Thus high residual levels of readily soluble nitrogen remain in the soil. Here again, it often happens that too much fertilizer is applied. The same holds for vinegrowing, especially over permeable limestone. In sugar beet farming, fertilizer nitrogen was formerly applied far in excess of the depletion. However, from 1980 until 1994 there was already a continuous decrease from 250 to 125 kg N per hectare in German sugar beet growing, on average [550].

In general, the danger of overapplication is less for mineral fertilizers than for organic fertilizers, since the nitrogen content in the mineral fertilizer, unlike that in manure, is known and constant. What is more, the mineral fertilizer can be applied more precisely with respect to both quantity and schedule. Finally, cost is an important factor in determining the rate of mineral fertilization.

Overapplication of organic fertilizers is a problem chiefly in heavily stock-oriented farming with liquid manure fertilization and in pasturage with grazing. Despite overapplication of organic fertilizers by a factor of one or two, compared to the residual nitrogen loss, mineral fertilizer N is often supplied in addition to improve yields. This is demonstrated by the total nitrogen balances of different farming types in Germany. The mean nitrogen surpluses were estimated for the financial year 1995/96 at 19 kg N per hectare for arable farms, 107 kg N per hectare for cattle farms, and 166 kg N per hectare for special pig and poultry farms [551].

9.1.2. Surface Waters

In common with the groundwater situation, many Western European rivers have shown a strong tendency towards increasing levels of dissolved nitrogen. As an example, in the period between 1954 and 1995 the nitrogen load, mainly as nitrate, from diffuse sources of the Rhine at the Lobith control station increased from 95 000 to 185 000 t N per hectare per annum [552].

The present share of diffuse sources in the total nitrogen input into surface waters in Germany is estimated at about 60 % [526, 553, 554], because the N input from point sources was drastically reduced since the mid-1980s due to the introduction of nitrification and denitrification treatments in sewage plants. Of the diffuse sources, the pathway via groundwater is highly dominant, accounting for roughly two-thirds. Drain water was responsible for an average input share of about 10 % of the diffuse nitrogen pollution of surface water in Germany. Hence, about three-quarters of total diffuse nitrogen input was due to leaching of nitrogen from upper soil layers, and nitrogen fertilization with both mineral and farm-produced fertilizers has an important impact on the level of leaching losses.

In connection with the nitrate N (and phosphorus) loading of rivers and wetlands, special attention should be paid to the drainage system in the agricultural area of the northern European lowland plains, with their intensive stockbreeding and liquid manure disposal. The danger of eutrophication not only by increasing phosphate inputs but also by rising nitrogen inputs into estuaries, coastal zones, and especially the tidal mud flats of the North and Baltic Sea coasts has come under discussion [555 – 557]. Sediments in these areas since about 1950 – 1960 display increasing contents of both P and N [558, 559].

9.1.3. Atmosphere

Agriculture is one source of problematic N compounds in the atmosphere: N_2O from nitrification and denitrification processes in the soil and, chiefly in stockbreeding areas, ammonia (Fig. 42).

N_2O Emissions. N_2O [*10024-97-2*], with an atmospheric residence time of 100 – 200 years, serves as a source of NO [*10102-43-9*]. In the upper stratosphere NO, along with HO radicals and halogenated hydrocarbons, contributes to the breakdown of ozone, which is associated with the danger of increased short-wavelength radiation on the earth and a correspondingly increased susceptibility to skin cancer in humans [560].

$$\begin{array}{l}
O_3 \xrightarrow{h\nu} O + O_2 \\
O + N_2O \longrightarrow 2NO \\
2NO + 2O_3 \longrightarrow 2NO_2 + 2O_2 \\
\hline
3O_3 + N_2O \longrightarrow 3O_2 + 2NO_2
\end{array}$$

Soil management is the most important agricultural N_2O source [561]; denitrification and nitrification are the responsible microbial processes [562, 563]. Intensive studies on N_2O emissions from agricultural soils carried out from the beginning of the 1990s gave average emission rates of 2 – 5 kg N_2O per hectare per annum for temporate zones [564 – 566], but much higher for tropical soils [567].

The total N_2O emission in Germany in 1990 was estimated by the Federal Environment Agency (UBA) at 143×10^3 t N per annum, with an agricultural contribution of 34 % [553].

The quantity of N_2O emitted from soils is determined by the content of available nitrogen, that is, by the level of N fertilization. Nitrogen fertilization was responsible for 50 – 80 % of the emissions, and between 1 and 3 % of the fertilized N was lost as N_2O [568 – 571].

A worldwide estimate of direct and indirect emissions of N_2O from nitrogen fertilization and nitrogen fixation is given in Table 36. The direct emissions of N_2O are estimated at 1.25 ± 1 % of the applied N. The indirect emissions are ascribed to N from past years' fertilization, crop residues, from subsurface aquifers, and from recent atmospheric depositions [571]. An additional 0.75 % of the applied N will eventually be evolved from these indirect sources [572]. With increasing nitrate levels in the soil, the denitrification ratio N_2O/N_2 shifts in favor of N_2O [573]. The average share of N_2O in the total denitrification loss was assessed at 8.5 % [574].

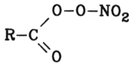
Ammonium-based fertilizers lead to higher N_2O emissions than nitrate-based fertilizers [569, 575]. Farm manures generally produce higher N_2O emissions, mainly due to the simultaneous application of quickly decomposable organic matter [576].

N_2O emissions due to N fertilization are mitigated by all measures to improve the efficiency of N use. The mitigation potential is estimated at up to 20 % [577].

NO_x ($NO + NO_2$) Emissions. NO_x, which has an average atmospheric residence time of 1.5 d, contributes to ozone synthesis in the troposphere:

$$NO_2 + O_2 \xrightarrow{h\nu} NO + O_3$$

The reverse reaction does not take place in the presence of carbon monoxide or reactive hydrocarbons, including methane, which is produced mainly by ruminants. Ozone can combine with unsaturated hydrocarbons from automobile exhausts to form ozonides, which react with NO_2 to yield peroxyalkyl nitrates



Ozone and the peroxy compounds are strong oxidizing agents with high phytotoxicity. They have been blamed for damage to vegetation in both forestry and agriculture.

The volume of NO_x emissions due to fertilization (from N reactions in the soil, nitrification more than denitrification [578]) and of plant NO_x emissions [579 – 581] is hard to assess. The contribution of agriculture to global NO_x emissions was estimated at 22 % (ca. 11 Tg NO_x N per annum), which consists of biomass burning (14 %) and the influence of mineral fertilization and manuring (each ca. 4 %) [582]. When the photooxidation of emitted NH_3 in the troposphere is taken into account, the figure rises to 27 %. However, NO_x is reabsorbed and metabolized by the plant, so that gross and net processes must be differentiated [583 – 587].

NH_3 Emissions. Ammonia emitted into the atmosphere reacts fairly rapidly (residence time < 9 d) to NH_4^+ and, after reaction with, say, SO_4^{2-}, is precipitated as ammonium sulfate, $(NH_4)_2SO_4$. Atmospheric NH_3 or NH_4^+ promotes the long distance transport of SO_2 or SO_4^{2-}. Ammonia and ammonium nitrogen forms do have fertilizing action, but in Western Europe the negative effects outweigh the beneficial ones in close-to-natural (forests, heath) and natural ecosystems (nature preserves, surface waters). Aside from the phytotoxic action of NH_3 in the area close to the emission source, deposition of NH_4^+ causes long-range damage:

1) Leaching of nutrients (e.g., K^+, Ca^{2+}, Mg^{2+}) out of the phyllosphere (leaves, needles) and the pedosphere (soil) followed by acidulation of the soil and waters [588 – 592]
2) Buildup of nitrogen in the pedosphere and nutrient imbalances in vegetation [589]
3) Injuries to mycorrhizae, the roots in symbiotic association with fungi [593]
4) Changes in the flora and fauna of terrestrial and aquatic ecosystems due to the promotion

Table 36. Estimates of direct and indirect global emissions of N_2O from application of fertilizer N (synthetic or animal waste) to agricultural soils and from soils growing biological N-fixing crops (10^6 t/a N_2O N) [577]

Region	Mineral N	Animal waste	N fixation	Total	Range
Africa	0.04	0.21	0.05	0.30	0.15 – 0.45
North and Central America	0.26	0.11	0.11	0.48	0.24 – 0.72
South America	0.03	0.22	0.09	0.34	0.17 – 0.51
Asia	0.75	0.52	0.19	1.46	0.73 – 2.19
Europe	0.27	0.22	0.02	0.51	0.26 – 0.77
Oceania	0.01	0.03	0.01	0.05	0.03 – 0.08
Former Soviet Union	0.17	0.18	0.03	0.30	0.19 – 0.57
Total	1.53	1.49	0.50	3.50	1.80 – 5.30

of nitrophilic species and the inhibition of nitrophobic species [589, 594]

5) Increased loss of N with leach water, especially in damaged coniferous forests [595 – 597]
6) Increased N inputs to surface waters [598], corresponding N buildups in marine sediments, especially in the North Sea and Baltic Sea coastal regions [558, 559]

Around the turn of the century (in remote regions even today) the mean annual depositions of atmospheric NO_3 N and NH_4^+ N were each ca. 1.3 kg/ha. Today, 10 – 15 kg/ha are deposited for each nitrogen form. On the basis of the filter capacity of the forest, the atmospheric N inputs may be increased by a factor of 1.2 – 2.0 (deciduous forest) or 3.0 (coniferous forest). In addition, a coniferous forest has a specific filtration capacity for NH_4^+ N but not for NH_3^- N [596, 599].

Recent measurements of the atmospheric nitrogen deposition into the soil – plant system with a new integral measurement system for wet, dry, and gaseous depositions even show annual net depositions of between 65 and 73 kg N per hectare at two locations in central Germany [600]. Clearly the earlier standard measurements underestimated the true magnitude of nitrogen deposition. Such nitrogen depositions exert a high pressure on natural or close-to-natural ecosystems because they greatly exceed the critical loads of these ecosystems.

The estimate of NH_3 emissions by agriculture is based on statistical figures of animal husbandry and fertilizer production and application, which all are multiplied by source-specific emission coefficients. Because of the different values of these specific coefficients given in the literature, all estimates of NH_3 emissions have a high range of uncertainty. An estimate for Germany (1992) resulted in the range from about 350 to 840 with a mean value of 577 Gg NH_3 N [601]. There are very large differences in the emission densities between and even within the federal states.

The estimates for Western Europe from different authors are in the range of 3.1 – 4.0 Tg/a NH_3 N [602]. As an example, Table 37 contains estimates of the anthropogenic NH_3 emissions from agriculture, industry, and other sources for 16 European countries. 90 % of the total emissions are due to agricultural activities, 74 % alone originates from animal husbandry (stabling, grazing, application of manure), and 12 % is attributed to the use of mineral fertilizers. The total emission is 4.0 Tg/a NH_3 N ± 30 %, that is, 2.2 – 5.2 Tg/a NH_3 N.

Worldwide, including natural emissions, mineral fertilizers account for 2 – 5 % and stockbreeding 12.5 % of the total emissions of about 120 Tg/a NH_3 N [560]. The high proportion due to stockbreeding in Western Europe is accounted for by the high population density of animals and by the changeover from solid manure to slurry manure, which is less laborious but higher in NH_3 emissions. In comparison with stockbreeding, NH_3 emissions are lower even when solid mineral fertilizers high in NH_4 or amide N (ammonium sulfate, diammonium phosphate, urea) are used. This is especially true for soils where the pH and the free lime content are high or where directly incorporating the fertilizer into the soil is not possible. Liquid fertilizers with NH_4^+, because they infiltrate the soil, emit less NH_3 than solid NH_4^+ fertilizers.

Based on the specific NH_3 emission coefficients of the various N fertilizers and their application, NH_3 emission rates from mineral fertilizers in Germany are calculated by different authors to be from 2.1 to 8.1 kg per hectare per annum NH_3 N [603].

Table 37. Anthropogenic ammonia emissions from 16 European countries [602]

Country	Animal husbandry	Mineral fertilizers	Cultivated plants	Industry	Other sources	Total
Belgium/Luxembourg	99	4.2	2.3	1.1	9.2	115
Germany	504	78.4	27.1	1.5	53.1	664
Denmark	97	7.5	4.2	0.4	9.5	119
Finland	36	2.7	3.9	0.7	3.8	47
France	564	127.6	46.1	2.0	64.3	804
Greece	57	18.6	13.8	0.5	7.8	98
Great Britain	366	55.9	26.9	1.4	39.1	489
Ireland	124	12.5	8.5	0.8	12.6	158
Italy	390	64.0	21.0	3.3	41.6	520
Netherlands	200	8.5	3.0	3.6	18.7	234
Norway	32	1.1	10.5	0.9	3.1	39
Austria	62	1.6	5.3	0.4	6.1	76
Portugal	59	6.2	6.8	0.3	6.3	78
Sweden	54	2.2	5.1	0.3	5.4	67
Switzerland	48	3.4	3.0	0.0	4.7	59
Spain	270	96.1	45.8	1.8	36.0	449
Total (abs.)	2961	490	224	19	321	4016
Total (rel.)	74	12	6	0.5	8	100

Apart from the impact of nitrogen fertilization on greenhouse gases, there is growing concern about its influence on the sink capacity of soils for methane, the most important greenhouse gas after CO_2. Oxidation by methanotropic bacteria in the soil is the only biological sink for methane. An adverse effect of N fertilization on methane oxidation was first reported in 1989 [604]. Later it was found that ammonium strongly inhibits methane oxidation, whereas nitrate has only a minor effect if at all [605 – 607]. This is due to the competition between NH_4^+ and CH_4 for the enzyme methane monooxygenase [608].

9.1.4. Biosphere

Nitrogen fertilizer may produce undesirable N forms in the crop and changes in the composition of flora and fauna in nearby close-to-natural or natural ecosystems.

Undesirable N Forms in Crop. Because of the potential formation of nitrosamines, crops should not contain too much nitrate. However, the nitrosation of substances such as vitamin C [*50-81-7*] and α-tocopherol [*59-02-9*] suppresses nitrosamine formation.

Fertilization with nitrogen alone increases the content of stored N forms (such as NO_3^- N, basic amino acids, amines, and amides, and lowers the content of vitamin C in vegetative plant parts. This is more true for NH_4^+ fertilization than for NO_3^- fertilization. The content of α-tocopherol is virtually unaffected [609]. A balanced NPK application, on the other hand, can raise the vitamin C content [610, 611]. This is important above all to vegetable farming, especially with regard to the NO_3^- content arising from fertilizer, since the nitrate intake of human beings is derived about 70 % from vegetables consumed if the NO_3^- content in drinking water is low (<10 mg/L). As a result, countries in Western Europe have adopted guidelines or maximum levels for nitrate in vegetables. Limits are imposed, for example, in the Netherlands, Austria, and Switzerland. The Federal Republic of Germany has established guidelines, e.g., for fresh lettuce and spinach, 3000 and 2000 mg/kg, respectively.

Biodiversity. The diversity of both faunal and floral communities is influenced by agriculture and fertilizer use. On a site-specific local scale, fertilizer use in general and nitrogen fertilization in particular promote the growth of crops more than that of accompanying flora. In grassland, heavy use of nitrogen inhibits the growth of many herbs and legumes.

High amounts of fertilizer salts or anhydrous ammonia may have adverse effects on earthworm population by direct contact. However, the detrimental effect on the total population is very low. The greater supply of fresh organic material that becomes available when soils are raised low to high fertility by fertilization has positive effects on both earthworms and soil microorganisms.

On a global scale the use of fertilizers has positive effects on biodiversity in reducing population pressure for cultivating unsuitable fragile soils, felling of rainforests, and overgrazing, that is, by reducing or preventing soil erosion and degradation.

9.1.5. Pedosphere (Soil)

Nitrogen in cultivated soil (root zone, 0 – 120 cm) is an asset for agriculture, because nitrogen reserves and availability in this region are an important criterion for soil fertility. However, in close-to-natural or largely natural ecosystems, atmospheric N inputs in the forest, heath, nature preserves, lakes, and rivers can lead, over a long period, to a buildup of nitrogen in the soils; the harmless removal of this N (possible only through denitrification) is of concern to ecologists.

9.1.6. Countermeasures

Measures aimed at preventing or overcoming nitrogen problems due to N fertilization in all environmental zones can be divided into direct measures and indirect measures. The aim of both is to minimize the residual nitrogen in the root zone at the end of the vegetation period and hence the leaching potential.

Direct Measures in Fertilization. For arable crops such as sugar beet [550], significant progress has been made in reducing the fertilizer-related nitrogen leaching potential. To provide an economically and an ecologically accurate nitrogen recommendation, the nitrogen supply from soil reserves is assessed by methods such as electroultrafiltration (EUF) or, if not measurable, by empirical estimation. Nitrogen fertilizer is added only to account for the difference between the demand of the crop and the supply from the soil. The guideline for the plant N demand over time is the nitrogen depletion with the harvest. Because of inevitable N losses (denitrification, leaching, etc.), roughly 20 – 30 % extra nitrogen must be supplied over and above the depletion. Optimal distributing systems apply the fertilizer uniformly. Most farmers follow these principles.

The only way to accurately find the actual nitrogen demand is a nitrogen balance for a single farm or field. The ecologically acceptable N level may be higher than, equal to, or lower than the optimal fertilization level: this fact represents a potential incompatibility between economics and ecology. It is very important in this concern, that the new German “Fertilizer Utilization Decree” contains a commitment of farmers to bookkeeping, thus calculating the balances of mineral nutrients at form level.

Farm-Produced Fertilizers. The most urgent nitrogen problem in Western Europe is that the livestock population in large regions has long been above acceptable levels. To comply with clean-air and clean-water requirements, the former liquid manure regulations of some states in Germany, that still permitted using liquid manure of three live-animal units per hectare of agricultural land, an amount still far beyond what is economically beneficial and compatible with the environment, were replaced in 1996 by a federal Fertilizer Utilization Decree with some special requirements for the application of farm-produced manures, including the following:

- Limiting gaseous NH_3 losses by appropriate technical measures, consideration of weather conditions, and the incorporation of liquid manure into unplanted soils immediately after application.
- Using liquid manure in autumn after the harvest of main crops only for subsequent catch or in combination with straw incorporation and only in limited amounts (equivalent to 40 kg of NH_4 N or 80 kg of total N per hectare).
- No liquid manure application in winter from November 15 to January 15.
- Limitation of farm manure application to 170 and 210 kg N per hectare per annum on arable land and grassland, respectively, including nitrogen in animal droppings on pastures. Up to 20 % of total N in manure may be subtracted to compensate unavoidable NH_3 losses during spreading.

Mineral Fertilizers. The matching of N fertilizer application to economic and ecological requirements is much easier with mineral fertilizers than with farm fertilizers, since the mineral products — in contrast to the farm-produced ones — are defined within narrow limits as to N content, N form, and availability.

The nitrogen form is of secondary importance, since NH_4^+ and amide N are usually converted in a few days, perhaps 1 – 2 weeks, to nitrate nitrogen in agricultural soils. Nitrification inhibitors, added to NH_4^+ fertilizers to retard the conversion of NH_4^+ toNO_3^-, may afford an extra measure of safety where there is no acute ground water nitrate problem; however, they are only a partial solution to the problem [612]. (Nitrification inhibitors may promote the liberation of NH_3 from NH_4^+ fertilizers, especially when the fertilizers are not incorporated in the soil [613].)

Controlled-release forms of N may represent an improvement from the ecological point of view when they make it possible to satisfy the crop N demand over time better than can be done with conventional nitrogen fertilizers, and when no substantial amount of nitrogen remains in the soil after the vegetation period.

Indirect Measures. All practices that lead to gains in yield without additional N alleviate environmental nitrogen problems due to fertilization.

Plant Cultivation. The selection of species and varieties and the planning of the entire rotation are crucial factors in reducing economically and ecologically undesired nitrogen losses. The *evergreen system,* that is, keeping fields covered with crop plants year-round, is a desirable goal; whenever possible, the intercrops should moderate N fertilization (nitrogen harvesting). This practice also protects against erosion. Fallow land should be avoided; semifallow area, such as under corn, sunflowers, or summer grains, should be minimized.

An extraordinary reduction of nitrate loss by leaching is achieved by overhead crop irrigation, and, the extreme case, by moderate spraying to avoid frost damage and possibly the loss of a crop in an early stage.

Plant Protection. Plant protection measures, whether mechanical (especially to combat weeds and grass), biological, or chemical, generally increase yield and thus better utilize the nitrogen supply. In this way they indirectly reduce ecologically undesirable nitrogen losses.

Plant Breeding. Nitrogen-efficient plant species and varieties produce more dry matter per unit of nitrogen delivered than do inefficient species.

Soil Tillage. Tillage also has a decisive effect on ecologically undesirable N losses. Tilling as deep as possible, while still preserving soil structure, aids the availability of the nitrogen and reduces the leaching loss by creating the optimal pore volume in combination with an ordered humus regime, thus optimizing the water regime and the supply of water to the crop.

9.2. Phosphorus

Environmental problems connected with phosphate fertilizers are eutrophication and the buildup of heavy metals.

9.2.1. Eutrophication

The pollution of nonflowing or low-circulation surface waters (lakes, estuaries, and coastal zones, especially tidal mud flats) with plant nutrients is to be avoided on account of eutrophication. This term refers to the excessive growth of algae and aquatic plants due to too great a supply of nutrients. Because the putrefaction of these organisms requires a great deal of oxygen, the water becomes depleted in oxygen. Fish die, and the biological purification of the water ceases to function. The lake has *turned over.*

The primary limiting factor for eutrophication is phosphate. Surface waters should contain ≤ 50 µg P per liter. Nitrogen can also become a factor for eutrophication when increased biomass growth takes place.

Figure 46 compares the amounts and main sources of phosphates in surface waters of Germany from 1975 to 1995 [554]. The P input by point sources was markedly decreased by improved sewage treatment practices and by the transition to phosphate-free detergents. Consequently, the share of diffuse sources in the total P input increased from nearly 20 % to about 50 %, although the absolute diffuse input also began to fall from ca. 1990 onwards. Soil erosion and surface runoff from agricultural fields are the most important diffuse sources (Fig. 47).

In contrast to nitrogen, phosphorus pollution via groundwater and drain water is not yet important, although vertical transport of this nutrient may create a pollution problem where the P

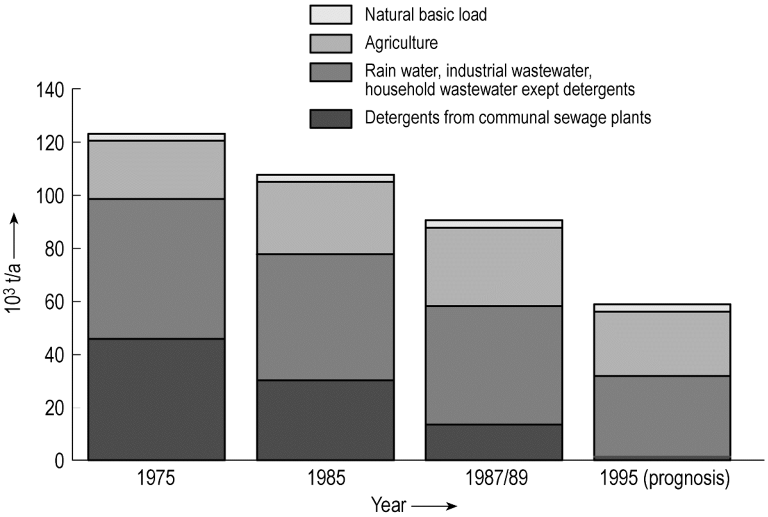


Figure 46. Changes in phosphorus input into surface waters in Germany from 1975 to 1995 [525, 526, 552, 554, 614, 615]

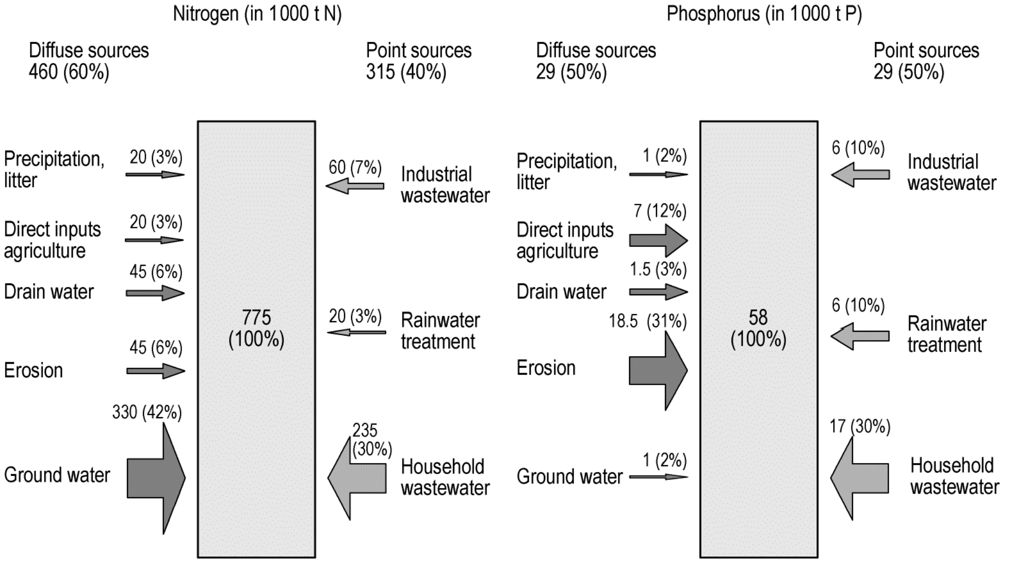


Figure 47. Nitrogen and phosphorus inputs into running waters by diffuse and point sources in Germany: prognosis for 1995 [553]

sorption capacity of deeper soil layers is already highly saturated. This has been reported for areas with high livestock densities in the Netherlands [616] and in north-western Germany [617].

The agricultural contribution to phosphorus in surface waters on a regional scale makes the implementation of efficient countermeasures in agriculture necessary [618, 619]:

- Prevention of erosion by field arrangement (e.g., reducing the slope length), crop management (mulched seeding, underseeding, changes in crop rotation), and soil management (tilling across the slope, improvement of soil structure and infiltration rate).
- Prevention of surface runoff from slopes by omitting the application of mineral or organic fertilizers in autumn and winter.
- Prevention of direct inputs of eroded soil and runoff water by planted margins along the banks of surface waters.
- Consequent adjustment of phosphorus fertilization to plant requirements: supply and re-

moval must be kept in balance on soils with optimum P supply status. On P-accumulated soils, fertilization can temporarily be reduced or even omitted.

In Germany, the implementation of countermeasures is accelerated by the German "Fertilizer Utilization Decree" of 1995.

Besides economic reasons, environmental concerns were also responsible for changes in mineral fertilizer consumption since 1985. As far as phosphorus is concerned, the balance surplus showed a mean annual decrease of 7 % for the period of 1990 – 1995 [551], in particular due to reduced application of mineral P fertilizer (mean application 11.0 kg P/ha in 1995 compared to 25.5 kg P/ha in 1985).

9.2.2. Heavy Metals Buildup

With regard to the impact of fertilizer use on heavy metals buildup in soils, the element cadmium is of primary concern. Fertilizer phosphates produced from phosphate rock contain cadmium [*7440-43-9*]. The amount depends on the origin of the rock and the digestion process employed. The cadmium content of phosphate rock varies from almost zero to about 700 mg/kg P. The acidification of phosphate rock partitions the Cd between the fertilizer and byproducts of phosphoric acid production such as phosphogypsum.

The Cd input into agricultural land by phosphate fertilizers in Germany was significantly decreased during the last two decades, due to both the preference of low-cadmium phosphate rock for fertilizer production and the dramatic decrease in mean phosphorus application rates. The mean Cd content is phosphorus fertilizers is now reported with about 100 mg/kg P [620]. The mean application rate in 1995/1996 was 11 kg P/ha. Based on these figures, the average annual Cd input is 1.1 g/ha, which compares to about 3.0 g/ha in 1980.

The quantities removed by the crops and by leaching are calculated at about 2.0 g Cd/ha. The background Cd contents in agricultural fields therefore, could not be augmented by mineral fertilizers alone, even if current application rates were doubled [621 – 623]. However, additional cadmium sources must be taken into account. Atmospheric input from industrial air pollution is the most important source in all industrial countries (3 – 6 g Cd/ha). Manures, sewage sludges, and biowaste composts may be locally or regionally important heavy metal sources [624]. Legal regulations in Germany allow annual maximum heavy metal inputs into soils that are much higher than the realistic inputs via mineral fertilizers. For cadmium these threshold values are 18 g/ha by atmospheric depositions, 10 g/ha by biowaste composts or 16.7 g/ha by sewage sludges.

10. Legal Aspects

Since the beginning of the mineral fertilizer industry, many countries have issued regulations to protect fertilizer users. These rules deal, in particular, with nutrient contents and with safety for plants, human beings, animals, and the environment.

Fertilizer regulations are based on special fertilizer legislation or else form part of a more comprehensive regulatory scheme that governs areas such as animal feeds or pesticides. As a rule, the government department of agriculture has jurisdiction over fertilizers.

The rules on fertilizers extend only to commerce in fertilizers (offering, selling, trading); in only a few cases do they cover other areas (Table 38).

Definition. Laws on fertilizers either contain a definition or simply refer to a list of fertilizers. A definition may be scientifically or pragmatically oriented. While mineral fertilizers present fewer difficulties, the diverse agents used for soil amendment are harder to define.

Examples:

Material, the main function of which is to provide plant food. (ISO)

The term "fertilizers" as used within this Law shall be defined as being any substance applied to the soil for the purpose of supplying nutrients to plants; for producing a chemical change in the soil which will contribute to the cultivation of plants; or which, when applied to the plant, will supply plant nutrients. (Japan)

Fertilizers are substances that are intended to be supplied directly or indirectly to crop plants in order to promote their growth, increase their yield, or improve their quality; excepted are . . . (Federal Republic of Germany)

Table 38. National and international regulations concerning fertilizers

Federal Republic of Germany	Düngemittelgesetz vom 15. November 1977 (*Bundesgesetzblatt I*, p. 2134)
	Düngemittelverordnung vom 19. November 1977 (*Bundesgesetzblatt I,* p. 2845)
France	*Journal officiel* du 29 juin 1980 (Loi No. 79 – 595 du 13 juillet 1979 relative à l'organisation du contrôle des matières fertilisantes et des supports de culture ; *Journal officiel* du 14 juillet 1979)
Great Britain	Statuory Instruments 1977 No. 1489 *The Fertilisers Regulations*
Italy	Legge 19 ottobre 1984, n. 748. Nouve norme per la disciplina dei fertilizzanti *Gazetta Ufficiale* 6. Novembre 1984
European Economic Community	Council Directive of 18 December 1975 on the approximation of the laws of the member states relating to fertilizers (76/116 EEC)
	Council Directive of 22 June 1977 on the approximation of the laws of the member states relating to sampling and methods of analysis of fertilizers (77/535 EEC)
Austria	Bundesgesetz vom 7. November 1985 über den Verkehr mit Düngemitteln, Bodenhilfsstoffen, Kultursubstraten und Pflanzenhilfsmitteln (Düngemittelgesetz – DMG)
Japan	Fertilizer Control Law of Japan. MAFF Ordinance No. 87, Juli 5, 1978
United States	Association of Official Analytical Chemists (AOAC), Washington, DC
International	International Organization for Standardization (ISO), Genève, Switzerland

In the regulations and annexes, fertilizers are systematically classified, for example, into straight and multinutrient fertilizers. The physical form, for example, in liquid fertilizers, may also figure in the classification.

Approval, Registration, Type Lists, Standards. In principle there are two ways of regulating the trade in fertilizers: type approval and individual approval of fertilizers. The European Economic Community (EEC) has chosen the following approach in the interest of harmonization of laws: A type list describes the fertilizers covered (type designation, minimum nutrient contents, expression of nutrients, method of production, essential ingredients, nutrient forms, and nutrient solubilities). Fertilizers that meet these requirements may be marketed provided the labeling rules in all member states are complied with.

Such a system exists in similar form in many of the developed countries. Allowance is made for the fact that many fertilizers are products well known in international trade, such as urea, triple superphosphate, and NPK fertilizers. The administrative cost is low. The type list must be supplemented from time to time to take account of technical development. As a rule, effectiveness must first be proved (plant tests), as must safety for human beings, animals, the soil, and the environment.

Another approach is individual licensing for each fertilizer offered by a manufacturer or importer. An administrative action must precede the sale of any product. The government thus has a complete picture of the registered fertilizers and of the suppliers. Often, approval is granted only for a certain time. Provisional approvals are usually possible.

Because both systems have advantages and drawbacks, many countries prefer a mixed approach: type approval and registration. Standards are defined for fertilizers. Manufacturers and importers must seek registration, which requires stated tests. The certificates granted often have only a limited term.

The choice of approach is dictated, above all, by the system of laws and government in each country, in particular by the degree of supervision desired by the state.

Labeling, Terminology, Packaging. Next to approval, labeling of the product on the package or accompanying documents is the most important rule. The prescribed manner of labeling varies greatly from country to country. Before doing business, it is therefore vital to have an exact knowledge of these regulations. In general, the following information is required as a minimum:

1) type designation or name of the fertilizer
2) guaranteed content of each nutrient
3) name and address of the person responsible for sale
4) weight of product

Special rules apply to trademarks and trade names. There are special rules for packaging and sealing; most of these are restricted to certain fertilizers.

Official Inspections, Sampling, Analysis. As part of the supervision of fertilizer marketing, the sampling and analysis methods to be employed in official inspections are set forth. The variety of methods and their continual development make a selection for official tests necessary. The official checking of the guaranteed nutrient contents must be governed by rules that state whether and to what extent, unavoidable deviations are tolerated. For example, the EEC has adopted definite unified tolerances for each type of fertilizer.

Fertilizer legislation also includes the action to be taken when violations occur (fines, seizure).

Finally, besides the special laws pertaining to fertilizers there are also provisions in other areas of legislation that must be observed in the fertilizer market. The regulations on transportation and storage and the rules aimed at preventing epidemics, important for organic fertilizers, should be kept in mind.

11. Economic Aspects

Consumption, production, and international trade of fertilizers are determined by technical, economic and legal factors, i.e., by output – input efficiencies, factor and product prices, and legal constraints. This applies to the single plot of an individual farm up to the agricultural area of entire nations and continents. While in developing countries consumption of fertilizers is still growing, in developed countries environmental concerns are making themselves felt, leading to legal and economic disincentives against unduly high fertilization rates. However, because of sustained world population growth, world consumption of mineral fertilizers will further increase within the next decades.

11.1. Economics of Fertilization

11.1.1. Input – Output Relationships: The Yield Function

Assessing economic benefits of fertilization is a relatively complex task, since the outputs of crop production processes are determined by numerous input factors, affecting the output level and being interdependent among each other. The precondition for economic considerations, therefore, is quantitative knowledge about (crop) yield functions. Although at present this knowledge is still not complete, it can safely be stated that plant growth obeys basic laws of nature, especially chemical laws. The relevant yield function for a crop — as Justus Liebig first showed with his "law of minimum" — can thus be written as:

$$y = \min\{b_1x_1;\ldots b_jx_j;\ldots b_mx_m\} \tag{1}$$

y = amount of crop output
x_j = supply of necessary inputs
b_j = partial output – input coefficients

The x_j comprise inputs which are controllable by the farmer (seed, fertilizers, pesticides, etc.), as well as those which are not controllable (solar energy, genetic yield potential, water in rainfed agriculture, etc.). The output level y is determined by the input whose supply is minimal compared to all other inputs. Given certain supplies of all but one particular input, the output increases proportionally with increasing supply of this input, until some other input becomes the minimum factor. Further augmentation of the variable input does not lead to any further output; it would be wasted. When a fertilizer is the variable input, the relationship is called a linear response and plateau function (LRP function; Fig. 48) [627].

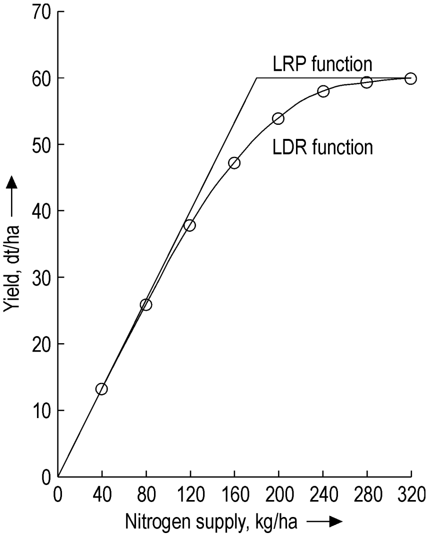


Figure 48. Types of yield function

The LRP function, however, is not compatible with results of fertilizer field experiments, investigated by means of regression analysis [628 – 630, 640]. Usually, these empirical investigations lead to curves shaped according to the "law of diminishing returns" (LDR function; Fig. 48). The difference between the two types of response function can be explained by the fact that available supplies of one or more of the other inputs vary from plant to plant in a plot (e.g., genetic potential, water) [641 – 643].

To simplify further discussion, it shall be assumed that the output (e.g., wheat) is only restricted by two inputs: the variable input x_v (e.g., nitrogen) and a given input x_g, whose amount varies randomly from plant to plant (e.g., genetic potential). Equation (1) then simplifies to:

$$y = \min\{b_g x_g ; b_v x_v\} \tag{2}$$

Assuming a discrete distribution for the amounts of x_g, Equation (2) can be expanded to:

$$y = \sum_{i=1}^{n} p_i \min\{b_g x_{gi} ; b_v x_v\} \quad \text{with} \quad \sum_{i=1}^{n} p_i = 1 \tag{3}$$

y = wheat output in dt/ha
i = number of classes in the discrete distribution of the genetic potential
p_i = probabilities of the different classes of the discrete distribution
x_{gi} = genetic potentials of the plants in the different classes of the discrete distribution, measured in dt/ha
x_v = variable supply of nitrogen, measured in kg/ha
b_g, b_v = partial input – output coefficients

If, e.g., $i = 5$, p_i = [0.1; 0.2; 0.4; 0.,2; 0.1], x_{gi} = [20; 40; 60; 80; 100], $b_g = 1$ and b_v = 0.33, increased amounts of nitrogen (in steps of 40 kg/ha) result in the plot yields shown as dots in Figure 48. Applying regression analysis leads to the LDR function also depicted. Although each plant grows according to a LRP function, the analysis of this small "experiment" suggests a law of diminishing returns.

The shape of the LDR function depends upon the variance of the spatial distribution of the input x_g within a plot. A smaller variance produces LDR curves that more closely resemble the LRP function. When the variance approaches 0, the LDR function transforms into a LRP function. This relation is especially important because modern plant breeding has reduced genetic variance of varieties (sometimes to zero), and modern land cultivation has homogenized soil conditions.

11.1.2. Factors Controlling the Optimal Nitrogen Fertilization Level

The above relation is of essential importance in determining the economically optimal supply of the variable input nitrogen. Assuming the LDR function of Figure 48, a wheat price of 11 €/dt, a nitrogen price of 0,6 €/kg, and a nitrogen delivery from the soil of 80 kg/ha, the optimal nitrogen fertilization rate can be derived as shown in Figure 49. The farmer tries to maximize the difference between the monetary return (LDR_1) and the nitrogen costs (NC_1). This maximum is obtained at the nitrogen input level (Nop_1) for which the slope of the monetary return curve equals the (constant) slope of the nitrogen cost line, that is, when marginal monetary returns equal marginal nitrogen costs [631].

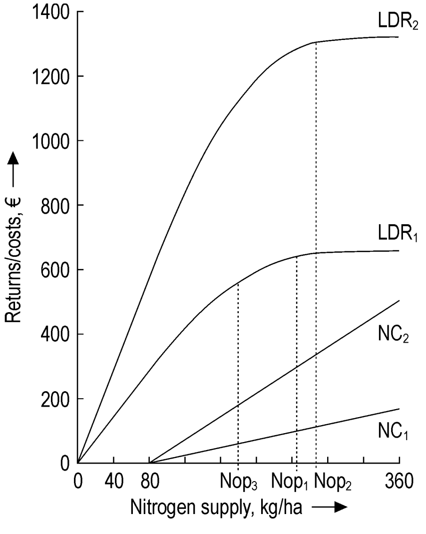


Figure 49. Economically optimal nitrogen supply in crop production, assuming the law of diminishing returns (LDR function)

Changes of output and/or input prices lead to different optimal nitrogen input levels and profitabilities. For example, doubling the wheat price to 22 €/dt results in the monetary return curve LDR_2. Tripling the nitrogen price to 1,8 €/kg results in the cost line NC_2. The first variation leads to the increased optimal nitrogen supply level Nop_2, the second variation to the decreased optimal nitrogen supply Nop_3. Generally speaking, increasing crop prices and/or decreasing factor prices result in higher fertilizer consumption, and vice versa.

If, however, the crop yield responds to variable nitrogen input levels according to an LRP function, then the farmer who tries to maximize the profitability would always provide the same nitrogen input level, regardless of price situations. Figure 50 shows monetary return functions for wheat prices of 11 €/dt (LRP_1), and 22 €/dt (LRP_2). In addition, the nitrogen cost lines, repeated from Figure 49, are depicted. Clearly, for all price situations the farmer would try to ensure the same optimal nitrogen input level Nop_1.

In modern agriculture, the yield functions are approaching LRP functions, so that price variations have less and less impact on levels of fertilization.

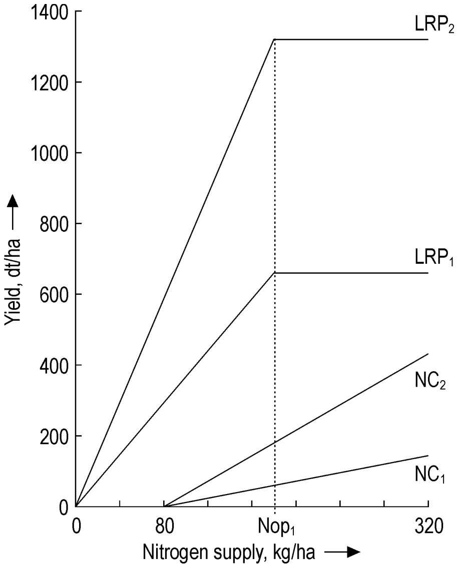


Figure 50. Economically optimal nitrogen supply in crop production, assuming linear response and plateau functions (LRP functions)

11.1.3. Factors Influencing the Optimal Nitrogen Fertilization Level

As can easily be derived from Equation (1), other factors, especially the levels of noncontrollable inputs for plant growth, exert a substantial influence on the optimal nitrogen input level. Firstly, the soil and climate conditions of a particular piece of land play a major role. Increased availabilities of solar energy and/or plant-available water allow for more productive fertilizer consumption, returning higher yields. As an example, Figure 51 shows the nitrogen response functions LRP_1 and LRP_2 for two parcels of land with different water conditions. The higher optimal yield y_2 of the "better" parcel can be obtained only if the nitrogen supply is increased from Nop_1 to Nop_2. Water and nitrogen are complementary inputs with respect to crop yield.

Secondly, modern plant breeding successively produces varieties with higher yield potentials, enabling the plants to consume water and/or solar energy more effectively. This, of course, leads to higher yields, provided the fertilizer input level is increased appropriately. Figure 51 may be also interpreted in terms two varieties of different productivity.

Thirdly, modern crop-protection agents keep the plants healthy during the vegetation period, enabling them to consume more solar energy and water. This again leads to higher yields, provided the fertilizer input level is adjusted accordingly. The situation with and without the application of modern pestizides can also be represented by the LRP functions of Figure 51.

Under a wide range of price situations, the farmer would make full use of favorable soil and climatic conditions, as well as of the advantages of improved seeds and crop-protection agents. As a rule, the additional monetary returns of the increased yields are much higher than the additional costs for fertilizers, seeds, and pesticides.

11.1.4. Environmental Aspects of Fertilization

Ecological concerns with respect to fertilization are becoming more and more important. They arise from the fact that farmers apply more fertilizers than may be consumed productively by the crops. Depending on soil conditions, some part of the surplus will not be stored in the soil to be used by the following crop, but will be leached into the underground, eventually contaminating the ground water.

However, even state-of-the-art fertilization causes some nitrogen surplus. This is due mainly to two facts: First, as discussed above, the levels of certain noncontrollable plant growth inputs are distributed randomly over a plot of land. Since the farmer does not know the exact locations, he will fertilize the whole field evenly or, in case of precision agriculture methods, at least larger parts of it. He will try to provide a nitrogen level such that the average marginal costs for the plot are equal to the average marginal monetary returns. Unavoidably, there will always be some low-yielding spots which receive too much fertilizer.

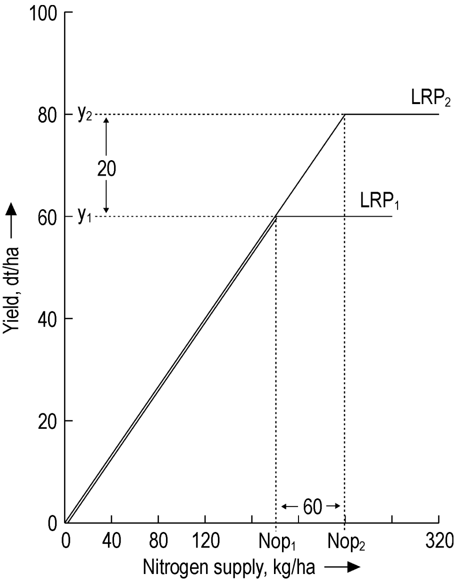


Figure 51. Effects of increased yield potentials on nitrogen requirement

Second, under most climatic conditions for rainfed agriculture, plant-usable water supply varies from year to year. Since the farmer does not know the water supply of a particular year in advance, he will always "shoot" for a "good" year. If, for example, in a good year the higher yield y_2 in Figure 51 is achievable, and in a "dry" year only the lower yield y_1, the farmer will nevertheless always provide for the higher nitrogen level Nop_2 instead of the lower level Nop_1. The reason is simple: the expected profitability value of strategy Nop_2 is under realistic price and weather conditions much higher than that of the strategy Nop_1.

If the farmer provided only for the low fertilization level Nop_1, in a good year he would lose the monetary return of 20 dt/ha (see Fig. 51), because the insufficient nitrogen supply would limit the yield. At a wheat price of 11 €/dt, this corresponds to a loss of 220 €/ha. At the higher nitrogen level Nop_2, in a dry year 60 kg/ha nitrogen would be wasted (Fig. 51). This corresponds to a loss of 36 €/ha.

These economically induced fertilizer surpluses can be reduced by further improvements of inputs, production techniques, and prognostic information. Seed varieties with less genetic variance and homogenization of soil conditions lead to less variance of the noncontrollable growth factors within a field. Splitting nitrogen fertilization into several applications as the vegetation period develops and new information about the water supply becomes available also reduces waste of nutrients. Finally, improved long-term weather forecasts would be most valuable in reducing the uncertainty involved in fertilizing decisions.

Strict legal constraints for nitrogen application rates, however, would not be the strategy of choice. It would lead to a waste of valuable yield potential and in addition to economic losses for farmers.

11.2. World Consumption, Production, and Trade

Consumption. World consumption of the three primary nutrients — nitrogen, phosphate and potash — reached a total of 135.0×10^6 t in 1996/97. The previous record level of 145.6×10^6 t in 1988/89 was once again not reached. The consumption figures broke down as follows [625] in 10^6 t:

Nitrogen	82.9 N
Phosphate	31.1 P_2O_5
Potash	21.0 K_2O

Over the past 10 years, agricultural consumption of fertilizers experienced a deep recession, mainly due to developments in Central and Eastern Europe, as well as in the former Soviet

Union. World consumption fell by 17 % from 1988/89 to 1993/94 and then recovered by 12 % up to 1996/97. Over the ten year period, nitrogen increased by 16 %, phosphate fell by 10 %, and potash fell by 19 %.

The consumption ratio N : P_2O_5 : K_2O was 1 : 0.6 : 0.5 in 1976/77; it changed in favor of nitrogen to 1 : 0.5 : 0.4 in 1986/87, and in 1996/97 it reached 1 : 0.4 : 0.25. While in North America and Western Europe the ratio is 1 : 0.4 : 0.4, it is less well balanced in other regions of the world (Table 39). Fertilizer consumption and production are given for fertilizer years, running from 1 July to 30 June. For example, 1996/97 is the period from 1 July 1996 to 30 June 1997.

In case only calendar year figures are available, e.g., 1996 is summarized under 1996/97. A regional analysis of fertilizer consumption shows that over 60 % is used in developing countries (in Asia, Latin America, Africa). The Asian markets are particularly important. About 50 % of all fertilizers consumed are applied in Asia. North America takes second place with 17 %, followed by Western Europe. Three decades ago, Western Europe was the world's largest fertilizer consumer; after 10 years, the Eastern Bloc had overtaken Western Europe; and another 10 years later, the developing countries have taken the lead — having increased their consumption tenfold in 30 years. This change corresponds to a mean annual growth rate of 8 %.

The intensity of fertilizer use, however, is still greatest in Western Europe. In terms of nutrient per hectare of agricultural area, Western Europe averaged 121 kg applied in 1996/97 (Table 40). The corresponding figure for the developing countries is 24 kg. In these countries, however, virtually no fertilizer is applied to pastureland. If the figures are referred to agricultural area minus pastureland, the rate in the developing countries was 88 kg of nutrients per hectare, 56 kg of this being N. Fertilizer application is extremely low in the former Soviet Union (8 kg/ha).

Three countries account for over half of world fertilizer consumption: China with 36.6×10^6 t, the United States with 21.2×10^6 t, and India with 14.3×10^6 t. Next on the list are India with 14.3×10^6 t, France with 5.1×10^6 and Brazil with 4.8×10^6.

In years to come, a further worldwide increase is expected. This growth will take place chiefly in Asia, Latin America and Africa. The recovery of fertilizer use in Central/Eastern Europe and the former Soviet Union is anticipated but will take time.

Production. A survey of production in 1996/97 showed that Asia ranks first as world fertilizer producer, mainly for nitrogen, but also for phosphate fertilizers, followed by North America, the leading potash producer (Table 41).

Over the past ten years the production pattern by region shows a considerable decrease in Western and Central/Eastern Europe (− 27 % and − 37 %, respectively) but above all in the former Soviet Union (− 50 %). In North America (+ 27 %) and especially Asia (+ 61 %) production increased markedly. While overall world production remained nearly stagnant (+ 3.5 %), nitrogen production increased by 18 %, but phosphate and potash dropped by 8 % and 16 %, respectively.

The leaders in production of fertilizers are China, the United States, and India. They are followed by Canada, the world's largest potash producer, and Russia (Table 42).

The rise in fertilizer production and consumption in recent decades could not have taken place without an enormous technical advance. Significant cost savings in ammonia production, the intermediate for nitrogen fertilizer production, resulted from the changeover from multitrain to single-train plants and the conversion to more economical feedstocks, mainly natural gas.

Due to improved product quality and well-balanced particle size spectrum, rational bulk transportation and easier application become possible. Higher analysis fertilizer grades brought savings in shipping and storage per unit of nutrient.

The fertilizer processes were optimized to decrease energy consumption. Emission reduction with modern techniques improved the environmental performance of the processes and at the same time increased the nutrient yield from the raw materials. These improvements are of great importance: the 149×10^6 t of nutrients produced worldwide in 1996/97 meant 430×10^6 t of fertilizers that had to be stored, transported, and applied (authors estimate).

Table 39. World nitrogen, phosphate and potassium consumption in millions of tonnes over the period 1976/77 – 1996/97 broken down by region/country [625] *

Region/country	Fertilizer season					
	1976/77		1986/87		1996/97	
	10^6 t	%	10^6 t	%	10^6 t	%
Nitrogen (N) fertilizer consumption						
Western Europe	8.8	19.0	11.4	15.9	10.1	12.2
Central/Eastern Europe	3.7	8.0	4.4	6.2	2.4	2.9
Former Soviet Union	7.3	15.7	11.5	16.1	2.8	3.4
North America	10.3	22.2	10.4	14.5	12.9	15.6
Latin America	2.2	4.7	3.8	5.3	4.1	4.9
Asia **	12.4	26.7	27.7	38.7	47.4	57.2
Africa	1.5	3.2	1.9	2.7	2.3	2.8
Other	0.2	0.4	0.4	0.6	0.9	1.1
World	46.4	100.0	71.5	100.0	82.9	100.0
Phosphorus (P_2O_5) fertilizer consumption						
Western Europe	5.8	21.6	5.3	15.3	3.7	11.9
Central/Eastern Europe	2.7	10.1	2.0	5.8	0.7	2.3
Former Soviet Union	4.9	18.3	9.1	26.2	0.9	2.9
North America	5.6	20.9	4.3	12.4	4.8	15.4
Latin America	2.0	7.5	2.8	8.1	2.9	9.3
Asia **	3.8	14.2	9.2	26.5	15.7	50.5
Africa	0.9	3.4	1.0	2.9	1.0	3.2
Other	1.1	4.1	1.0	2.9	1.4	4.5
World	26.8	100.0	34.7	100.0	31.1	100.0
Potassium (K_2O) fertilizer consumption						
Western Europe	5.5	5.7	5.9	22.6	4.3	20.5
Central/Eastern Europe	2.9	3.0	2.8	10.7	0.7	3.3
Former Soviet Union	5.6	5.8	6.7	25.7	1.2	5.7
North America	5.5	5.7	4.8	18.4	5.2	24.8
Latin America	1.2	1.2	1.9	7.3	2.6	12.4
Asia **	1.8	1.9	3.4	13.0	6.2	29.5
Africa	0.3	0.3	0.4	1.5	0.4	1.9
Other	0.2	0.2	0.2	0.8	0.4	1.9
World	23.0	23.9	26.1	100.0	21.0	100.0
Total fertilizer consumption ($N + P_2O_5 + K_2O$)						
World	96.2		132.3		135.0	

* *FAO Fertilizer Yearbook* 1980, 1990 and 1997.
** Excluding Asian republics of former Soviet Union.

Table 40. Nutrient use per hectare of agricultural area, [625, 632]

Region	Nutrient application, kg/ha			
	N	P_2O_5	K_2O	Total
Western Europe	67.6	24.7	28.8	121.2
Central/Eastern Europe	36.1	10.6	9.9	56.6
Former Soviet Union	4.8	1.5	2.1	8.4
North America	26.0	9.8	10.5	46.4
Other	15.2	5.8	2.7	23.6
World average	16.9	6.3	4.3	27.5

[a] Consumption: FAO Fertilizer Yearbook, Agricultural Area: FAOSTAT Database results

World Trade. Recent decades have seen a sharper rise in world trade than in consumption. Because of the limited number of potash deposits, the ratio of trade to consumption is highest for potash, with 91 %. Some 40 % of phosphate and 29 % of nitrogen are sold internationally (Table 43).

In nitrogen, Russia and the USA have the largest exports, but Canada, Ukraine, and the Netherlands are also important in the world market. The most important importing regions are China and the USA.

American exporters dominate the phosphate market, with sales in all regions, but primarily in the developing countries in Asia, Latin America

Table 41. World fertilizer production by nutrient and region 1996/97 [625]

Region	Nutrient production, 10^6 t							
	N		P_2O_5		K_2O		Total	
	1986/87	1996/97	1986/87	1996/97	1986/87	1996/97	1986/87	1996/97
Western Europe	11.8	9.5	4.4	2.9	8.3	5.4	24.5	17.8
Central/Eastern Europe	6.1	4.8	2.8	0.9	0.0	0.0	8.9	5.6
Former Soviet Union	15.0	8.7	8.5	2.5	10.2	5.5	33.7	16.7
North America	13.6	19.3	9.4	11.3	8.2	8.9	31.2	39.5
Latin America	3.0	3.2	1.9	1.8	0.1	0.4	5.0	5.4
Asia *	26.0	42.6	7.7	11.5	2.0	3.2	35.7	57.4
Africa	1.7	2.7	1.9	2.5	0.0	0.0	3.6	5.2
Oceania	0.2	0.3	0.8	0.7	0.0	0.0	1.0	1.0
World	77.4	91.1	37.4	34.1	28.8	23.4	143.6	148.6
World supply **	72.6	85.8	34.9	32.2	26.1	21.8	133.6	139.7

* Excluding Asian republics of former Soviet Union.

** Available world supply was arrived at by deducting from production estimated amounts for technical uses, further processing, transport, storage, and handling losses.

Table 42. Fertilizer production by country, 1996/97 [625]

Country	Fertilizer production, 10^6 t			
	N	P_2O_5	K_2O	Total
China	20.1	5.8	0.2	26.1
United States	12.5 *	10.9	0.8	24.2
India	8.6	2.6	0.0	11.2
Canada	2.7 *	0.4	8.1	11.2
Russia	4.9	1.6	2.6	9.1

* Author’s estimate (available supply)

Table 43. World fertilizer trade in millions of tonnes (exports) (10^6 t) [625] * .

Nutrient	Fertilizer season		
	1976/77	1986/87	1996/97
N	8.5	17.4	24.2
P_2O_5	4.4	9.5	12.4
K_2O	13.7	17.6	19.1
Total	26.6	44.5	55.7

* *FAO Fertilizer Yearbooks*

and Africa. The largest exporters of potash are Canada and Germany, followed by Belarus and Russia.

The largest exporters and importers in 1996/97 are listed in Table 44.

Types of Fertilizers. As the quantities produced and applied have increased, the importance of fertilizer grades has changed. Low-analysis grades have decreased, while highly concentrated grades such as urea, triple superphosphate, and NPK fertilizers have gained (Fig. 52). Sulfur-containing fertilizers have gained importance to cope with sulfur deficiencies.

Urea has become the preferred nitrogen fertilizer, especially in the developing countries. In Western Europe, for example, ca. 80 % of nitrogen consumption is in the form of ammonium nitrate, calcium ammonium nitrate, and ammonium nitrate-based multinutrient fertilizers. Phosphate consumption is dominated by multinutrient fertilizers. In the case of potash, straight potassium chloride is the most important grade, but potassium sulfate is of growing importance due to its sulfur contents.

11.3. Future Outlook

The decisive factors for the development of fertilizer demand are population growth and changes in the available income per capita. A growing world population needs more food and fiber. In addition, a wealthier population has a

Table 44. Major exporting and importing countries for nitrogen, phosphate, and potash fertilizers, 1996/97 [625]

Country	Exports, 10^6 t	Country	Imports, 10^6 t
Nitrogen (*N*)			
Russia	3.6	China	4.7
United States	3.0	United States *	2.0
Ukraine	1.2	France	1.3
Netherlands	1.2	India	1.2
Canada *	1.3	Germany	1.2
Phosphate (P_2O_5)			
United States	5.7	China	2.8
Russia	1.2	India	0.7
Morocco	0.8	Australia	0.7
Tunisia	0.7	France	0.6
Netherlands	0.4	Thailand	0.5
Potassium (K_2O)			
Canada	7.9	United States	5.2
Germany	2.6	Brazil	1.8
Belarus	2.0	France	1.1
Russia	1.9	India	0.7
Israel	1.2	Malaysia	0.6

* Author's estimates.

higher daily energy intake per capita and it generally consumes a higher share of animal products (Table 45). Compared to direct human consumption, three to four times more plant products such as cereals are necessary to produce the same amount of energy in the form of animal products like milk, eggs, and meat.

11.3.1. Food Situation

Since the 1950s world food production per capita has continuously increased, although world population has more than doubled (from 2.5 to almost 6.0 billion). New crop varieties and improved production techniques enabled a substantial growth of average yields. A significant advance was the broader use of effective cereal fungicides in industrialized countries and the introduction of high-yielding varieties of rice, wheat, and maize in several developing countries, known in the 1970s as the "green revolution". These varieties, bred for tropical and subtropical regions, already offer a higher yield potential under traditional growing conditions. But their full potential can only be exploited when crop husbandry and plant nutrition are adapted to their needs, and agrochemicals provide protection against insects, diseases, and competition from weeds. In many cases they rendered the use of fertilizers and agrochemicals economic for the first time. The average yields of cereals, the most important staple food of humans, increased substantially (Table 46).

According to the FAO, on average each kilogram of fertilizer nitrogen applied to the soil produces about 12 kg of cereal units (1 kg of cereal unit is equal to the nutritional value of 1 kg of barley); therefore, it can be calculated that the food for half of the world's population can only be provided due to the use of $(75 - 80) \times 10^6$ t nitrogen in mineral fertilizers annually. Nevertheless, 840 million individuals still suffer from undernutrition and an estimated 20 million die annually of hunger and undernutrition-related diseases. Civil wars, natural disasters, and poverty, often related to unemployment, are the main reasons for starvation.

Growth in Food Demand. The 1996 update of the UN World Population Prospect shows that the rate of world population growth has declined to 1.48 % per annum, but this still means an additional 80 million humans to be fed every year. By the year 2020 world population is predicted to reach 7.67 billions. Since economic growth is expected to continue, a larger part of the population will be able to spend more money on food. Thus an increased demand per capita for plant products to be used as animal feed must be taken into account. The demand for cereals is expected to increase by 41 % from 1993 to 2020, that for meat by 63 %, and the consumption of tubers and root is estimated to rise by 40 % [634].

Table 45. Dietary energy supply per capita by economic group 1969 – 1971 and 1990 – 1992 [633]

Country Group	Total kcal/d		% animal	
	1969 – 71	1990 – 92	1969 – 71	1990 – 92
Industrialized	3120	3410	30.4	29.8
Transition	3330	3230	24.4	27.6
Low-income	2060	2430	6.1	9.3
Least developed	2060	2040	6.6	6.0
World	2440	2720	15.6	15.7

Table 46. World production and average yields of cereals 1972 – 1974 and 1996/97

	Production, 10^6 t		Yield, t/ha	
	1972 – 74	1996 – 97	1972 – 74	1996 – 97
Wheat	359	581	1.66	2.53
Maize	300	562	2.75	4.02
Barley	164	155	1.88	2.33
Rye, Oats	81	54	1.68	1.85
Rice	325	558	3.23	3.76
Total	1229	1910	2.19	3.11

Agricultural Land Use. More than 70 % of the world's surface is covered by water. Of the 13.4 billion hectares of dry land, 4.7 billion hectares are used by agriculture. The major portion is covered by extensively used grasslands, often in low-rainfall areas. Most of the food is supplied by the 1.4 billion hectares of arable land — a mere 10 % of the dry land. Much of the remaining area is not suitable for intensive agricultural production since it is either too dry, too steep, too cold, or infertile. The majority of soils usable for arable crops are covered by biotopes such as rain forests. There is no agreement to which extent they should be used for agriculture and how much must be preserved. FAO [635] calculated that Sub-Saharan Africa and Latin America have the most land reserves with crop-production potential.

At the same time 7 million hectares agricultural land are lost annually due to erosion and salination. The agricultural area available per capita declined from 0.44 ha (1960) to 0.27 ha (1990) and is expected to shrink further to 0.17 ha by 2020. Therefore FAO estimates that although newly cleared land may supply 21 % of the necessary increase in food production, and more frequent use of existing arable land 13 %, the most important contribution (66 %) must come from higher yields on soils already under cultivation. Although neither the quality of soils nor the agroclimatic conditions will allow the same high yield to be achieved everywhere, the wide variation in actual yields offers a vast potential for further improvement (Figure 53).

Intensity of Agricultural Production. The intensity of agricultural production is highest in industrialized and transition economies, where the purchasing power for food is high. Attractive markets create an efficient production system, whereas the subsistence farmer cannot invest in yield-raising inputs. Annual nutrient application rates therefore vary widely (Figure 53). Western European countries, Egypt, Saudi Arabia, and Mexico for example apply on average more than 200 kg N + P_2O_5 + K_2O per hectare wheat and harvest 4 – 7 t of grain, whilst countries using less than 50 kg plant nutrients obtain barely more than 2 t per hectare [636]. This of course can also be the result of unfavorable growing conditions, primarily insufficient supply of water, but for most countries it reflects the socio-economic situation.

Wheat is the crop which receives most (22 %) of the fertilizer nutrients, followed by rice and maize (17 % each). Cereals in total count for 65 % of the nutrient consumption, while 9 % are used on oil crops, 5 % each on vegetables and sugar beet/cane). Thus, fertilizers are predominately used for food production. Fiber crops, tobacco, and stimulants receive 4 and 2 %, respectively [636].

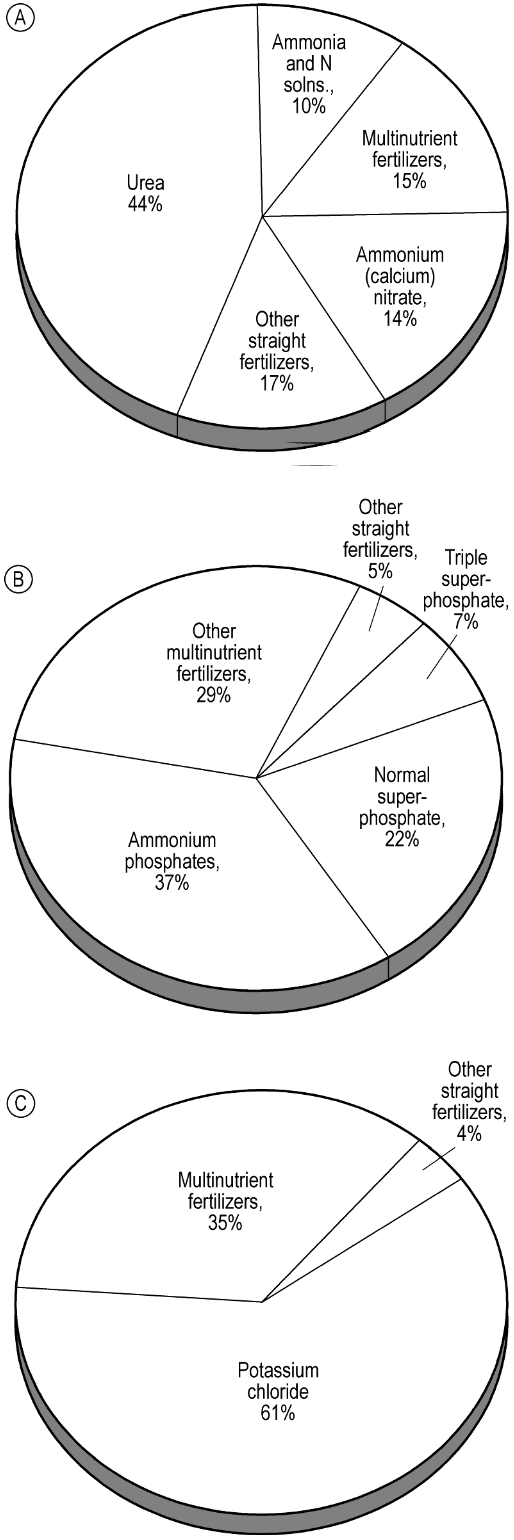


Figure 52. World fertilizer consumption by type, 1996/97 preliminary [632]
A) Nitrogen fertilizer; B) Phosphate fertilizer; C) Potassium fertilizer

In the past countries with economic and population growth have increased their fertilizer consumption (Table 47), whereas those with traditionally high consumption only show moderate growth (e.g., United States, Canada, Spain) or a decrease in consumption. This is the case for most EU countries, where nutrient levels in the soil have mostly been built up to the desirable level, environmental concern has led to strict regulations, and changes in agricultural policy, such as leaving arable land fallow, have been introduced. Changes of the economic system in the former centrally planned economies resulted in a dramatic decline in agricultural production and consequently in fertilizer consumption.

Table 47. Development of fertilizer use in the 20 countries with the highest actual nutrient consumption 1985/86 – 1995/96 in 10^6 t N + P_2O_5 + K_2O [637]

	1985/86	1995/96
China	16 852	35 527
USA	17 831	20 113
India	8504	13 876
France	5695	4915
Brazil	3197	4309
Germany	4823	2818
Indonesia	1972	2512
Pakistan	1511	2443
Canada	2325	2436
UK	2524	2264
Italy	2162	1883
Spain	1734	1817
Australia	1155	1735
Russian Fed.		1700
Turkey	1427	1700
Japan	2034	1642
Poland	3413	1511
Vietnam	386	1448
Thailand	434	1443
Malaysia	611	1247
World	128 613	130 865

11.3.2. Development of Fertilizer Consumption

World fertilizer consumption will continue to rise by more than 2 % per annum from 1996/97 to 2002/03 [638, 639]. The rate of growth will be highest in the densely populated countries of South Asia (+ 5.2 %), in Latin America (+

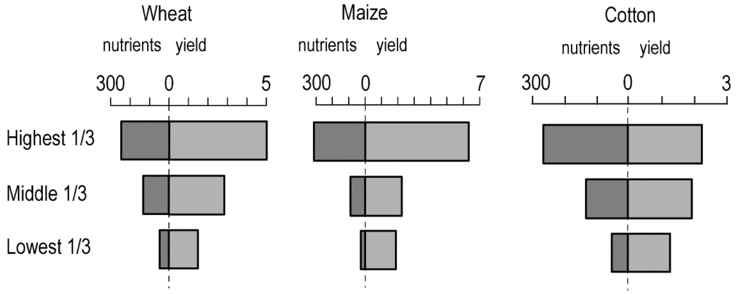


Figure 53. Average nutrient application rates (kg N + P_2O_5 + K_2O per hectare) and average yields (t/ha) of countries with high, medium, and low fertilizer application rates in 1995 [636]

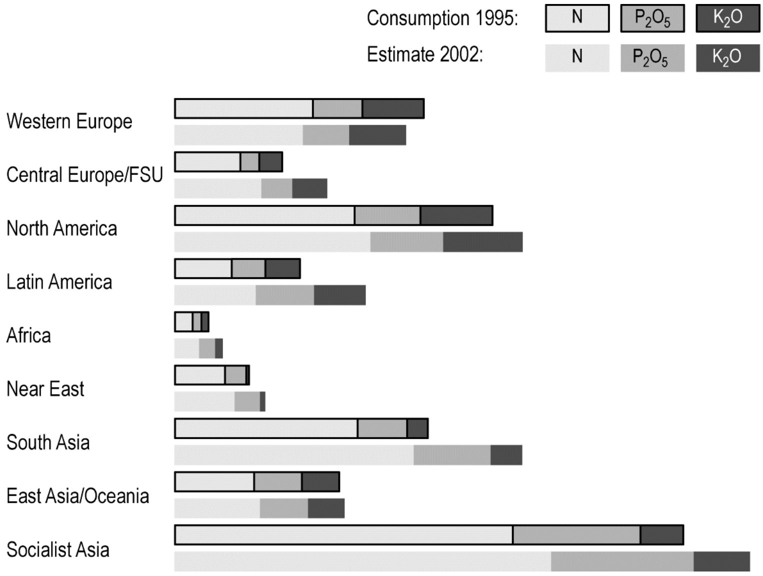


Figure 54. Fertilizer consumption forecast by region 1995 – 2002 [638]

5.0 %), Africa (+ 4.9 %) and Central Europe (+ 4.4 %) (Figure 54). The estimated increase in Central Europe signals a recovery from economic depression, while the growth rate in Africa simply reflects the low base. For Western Europe, a further decline in fertilizer consumption is forecast since the agricultural area in this densely populated, industrialized region will continue to decline, and more efficient use of organic manures (farmyard manure, sewage sludge, etc.) will be necessary to achieve the goals set for the protection of the environment.

12. References

1. K. Scharrer in, W. Ruhland (ed.): *Handbuch der Pflanzenphysiologie*, vol **IV**, Springer Verlag, Berlin-Göttingen-Heidelberg 1958, pp. 851 – 866.

Specific References

2. J. N. Burnell in R. D. Graham et al. (eds.): *Manganese in Soil and Plants*, Academic Press, London 1988, pp. 125 – 137.
3. H. Marschner: *The Mineral Nutrition of Higher Plants*, Academic Press, London 1993.

4. K. H. Falchuk, L. Ulpino, B. Mazus, B. L. Valee, *Biochem. Biophys. Res. Commun.* **74** (1977) 1206 – 1212.
5. M. G. Guerrero, J. M. Vega, M. Losada, *Ann. Rev. Plant Physiol.* **32** (1981) 169 – 204.
6. S. J. Brodrick, K. E. Giller, *J. Exp. Bot.* **42** (1991) 1339 – 1343.
7. J. v. Liebig: *Die organische Chemie in ihrer Anwendung auf Agrikultur and Physiologie*, Vieweg, Braunschweig 1841.
8. G. Hehl, K. Mengel, *Landwirtsch. Forsch. Sonderh.* **27** (1972) no. 2, 117 – 129.
9. A. K. Goswami, J. S. Willcox, *J. Sci. Food Agric.* **20** (1969) 592 – 595.
10. S. Haneklaus, E. Evans, E. Schnug, *Sulphur in Agriculture* **16** (1992) 31 – 34.
11. H. W. Scherer, A. Lange, *Biol Fertil Soils* **23** (1996) 449 – 453.
12. E. Saalbach, *Angew. Bot.* **58** (1984) 147 – 156.
13. E. H. Birnbaum, W. M. Dugger, B. C. A. Beasley, *Plant Physiol.* **59** (1977) 1034 – 1038.
14. H. E. Goldbach, *J. Trace Microprobe Techn.* **15** (1997) 51 – 91.
15. W. D. Loomis, R. W. Durst, *Biofactors* **3** (1992) 229 – 239.
16. G. K. Judel, *Landwirtsch. Forsch. Sonderh.* **34** (1977) no. 2, 103 – 108.
17. D. Werner, R. Roth, *Inorganic Plant Nutrition*. Encycl. Plant Physiol., New Ser. 15 B (1983) 682 – 694.
18. Y. Miyake, E. Takahashi, *Soil Sci. Plant Nutr. (Tokyo)* **29** (1983) 463 – 471.
19. A. D. M. Glass, M. Y. Siddiqi in P. B. Tinker, A. Läuchli (eds): *Advances in Plant Nutrition*, Praeger, New York 1984, vol. 1, pp. 103 – 147.
20. R. G. Wyn Jones, A. Pollard, *Inorganic Plant Nutrition*. Encycl. Plant Physiol. New Ser. 15 B, (1983) 528 – 562.
21. K. Mengel in R. D. Munson (ed): *Potassium in Agriculture*, American Society of Agronomy, Madison, Wis. 1985, pp. 397 – 411.
22. T. R. Peoples, D. W. Koch, *Plant Physiol*, **63** (1979) 878 – 881.
23. D. T. Clarkson, J. B. Hanson, *Annu. Rev. Plant Physiol.* **31** (1980) 239 – 298.
24. R. F. Hüttl, H. W. Zöttl, *Forest Ecol. Management* **61** (1993) 325 – 338.
25. C. R. Caldwell, A. Haug, *Physiol. Plant.* **54** (1982) 112 – 118.
26. J. B. Hanson in P. B. Tinker, A. Läuchli (eds): *Advances in Plant Nutrition*, Praeger, New York 1984, vol. 1, pp. 149 – 208.
27. C. B. Shear, *Hort. Science* **10** (1975) 361 – 365.
28. H. Marschner, *Neth. J. Agric. Sci.* **22** (1974) 275 – 282.
29. L. C. Campell, R. O. Nable in R. D. Graham, R. J. Hannan, N. C. Uren (eds.): *Manganese in Soils and Plants*, Kluwer Academic Press, Dordrecht 1988.
30. S. Spiller, N. Terry, *Plant Physiol.* **65** (1980) 121 – 125.
31. K. Mengel, G. Geurtzen, *J. Plant Nutr.* **9** (1986) 161 – 173.
32. J. C. G. Ottow, G. Benckiser, I. Watanabe, S. Santiago, *Trop. Agric. (Trinidad)* **60** (1983) 102 – 106.
33. K. Mengel, E. A. Kirkby: *Principles of Plant Nutrition*, 4th ed., International Potash Institute, Berne 1987.
34. D. Schroeder: *Soils – facts and concepts*, International Potash Institute, Berne 1984.
35. N. C. Brady: *The Nature and Properties of Soils*, Macmillan Publishing Co., New York 1984.
36. F. Scheffer, P. Schachtschabel: *Lehrbuch der Bodenkunde*, 14th ed., Enke Verlag, Stuttgart 1998.
37. R. Dudal in *SEFMIA Proc. Intern. Seminar on Soil Environment and Fertility Management in Intensive Agriculture*, Society of Science of Soil and Manure of Japan, Tokyo 1977, pp. 78 – 88.
38. Soil Taxonomy of the Soil Conservation Service, U.S. Department of Agriculture, Handbook no. 436.
39. E. N. Gapon, *J. Gen. Chem. USSR* **3** (1933) 144 – 152.
40. R. J. Haynes, *Adv. Agron.* **37** (1984) 249 – 315.
41. R. L. Parfitt, *Adv. Agron.* **30** (1978) 1 – 50.
42. C. D. Foy, R. L. Chaney, M. C. White, *Annu. Rev. Plant Physiol.* **29** (1978) 511 – 566.
43. C. E. Kallsen, T. W. Sammis, E. J. Gregory, *Agron. J.* **76** (1984) 59 – 64.
44. R. L Tate, *Soil Microbiology*, Wiley & Sons, New York 1995.
45. K. Mengel, *Adv. Soil Sci.* **2** (1985) 65 – 131.
46. G. L. Terman, *Adv. Agron.* **31** (1979) 189 – 223.
47. R. Vandré, J. Clemens, *Nutrient Cycling in Agrosystems.* **47** (1997) 157 – 165.
48. R. J. Buresh, S. K. DeDatta, *Adv. Argon.* **45** (1991) 1 – 59.
49. S. K. DeDatta, R. J. Buresh, *Adv. Soil Sci.* **10** (1989) 143 – 169.
50. N. K. Savant, S. K. DeDatta, *Adv. Agron.* **35** (1982) 241 – 302.
51. J. H. G. Slangen, P. Kerkhoff, *Fert. Res.* **5** (1984) 1 – 76.

52. L. Hendriks, N. Claassen, A. Jungk, *Z. Pflanzenernaehr. Bodenkd.* **144** (1981) 486 – 499.
53. P. H. Nye, *Adv. Agron.* **31** (1979) 225 – 272.
54. M. Silberbush, S. A. Barber, *Agron. J.* **75** (1983) 851 – 854.
55. C. A. Neyra, J. Döbereiner, *Adv. Agron.* **29** (1977) 1 – 38.
56. V. Römheld, H. Marschner, *Adv*, Plant Nutr. 2 (1986) 155 – 204.
57. R. Perrin, *Soil Use Manag.* **6** (1990) 189 – 195.
58. H. Marschner, B. Dell in A. D. Robson et al. (eds.): *Management of Mycorrhizas in Agriculture, Horticulture and Forestry*, 1994 , 89 – 102.
59. A. Finck: *Dünger und Düngung - Grundlagen und Anleitung zur Düngung der Kulturpflanzen*, VCH Verlagsgemeinschaft, Weinheim, Germany 1992.
60. A. L. Page, R. H. Miller, D. R. Keeney: *Methods of Soil Analysis - Chemical and microbiological properties*, 2nd ed., **part 2**, American Society of Agronomy, Inc., Madison, WI 1982.
61. E. Sibbesen, *J. Sci. Food Agric.* **34** (1983) 1368 – 1374.
62. G. Hoffmann, *Methodenbuch*, vol. **1, Untersuchung von Böden**, VDLUFA-Verlag, Darmstadt 1991/1997.
63. K. Németh, *Plant and Soil* **83** (1985) 1 – 19.
64. K. Németh, J. Maier, K. Mengel, *Z. Pflanzenernaehr. Bodenk.* **150** (1987) 369 – 374.
65. A. Link, Ph. D. Thesis, University of Hannover, Grauer Verlag Stuttgart 1997.
66. R. J. Poole, *Annu. Rev. Plant Physiol.* **29** (1978) 437 – 460.
67. E. A. Mitscherlich: *Bodenkunde für Landwirte, Forstwirte und Gärtner*, 7th ed., Verlag Paul Parey, Berlin – Hamburg 1954, p. 168.
68. S. P. Ceccotti, D. L. Messick, *Agrofood Industry hi-tech* **5** (1994) 9 – 14.
69. A. Vömel, *Z. Acker Pflanzenbau* **123** (1965/1966) 155 – 188.
70. U. Köpke: "Optimized Rotation and Nutrient Management in Organic Agriculture," in H. vanKeulen, E. A. Lantinga, H. H. van Laar (eds.): *Proc. Workshop Mixed Farming Systems in Europe*, Dronten, The Netherlands 1998.

General References

71. *Guidelines of the Council of the European Communities for the Harmonization of Legal Provisions in the Member States Concerned with Fertilizers*, 1975.

Specific References

72. J. Norden, *Raiffeisen* 1979, 50 – 55.
73. F. P. Achorn, W. C. Scott, J. A. Willbanks, *Fert. Solution* **14** (1970) 40.
74. V. Buhlmann, *Vereinigte Landwesenkaufleute* 1980, no. 3, 20, 22, 24.
75. J. Norden, *DIZ* (1978) 256 – 260, 512 – 515.
76. *Farm Chem.* **137** (1974) no. 10, 10.
77. T. P. Hignett, *Chem. Technol.* **2** (1972) 627 – 637.
78. T. P. Hignett (ed.): *Fertilizer Manual*, Martinus Nijhoff, Dr. W. Junk Publishers, Dordrecht – Boston – Lancaster 1985, p. 129.
79. D. M. Sloan, R. W. Veales, *J. AOAC* **60** (1977) 876.
80. R. Kümmel, *Chem. Techn. (Leipzig)* **25** (1973) 732.
81. W. R. Grace, NL-A 6 414 487, 1964.
82. *Derakane-Vinylesterharze*, DOW Chemical Europe (1977) Nov., p. 6.
83. *Handbuch der chemischen Beständigkeit der Dynamit Nobel AG*, 1982, p. 60.
84. W. von Beackmann, D. Funk, *3R, Rohre Rohrleitungsbau Rohrleitungstransp.* **17** (1978) 443.
85. L. G. Croysdale, W. E. Samuels, J. A. Wagner: "Urea – Ammonium Nitrate: Are They Safe?," *Chem. Eng. Prog.* **61** (1965) no. 1, 72 – 77.
    J. F. Anderson: "Explosions and Safety in Handling Urea – Ammonium Nitrate Solutions, *Saf. Air Ammonia Plants* **9** (1967) 70 – 71.
    Van Dolah et al.: "Explosion Hazards of Ammonium Nitrate under Fire Exposure," *Rep. Invest. U.S. Bur. Mines* no. 6773 (1966).
    Th. M. Groothiuzen: *Danger Aspects of Liquid Ammonium Nitrate. Part I. Detonation Properties*, report no. M3038–1 (1979).
    Th. M. Groothuizen: *Thermische stabiliteit van een ureum-ammonium-nitraatoplossing bij 60 °C*, report no. 484/485/70, Opdracht NSM-NV no. 9139 (1970).
86. J. M. Potts (ed.): "Fluid Fertilizers," Bulletin Y 185, Tennessee Valley Industry, Muscle thoals, Alabama 1984.
87. R. P. Rilo, *Zh. Prikl. Khim. (Leningrad) USSR* **50** (1977) 1676;
    J. Appl. Chem. Russ. (Engl. Transl.) **50** (1977) 1610.
88. A. L. Huhti, P. A. Gartaganis, *Can. J. Chem.* **34** (1956) 785.
89. W. P. Moore, "Liquid Fertilizers Have Long Storage Life," *Chem. Eng. News* **49** (1971) no. 44, 37.

90. E. U. Huffman, *New Developments in Fertilizer Technology*, Tennessee Valley Authority, Muscle Shoals, Ala. 1974.
91. A. Alon: "Recent Developments in Phosphoric Acid Manufacture," *ISMA Technical Conference*, Edinburgh, 14th to 16th Sept. 1965, Chap. V.
92. M. S. Casper, *Liquid Fertilizers*, Noyes Data Corp., Park Ridge, N.J., 1973.
93. A. V. Slack: *Fertilizer Developments and Trends*, Noyes Development Corp., Park Ridge, N. J., 1968, p. 344.
94. *Nitrogen* 1971, no. 4, 30.
95. R. D. Young: "Advances in Fertilizer Technology That Will Have Significant Impact," *Agric. Chem.* **26** (1971) 12 – 16, 29 – 31.
96. R. S. Meline, C. H. Davis, R. G. Lee, *Farm Chem.* **133** (1970) no. 11, 26, 28, 30.
97. National Fertilizer Solutions Association: Fluid Fertilizer Manual, Peoria, IL 1985.
98. Ugine Kuhlmann, DE-OS 2 100 413, 1971.
99. G. V. Kostyukhova, N. N. Malakhova, V. M. Lembrikoc, L. M. Soleveva, *Zh. Prikl. Khim. (Leningrad)* **51** (1978) 3;
    J. Appl. Chem. USSR (Engl. Transl.) **51** (1978) 1.
100. J. Silverberg, Assoc. Am. Fert. Control Off., Off. Publ., no. 21 168.
101. M. F. Abd El-Hameed, "Experimentation on the Use of Urea – Ammonium Sulphate (UAS) Liquid Fertilizer in Kuwait." Preprint J. F. Techn. Conf. (1984).
102. *Nitrogen*, 1985, no. 153, 20 – 31.
103. "Phosphoric Acid Sludge: An Inept Phosphatic Material?" *Phosphorus Potassium* 1985, no. 135, 26.
104. "Suspension Fertilizers without Polyphosphates," *Phosphorus Potassium* 1977, no. 89, 31.
105. J. A. Wilbanks: "Suspensions and Slurries," *Agric. Chem.* **22** (1967) 37.
106. "New Developments in Fertilizer Technology, 9th Demonstration," Tennessee Valley Authority, Muscle Shoals, Ala., 1972, pp. 53 – 55.
107. H. E. Mills, *Fert. Solutions* **6** (1962) no. 6, 38.
108. A. V. Slag, *Farm Chem.* **128** (1965) no. 5, 24.
109. M. N. Nabiev, A. F. Glagoleva, *Uzb. Khim, Zh.* 1960 no. 4, 3.
110. BASF, DE-AS 1 592 567, 1965.
111. W. C. Scott, J. A. Wilbanks, L. C. Faulkner: "Fluid Fertilizer," *Proc. Annu. Meet. Fert. Ind. Round Table* **25** (1975) 87.
112. "Urea-Ammonium Nitrate Solutions," *Nitrogen*, 1971, no. 69, 30 – 31.
113. S. H. Wittwer, F. G. Teubner, *Annu. Rev. Plant Physiol.* **10** (1959) 13 – 32.
114. W. Franke, *Planta* **55** (1960) 533 – 541;
    Planta **61** (1964) 1 – 16;
    Z. Pflanzenkr. (Pflanzenpath.) Pflanzenschutz, Sonderh. **8** (1977).
115. H.-P. Pissarek, *Dtsch. Landw. Presse* **22** (1972) no. 10.
116. G. Jürgens, H. Ramstetter, *Dtsch. Weinbau* **35** (1980) no. 19, 715 – 717.
117. A. Buchner, H. Sturm, *Gezielter düngen*, DLG-Verlag, Frankfurt 1985, pp. 148 – 155.
118. W. Bergmann, A. Hennig, *Chem. Tech. (Leipzig)* **25** (1973) 391 ff.
119. *Farm Chemicals Handbook '86*, Meister Publishing Co., Willoughby, Ohio, 1986.
120. BASF, DE 2 313 921, 1973 (J. Jung, B. Leutner, H. Sturm).
    C. A. Whitcomb, EP 0 023 364, 1980, prior. US 61 842, 1979.
121. BASF, EP 0 053 246, 1981 (B. Leutner et al.), DE 3 044 903, prior., 1980;
    EP-A 0 173 089
    =DE-OS 3 427 980 1984 (A. Jungbauer, B. Leutner, G. F. Jürgens)
122. G. Jürgens: "Spurennährstoffe in die ähre," *Bauernblatt für Schleswig-Holstein* **33** (1979) no. 129, 24.
123. G. Jürgens, *Chemie und Technik in der Landwirtschaft* 1983, no. 4, 128 – 129.
124. A. Amberger: *Pflanzenernährung*, 4t ed., UTB 846, Eugen Ulmer Stuttgart, 1996.
125. A. Finck: "Fertilizers and their efficient use," in D. J. Halliday, M. E. Trenkel, W. Wichmann (eds.): *IFA (1992): World Fertilizer Use Manual*, International Fertilizer Industry Association, Paris 1992.
126. Association of American Plant Food Control Officials (AAPFCO) (ed.): *Official Publication No. 48*, Association of American Plant Food Control Officials, Inc., West Lafayette IN, 1995.
127. M. E. Trenkel: *Controlled-Release and Stabilized Fertilizers in Agriculture*, (FAO) IFA, Paris 1997.
128. IFA (ed.): *World Fertilizer Consumption*, International Fertilizer Industry Association, Paris 1996.
129. R. Powell: *Controlled Release Fertilizer*, Noyes Development Corp., Park Ridge, 1968.
130. J. Araten: *New Fertilizer Materials*, Noyes Development Corp., Park Ridge, N. J., 1968.

131. H. Petersen: "Synthesis of Cyclic Ureas by Ureidoalkylation," *Synthesis* 1973, 243 – 244, 262, 264.
132. A. V. Slack: *Fertilizer Development and Trends*, Noyes Development Corp., Park Ridge, N. J., 1968, p. 153 – 156.
133. H. Petersen: "Grundzüge der Aminoplastchemie," *Kunststoff-Jahrbuch*, 10th ed., Wilhelm Parnsegau Verlag, Berlin, 1968, pp. 30 – 107.
134. R. J. Church: "Chemistry and Processing of Urea and Ureaform," in V. Sauchelli (ed.): *Fertilizer Nitrogen Its Chemistry and Technology,* Reinhold Publ., New York 1964.
135. BASF (ed.): *Die Landwirtschaftliche Versuchsstation Limburgerhof 1914 – 1964. 50 Jahre landwirtschaftliche Forschung in der BASF*, BASF Aktiengesellschaft, Limburgerhof 1965.
136. R. Hähndel, "Langsamwirkende Stickstoffdünger — ihre Eigenschaften und Vorteile," *Mitt Landbau* (1986) 4.
137. DuPont, US 2 766 283, 1951 (E. T. Darden) = DE 1 002 765, 1952.
138. DuPont, CA 550 618, 1954 (H. M. Kvalnes, E. T. Darden), US prior., 1953/1954.
139. Allied Chemical, US 2 644 806, 1950 (M. A. Kise),
US 2 845 401, 1955 (C. E. Waters).
140. J. M. O'Donnell, US 2 916 371, 1956.
141. Hercules Powder, US 3 227 543, 1965 (J. M. O'Donnell).
142. Borden Co., US 2 810 710, 1955 (D. R. Long).
143. Fisons, GB 789 075, 1954 (A. L. Whynes).
144. O. M. Scott & Sons, US 3 076 700 ,1957 (V. A. Renner);
DE-OS 1 592 751, 1963 (V. A. Renner, R. H. Czurak).
145. Unpublished results of the BASF Ammonia Laboratory, 1962.
146. T. Ushioda, *Jpn. Chem. Q* **5** (1969) no. 4, 27.
147. E. Rother: "Depotdünger," 1975, and "Arbeiten zur Entwicklung eines Herstellverfahrens für Mehrnährstoffdünger mit Langzeitstickstoff," 1985, both internal BASF reports.
148. H. Schneider, L. Veegens: "Practical Experience with Ureaform Slow Release Nitrogen Fertilizer During the Past 20 Years and Outlook for the Future', *Proc. Fert. Soc.* **180** (1979) 4 – 39.
149. Aglukon company broschure: *"Nutralene, Nitroform, AZOLON — Biologically Controlled Nitrogen Release,"* Aglukon Spezialdünger GmbH, Düsseldorf 1993.
150. J. Jung, J. Dressel, *Landwirtsch. Forsch. Sonderh.* **26/I** (1971) 131.
151. Mitsubishi, DE 1 146 080, 1961 (M. Hamamoto, J. Sakaki).
Mitsubishi, US 3 322 528, 1961 (M. Hamamoto).
152. Mitsubishi, DE 1 543 201, 1965 (S. Kamo, N. Yanai, N. Osako), JA prior (1964);
GB 1 099 643, 1965, JA prior (1964).
Hoechst, DE 1 303 018, 1963 (H. Schäfer, P. Krause);
DE 1 244 207, 1962 (U. Schwenk, F. Kalk, H. Schäfer).
BASF, DE-OS 1 618 128, 1967 (G. Rössler);
DE 2 355 212, 1973 (O. Grabowsky et al.).
153. BASF, DE 1 081 482, 1959 (J. Jung et al.)
154. BASF, DE 1 176 39, 1963 (H. Kindler et al.);
DE 1 244 ;207, 1962 (H. Brandeis, H. Petersen, A. Fikentscher).
155. Chisso Corp., JP 492 348, 1967;
DE-OS 1 670 385, 1966 (K. Fukatsu et al.);
US 3 488 351, 1966. (K. Fukatsu et al.).
156. C. J. Pratt, R. Noyes: *Ureaform in Nitrogen Fertilizer Chemical Process*, Noyes Development Corp., Pearl River, N. Y., 1965, pp. 232 – 234.
157. BASF: *Produktinformation für Erwerbsgartenbau, Landschaftsbau und Landwirtschaft,* COMPO GmbH, Münster 1995.
158. J. Jung, *Z. Pflanzenernaehr. Dueng. Bodenkd.* **94** (1961) 39;
J. Jung, C. Pfaff, *Die Landwirtschaftliche Versuchsstation Limburgerhof 1914 bis 1964*, BASF, Ludwigshafen 1964.
159. A. J. Patel, G. C. Sharma, *J. Am. Soc. Hortic, Sci.* **102** (1977) no. 3, 364 – 367.
160. BASF, DE-OS 1 467 377, 1982 (J. Jung et al.).
161. *Chem. Ing. Tech.* **46** (1974) A 100;
Chem. Age (London) **108** (1975) no. 2852, 17 – 18.
162. Hoechst, DE-OS 2 308 941, 1973.
163. W. Riemenschneider: "A New Simple Process for Manufacturing Oxamide," in *Prod. Tech. Plant Nutr. Effic. Br. Sulphur Corp. Int. Conf. Fert., 2nd, 1978*, (1978 – 1979) 1 – 17.
164. *Eur. Chem. News* **24** (1973) no. 604; **24** (1973) no. 609.
T. Okada, *J. Ammonium Industry* **1** (1975) no. 2, 28;
Nitrogen 1979, no. 117, 43.
165. T. Fujita, personal communication, 1996.
166. G. L. Bridger et al., *J. Agric. Food Chem.* **10** (1962) 181.

167. M. L. Salutzky, R. P. Steiger, *J. Agric. Food Chem.* **12** (1962) 486 – 491.
168. Mitsui Toatsu Chem., JP-Kokai 067 089/82, 1980.
Nugata Sulphuric Acid Co, JP 7 035 210, (Prior) 1966;
Chem. Abstr. **75** (1971) 34 643.
169. Wintershall AG, DE-OS 1 792 725, 1963 (W. Jahn-Held);
DE1 252 210, 1962 (W. Jahn-Held);
DE 1 265 726, 1964 (W. Jahn-Held),
DE 1 592 810, 1963 (W. Jahn-Held),
DE 1 592 811, 1963 (W. Jahn-Held).
F. Müller, DE 1 924 284, 1969.
Kali & Salz, DE 3 204 238, 1982;
DE 3 216 973, 1982.
Knapsack, DE 1 260 450, 1966 (W. Kern, J. Cremer, H. Harnisch).
170. Monsanto, GB 1 226 256, 1968.
171. BFG Glass Group, BE 878 884, 1978.
172. J. Jung. *Z. Pflanzenernähr. Düng Bodenkd.* **91** (1960) 122 – 130.
Archer Daniels Midland, US 3 223 518, 1961 (L. J. Hansen),
DE 1 254 162, 1960 (L. J. Hansen).
173. M. J. Brown, R. E. Luebs, P. F. Pratt, *Agron. J.* **58** (1966) no. 2, 175 – 178.
J. J. Oertli, O. R. Lunt, *Soil Sci. Soc. Am. Proc.* **26** (1962) 579 – 587.
174. Aglukon company brochure: *“Plantacote — The System of Crop-Specific Plant Nutrition,”* Aglukon Spezialdünger GmbH, Düsseldorf, 1992.
175. T. Fujita, “Invention of fertilizer coating technology using polyolefin resin and manufacturing of polyolefin coated urea,” *Jap. J. Soil Sci. Plant Nutr.* **67** (1996) 3.
176. T. Fujita et al.: *MEISTER with controlled availability — Properties and efficient utilization,* Chisso-Asahi Fertilizer Co., Ltd., Tokyo.
177. T. Fujita: *“Technical Development, Properties and Availability of Polyolefin Coated Fertilizers,”* Proceedings Dahlia Greidinger Memorial International Workshop on Controlled/Slow Release Fertilizers, Technion – Israel Institute of Technology, Haifa, 7 – 12 March 1993.
178. Chisso Corp., CA 1 295 849 ,1992 (T. Fujita, S. Yoshida, K. Yamahira).
179. Chisso Corp., CA 1 295 848 ,1992 (T. Fujita, Y. Yamashita, S. Yoshida, K. Yamahira).
180. T. Fujita, S. Maeda, M. Shibata, C. Takahashi: *“Research & development of coated fertilizer,”* Proceedings Fertilizer, Present and Future, Japan. Society of Soil Science and Plant Nutrition, Tokyo 1989, pp. 78 – 100.
181. T. Fujita, S. Maeda, M. Shibata, C. Takahashi: *“Research & development of coated fertilizers,”* Japanese Society of Soil Science & Plant Nutrition, Proceedings of the Symposium on Fertilizer, Present and Future, Sept. 25 – 26, Tokyo 1989.
182. H. M. Goertz: *“Technology Developments in Coated Fertilizers,”* Proceedings Dahlia Greidinger Memorial International Workshop on Controlled/Slow Release Fertilizers, Technion – Israel Institute of Technology, Haifa, 7 – 12 March 1993.
183. S. P. Landels: *Controlled-Release Fertilizers: Supply and Demand Trends in U.S. Nonfarm Markets*, SRI International, Menlo Park, CA 1994.
184. W. P. Moore: *“Reacted Layer Technology for Controlled Release Fertilizers,”* Proceedings Dahlia Greidinger Memorial International Workshop on Controlled/Slow Release Fertilizers, Technion – Israel Institute of Technology, Haifa, 7 – 12 March 1993.
185. S. Shoji, A. T. Gandeza: *Controlled Release Fertilizers with Polyolefin Resin Coating*, Kanno Printing Co. Ltd., Sendai 1992.
186. The O.M. Scott & Sons Co., US 5 089 041 ,1992 (H. E. Thompson, R. A. Kelch).
187. Archer Daniels Midland, DE-AS 1 242 573, 1964 (Le Roy B. Sahtin), US prior., (1963).
Archer Daniels Midland, US 3 264 088, 1965 (L. J. Hansen).
Sierra Chemical Europe, EP-A 184 869, 1985; NL prior., 1984 (J. M. H. Lembie).
188. Chisso Asahi Fertilizer Co., JP 634 150, 1972, 650 860, 1972, DE-AS 2 461 668, 1974 (T. Fujita et al.), JP prior., 1973; US 4 019 890, 1974 (T. Fujita et al.), JP prior., 1973.
189. Chisso Asahi Fertilizer Co., DE 2 834 513, 1978 (T. Fujita et al.), JP prior., 1978.
190. RLC Technologies, L.L.C., US 5 599 374, 1997 (J. H. Detrick);
US 5 547 486, 1996 (J. H. Detrick, F. T. Carney, Jr. US 5 374 292, 1993 (J. H. Detrick, F. T. Carney, Jr.
US 4 969 947, 1990 (W. P. Moore); US 4 804 403, 1989 (W. P. Moore);
US 4 711 659, 1987 (W. P. Moore).
191. Pursell Inc. company brochure: *“POLYON Polymer Coatings and the RLC Process,”* Pursell Industries, Inc., Sylacauga, Alabama 1995.
192. H. J. Detrick, PURSELL Technologies Inc., personal communication, 1997.

193. D. W. Rindt, G. M Bloin, J. G. Getsinger, *J. Agric. Food Chem.* **16** (1968) 773 – 778.
194. *Ag Chem Commer. Fert.* **28** (1973) no. 2, 14 – 15;
 Chem. Eng. (N. Y.) **81** (1974) Dec. 23, 32 – 33.
 Sulphur Inst. J. **10** (1974) no. 3/4, 7.
195. S. F. Allen et al., *Crops and Soils* **21** (1968) no. 3;
 Agron. J. **63** (1971) 529.
196. D. W. Rindt, G. M. Bloin, O. E. Moore, *J. Agric. Food. Chem.* **19** (1971) no. 5, 801 – 808.
197. Tennessee Valley Authority, US 3 295 950, 1965 (G. M. Bloin, D. W. Rindt);
 US 3 342 577, 1966 (G. M. Bloin, D. W. Rindt);
 US 3 903 333, 1972; (A. R. Shirley, R. S. Meline).
 O. M. Scott & Sons, US 4 042 366, 1976 (K. E. Fersch, W. E. Stearus).
198. RLC Technologies, L.L.C., US 5 599 374 ,1997 (J. H. Detrick).
199. Bayer, DE-AS 2 240 047, 1972; DE-OS 3 020 422, 1980; EP 46 896, 1981; EP-A 95 624, 1983 (H. Heller, D. Schäpel).
200. Bayer, EP 90 992, 1983, DE 3 212 537, 1982 (H. Brunn et al.).
201. B. Crawford: *Florida Commercial Fertilizer Law. Rules and Regulations*, State of Florida, Department of Agriculture and Consumer Services, Tallahassee FL, 1995.
202. Bundesminister für Ernährung, Landwirtschaft und Forsten: *Verordnung zur Änderung düngemittelrechtlicher Vorschriften*, 1995, BGBl. I.
203. G. Kluge, G. Embert: *Das Düngemittelrecht mit fachlichen Erläuterungen*. Bonn 1996.
204. T. Fujita, personal communication, 1997.
205. A. Amberger: *Pflanzenernährung*, 4th ed., **Taschenbücher 846**, Verlag Eugen Ulmer, Stuttgart 1996, pp. 156, 157.
206. K. Mengel: *Ernährung und Stoffwechsel der Pflanze*, VEB Gustav Fischer Verlag, Jena 1968, pp. 287, 289.
207. Bundesrat, Drucksache 239/96 *Stellungnahme der Bundesregierung zu der Entschließung des Bundesrates zur Verordnung zur Änderung düngemittelrechtlicher Vorschriften,* Bundesanzeiger Verlagsgesellschaft mbH, Bonn 1996.
208. A. Amberger: “Potential of the Nitrification Inhibitor Dicandiamide to Control Nitrogen Management and Environmental Pollution,” *Proceedings, Dahlia Greidinger Memorial International Workshop on Controlled/Slow Release Fertilizers, Technion,* Israel Institute of Technology Haifa, March 7 – 12 1993.
209. B. Scheffer, “Application of nitrogen fertilizers with nitrification inhibitors in water drainage areas,” *GWF, Gas Wasserfach: Wasser/Abwasser* **135** (1994) 15 – 19.
210. B. Scheffer: “Nitratgehalte im Dränwasser bei Einsatz stabilisierter Stickstoffdünger,” Stabilisierte Stickstoffdünger — ein Beitrag zur Verminderung des Nitratproblems, Proccedings: 15./16. Oktober 1991, Würzburg, Publisher; BASF Aktiengesellschaft, Limburgerhof/SKW Trostberg AG, 1991, pp. 83 – 94.
211. P. Schweiger: “Wege zur Minimierung des Nitratproblems,” Proceedings: Stabilisierte Stickstoffdünger — ein Beitrag zur Verminderung des Nitratproblems. Fachtagung: 15./16. Oktober 1991, Würzburg. Publisher; BASF Aktiengesellschaft, Limburgerhof/SKW Trostberg AG, 1991, pp. 59 – 69.
212. W. Zerulla: “$N_{\min}$ — Gehalte im Boden nach der Düngung bzw. nach der Ernte,” Proceedings: Stabilisierte Stickstoffdünger — ein Beitrag zur Verminderung des Nitratproblems. Fachtagung: 15./16. Oktober 1991, Würzburg. Publisher; BASF Aktiengesellschaft, Limburgerhof/SKW Trostberg AG, 1991, pp. 111 – 119.
213. H. Sturm, A. Buchner, W. Zerulla: *Gezielter düngen. Integriert, wirtschaftlich, umweltgerecht*, VerlagsUnion Agrar, DLG-Verlags-GmbH, Frankfurt a.M. 1994, pp. 90 – 95.
214. K. F. Bronson, A. R. Mosier, “Suppression of methane oxidation in aerobic soil by nitrogen fertilizers, nitrification inhibitors, and urease inhibitors,” *Biol. Fertil. Soils* **17** (1994) 4, 263 – 280.
215. K. F. Bronson, A. R. Mosier: “Effect of Nitrogen Fertilizer and Nitrification Inhibitors on Methane and Nitrous Oxide in Irrigated Corn,” *Biochemistry of Global Change. Radiatively Active Trace Gases*, Chapman & Hall, New York – London 1993.
216. K. F. Bronson, A. R. Mosier, S. R. Bishnoi, “Nitrous Oxide Emissions in Irrigated Corn as Affected by Nitrification Inhibitors,” *Soil Sci. Soc. Am. J.* **56** (1992) 1, 161 – 165.
217. H.-J. Klasse: “Versuchsergebnisse zur Wirkung stabilisierter Stickstoffdünger auf die Nitratverlagerung bzw. -auswaschung. $N_{\min}$ — Gehalte im Boden nach der Düngung bzw. nach der Ernte,” Proceedings: Stabilisierte

Stickstoffdünger — ein Beitrag zur Verminderung des Nitratproblems. Fachtagung: 15./16. Oktober 1991, Würzburg. Publisher; BASF Aktiengesellschaft, Limburgerhof/SKW Trostberg AG, 1991, pp. 103 – 110.

218. M. Koshino: *The Environmental Protection Framework Concerning Fertilizer Use in Japan*, National Institute of Agro-Environmental Sciences, Department of Farm Chemicals, Tsukuba 1993.
219. C. A. Grant, S. Jia, K. R. Brown, L. D. Baily: "Volatile losses of NH_3 surface-applied urea and urea ammonium nitrate with and without the urease inhibitors NBPT or ammonium thiosulphate," *Canadian Journal of Soil Science* **76** (1996) 3.
220. C. J. Watson et al., "Soil properties and the ability of the urease inhibitor N-(n-butyl) thiophosphoric triamide (nBTPT) to reduce ammonia volatilization from surface-applied urea," *Soil Biol. Biochem.* **26** (1994) 9, 1165 – 1171.
221. C. A. Grant, R. Ferguson, R. Lamond, A. Schlegel, W. Thomas: "Use of Urease Inhibitors in the Great Plains," *Proceedings Great Plains Soil Fertility Conference,* Denver, Co 1996.
222. M. E. Trenkel: *Controlled-Release and Stabilized Fertilizers in Agriculture*, (FAO) IFA, Paris 1997, p. 12.
223. J. A. Delgado, A. R. Mosier: "Mitigation alternatives to decrease nitrous oxides emissions and urea – nitrogen loss and their effect on methane flux," *J. Environ. Qual.* **25** (1996) 5.
224. A. Amberger: "Mobilization of rock phosphates in soil," *2nd African Soil Science Society Conference,* Cairo 1991.
225. F. Bayrakli, S. Gezgin: "Controlling ammonia volatilization from urea surface applied to sugar beet on a calcareous soil," *Commun. Soil. Sci. Plant Anal.* **27** (1996) 9, 10.
226. Z. P. Wang, O. van Cleemput, L. Baert: "Movement of urea and its hydrolysis products as influenced by moisture content and urease inhibitors," *Biol. Fertil. Soils* **22**, (1994) 1/2.
227. Z. P. Wang, O. van Cleemput, P. Demeyer, L. Baert: "Effect of urease on urea hydrolysis and ammonia volatilization," *Biol. Fertil. Soils* **11** (1991) 1, 43 – 47.
228. Z. P. Wang, L. T. Li, O. van Cleemput, L. Baert: "Effect of urease inhibitors on denitrification in soil," *Soil Use Manage.* **7** (1991) 4, 230 – 233.
229. B. Zacherl, A. Amberger: "Effect of the nitrification inhibitors dicyandiamide, nitrapyrin and thiourea on Nitrosomonas europea," *Fert. res.* **22** (1990) 37 – 44.
230. J. K. R. Gasser: "Nitrification Inhibitors — Their Occurence, Production and Effects of their Use on Crop Yields and Composition," *Soils Fert.* **33** (1970) 547 – 554.
231. K. Sommer, *Nitrifizide,* Landw. Forschung Sond. 27/II, 1972, pp. 64 – 82.
232. US 3 135 594, 1964 (Cleve A. I. Goring), Serial No. 653, 065 1957 expired in 1981; continuation-in-part of copending application.
233. US 3 424 754, 1969 (William H. Taplin III.), expired in 1986.
US 3 420 833, 1969 (William H. Taplin), expired in 1983.
234. DowElanco(ed.): *Quick Guide to Nitrogen Management,* DowElanco, Champaign, IL.
235. DowElanco(ed.): *References on N-Serve® Nitrogen Stabilizer — Bibliography,* DowElanco, Champaign, IL 1989.
236. J. Huffman, DowElanco, personal communication, 1997.
237. W. Zerulla, BASF Aktiengesellschaft, personal communication, 1996.
238. US 3 135 594, 1964 (Cl. A. I. Goring).
239. US 5 106 984, 1992 (M. E. Halpern, J. A. Orvik, J. Dietsche);
EP 0 306 547 B1, 1992 (M. E. Halpern, J. Dietsche, J. A. Orvik, B. J. Barron).
240. FR 1 232 366, 1960 (L. Soubies, R. Gadet).
241. S. Hallinger: "*Untersuchungen zur biologischen Metabolisierung von Dicyandiamid,* Technische Universität München," Isnstitut für Bodenkunde, Pflanzenernährung und Phytopathologie, Lehrstuhl für Pflanzenernährung, Dissertation, 1992.
242. M. Hauser, K. Haselwandter: "Degradation of Dicyandiamide by Soil Bacteria," *Soil Biol. Biochem.*, **22** (1990) 113 – 114.
243. K. Vilsmeier: "Fate of ammonium-N in pot studies as affected by DCD addition," *Fert. res.* **29** (1991) 3, 187 – 189.
244. K. Vilsmeier: "Turnover of ^{15}N-Ammonium Sulfate with Dicyandiamide under Aerobic and Anaerobic Soil Conditions," *Fert. Res.* **29** (1991) 191 – 196.
245. R. Roll: *"Zur Toxikologie von Dicyandiamid,"* Proceedings: Stabilisierte Stickstoffdünger — ein Beitrag zur Verminderung des Nitratproblems. Fachtagung: 15./16. Oktober 1991, Würzburg. BASF Aktiengesellschaft, Limburgerhof/SKW Trostberg AG, 1991, pp. 77 – 82.

246. US 4 764 200, 1988 (O. Meiss, R. E. Nitzschmann);
DE 4 128 828 A1, 1993 (K. Engelhardt, H. Dittmar, S. Luther).
247. US 4 994 100, 1991 (A. R. Sutton, Ch. W. Weston, R. L. Balser).
248. US 5 352 265, 1994 (Ch. W. Weston, L. A. Peacock, W. L. Thornsberry, Jr., A. L. Sutton).
249. DD 222 471, 1985 (H. J. Herbrich et al.).
250. DD 247 894, 1987 (K. Gunther et al.).
251. US 4 975 107, 1990 (K. E. Arndt et al.),
US 4 969 946, 1990 (K. E. Arndt et al.),
US 4 545 803, 1985 (K. E. Arndt et al.).
252. DE 4 446 194, 1996 (J. Dressel et al.),
DE 4 137 011, 1993 (R. Kästner et al.),
DE 3 820 739, 1990 (U. Baus et al.),
DE 3 820 738, 1990 (U. Baus et al.),
DE 3 409 317, 1985 (H. Bohm et al.).
253. DE 4 405 393, 1995 (M. Grabarse et al.),
DE 4 405 392, 1995 (M. Grabarse et al.),
DE 4 237 688, 1994 (I. Berg et al.),
DE 4 237 687, 1994 (M. Grabarse et al.),
DE 4 219 661, 1994 (M. Grabarse et al.),
DE 4 218 580, 1993 (H. J. Hartbrich et al.),
DE 4 211 808, 1993 (H. Böhland et al.),
DE 4 018 395, 1991 (M. Grabarse et al.),
DD 273 829, 1990 (H. J. Hartbrich et al.),
DD 279 470, 1990 (H. J. Halbenz et al.),
254. DD 260 486, 1989 (H. Carlson et al.),
255. RU 2 046 116, 1996 (L. A. Gorelik et al.).
256. SU 1 680 683, 1992 (O. V. Kuznetsova et al.).
257. US 4 523 940, 1985 (K. E. Arndt et al.),
US 4 522 642, 1985 (K. E. Arndt et al.).
258. DE 4 128 828 A1, 1993 (H. Dittmar et al.).
259. WO 98/05607, 1998 (Th Barth et al.)
260. S. Kincheloe: "The manufacture, agronomics and marketing of Agrotain," IFA Agro-Economics Committee Conference: 'Plant Nutrition in 2000', Tours, June 1997.
261. S. Kincheloe, A. R. Sutton: "The Manufacture, Agronomics and Marketing of agrotain," Book of Abstracts, 212th ACS National Meeting, American Chemical Society, Washington, D.C. 1996.
262. F. J. Dentener, P. C. Crutzen: "A Three-Dimensional Model of the Global Ammonia Cycle," *Atmos. Chem.* **19** (1994) 331 – 369.
263. W. H. Schlesinger, A. E. Hartley: "A Global Budget for NH_3," *Biogeochem.* **15** (1992) 191 – 211.
264. A. Finck: *Dünger und Düngung*, Verlag Chemie, Weinheim – New York 1979, pp. 52, 59.
265. US 4 530 714, 1985 (J. F. Kolc, M. D. Swerdloff, M. M. Rogic, L. L. Hendrickson, M. van der Puy).
266. Ch. F. Wilkinson: *N-(n-butyl) thiophosphoric triamide (NBPT, Agrotain®): A Summary of its Chemistry, Toxicology, Ecotoxicology and Environmental Fate,* IMC-Agrico Company, Mundelein, IL 1996, p. 6.
267. IMC Agrico (ed.): *Material Safety Data Sheet , AGROTAIN® Urease Inhibitor,* IMC-Agrico Company, Mundelein, IL 1995.
268. US 5 352 265, 1994 (C. W. Weston et al.),
US 5 364 438, 1994 (C. W. Weston et al.).
269. US 5 698 003, 1997 (B. A. Omilinsky et al.).
270. Ministére de L'Environment de la République Français: "Bonne pratiques d'épandage et de stockage des fertlisants," Journal Officiel de La Republique Française, Jan. 5, 1994.
271. Bundesminister für Ernährung, Landwirtschaft und Forsten: *Verordnung zur Änderung düngemitelrechtlicher Vorschriften,* Bundesgesetzblatt Jahrgang 1995, Teil I., Bonn 1995.
272. G. Kluge, G. Embert: *Das Düngemittelrecht mit fachlichen Erläuterungen 1992*, Landwirtschaftsverlag GmbH, Münster – Hiltrup 1992.
273. KrW/AbfG: Kreislaufwirtschafts- und Abfallgesetz, Gesetz zur Vermeidung, Verwertung und Beseitigung von Abfällen, BGBl. I (1994) p. 2705.
274. G. Kluge, G. Embert: *Das Düngemittelrecht mit fachlichen Erläterungen, (inkl. 1. Supplement 1997)*, Landwirtschaftsverlag GmbH, Münster – Hiltrup 1996.
275. R. Gutser, *VDLUFA Schriftenreihe* **44** (1996), 29 – 43.
276. AbfKlärV: Klärschlammverordnung, BGBl. I (1992)
277. K. Severin, *VDLUFA Schriftenreihe* **44** (1996) 85 – 101.
278. R. Gutser, K. Teicher, P. Fischer, *Acta Horticulturae* **150** (1984) 175 – 184.
279. A. Fink: *Dünger und Düngung*, VCH Verlagsgesellschaft, Weinheim, Germany 1992, pp. 164 – 174.
280. E. Knickmann: "Handelshumusdüngemittel", in K. Scharrer, Linser (eds.): *Handbuch der Pflanzenernährung und Düngung*, Springer-Verlag, Wien 1968, pp. 1400 – 1431.
281. "Abfallstoffe als Dünger", *VDLUFA-Schriftenreihe* **23** (1988).
282. "Sekundärrohstoffe im Stoffkreislauf der Landwirtschaft", *VDLUFA-Schriftenreihe* **44** (1996).

283. R. Gutser, *Z. Branntweinwirtschaft* **138** (1998) 2 – 6.
284. U. Bayer, Diss. Techn. Univ. München, 1987.
285. T. v. Tucher, Diss. Techn. Univ. München, 1990.
286. Bundesministerium für Umwelt, Naturschutz- und Reaktorsicherheit: Entwicklung der Schwermetallgehalte von Klärschlämmen in der BRD von 1974 – 1994, Informationsblatt 1996.
287. A. Gronauer et al.: Bioabfallkompostierung — Verfahren und Verwertung, Bayerisches Landesamt für Umweltschutz, Schriftenreihe Heft 139 (1997).
288. P. Fischer, M. Jauch, *VDLUFA Schriftenreihe* **33** (1991) 751 – 756.
289. M. Bertoldi, P. Sequi, B. Lemmes, T. Papi: "The Science of Composting," *European Comm. Int. Symp.*, Udine 1995, Blackie Academic & Professional, an imprint of Chapman – Hall, 1996.
290. J. Köhnlein, H. Vetter: "Die Stalldüngerrotte bei steigender Stroheinstreu," *Z. Pflanzenernähr. Düng. Bodenkd.* **63** (1953) no. 108, 119 – 141.
291. G. J. Kohlenbrander, L. C. N. de la Lande Cremer: *Stahlmest en Gier*, H. Veenman & Zonen, Wageningen 1967.
292. H. Koriath und Kollektiv: *Güllewirtschaft, Gülledüngung*, VEB Deutscher Landwirtschaftsverlag, Berlin 1975.
293. K. Rauhe: "Wirtschaftseigene Düngemittel" in *Handbuch der Pflanzenernährung und Düngung*, vol. **2**, Springerverlag, Wien-New York, 1968 pp. 907 – 943.
294. D. Strauch, W. Baader, C. Tietjen: *Abfälle aus der Tierhaltung*, Verlag Eugen Ulmer, Stuttgart 1977.
295. H. Vetter, G. Steffens: *Wirtschaftseigene Düngung*, DLG-Verlag, Frankfurt 1986.
296. *Faustzahlen für die Landwirtschaft*, 10th ed., Landwirschaftsverlag, Münster-Hiltrup 1983.
297. A. Amberger: "Gülle – ein schlechtgenutzter Dünger," *DLG-Mitteilungen* **2**, 1982 pp. 78 – 80.
298. J. C. Brogan (ed): *Nitrogen Losses and Surface Run-off from Landspreading of Manures*, Martinus Nijhoff/Dr. W. Junk Publishers, Den Hague-Boston-London 1981.
299. K. Früchtenicht, H. Vetter: "Phosphatzufuhr und Phosphatwirkung aus organischer Düngung," in *Phosphatdüngung aus heutiger Sicht*, Arbeitskreis Phosphat der deutschen Düngerindustrie, Hamburg 1983.
300. J. K. R. Gasser: *Effluents from Livestock*, Applied Science Publishers, London 1980.
301. T. W. G. Hucker, G. Catroux: *Phosphorus in Sewage Sludge and Animal Waste Slurriers*, Reichel, Dordrecht 1981.
302. G. Schechtner: "Nährstoffwirkung und Sonderwirkungen der Gülle auf dem Grünland," in *Bericht über die 7. Arbeitstagung "Fragen der Güllerei"*, Bundesversuchsanstalt für alpenländische Landwirtschaft, 1981, pp. 135 – 196.
303. J. H. Voorburg: *Utilization of Manure by Land Spreading*, Janssen Services, London 1977.
304. L. Diekmann: "Schadgase aus Flüssigmist" in *Rationalisierungskuratorium für Landwirtschaft* (*RKL*), 1983, pp. 839 – 885.
305. P. Förster: "Einfluß hoher Güllegaben und üblicher Mineraldünger auf die Stoffbelastung (NO_3, NH_4, P und SO_4) im Boden und Grundwasser in Sandböden Nordwestdeutschlands," *Z. Acker Pflanzenbau*, **137** (1973) 270 – 286.
306. W. R. Kelly: *Animal and Human Health Hazards Associated with the Utilization of Animal Effluents*, Commission of the European Community, Luxembourg 1978.
307. H. Kuntze: "Düngung und Gewässergüte," *Landwirtsch. Forsch. Sonderh.* **35** (1979) 14 – 24.

General References

308. *Fertilizer Manual, Development and Transfer of Technology*, Series no. 113, UNIDO, United Nations, New York 1980.
309. A. Schmidt: *Chemie und Technologie der Düngemittelherstellung*, Hüthig-Verlag, Heidelberg 1972.
310. A. J. More (ed.): *Granular Fertilizers and Their Production*, The British Sulphur Corp., London 1977.
311. *Fertilizers: Ammonium Phosphates*, **Process Economics Program Report no. 127**, SRI International, Menlo Park, Ca., 1979.
312. F. T. Nielsson: *Manual of Fertilizer Processing*, vol. **5 of the Fertilizer Science and Technology Series**, 1987.

Specific References

313. *Kirk-Othmer*, **10** (1980) 31 – 125.
314. T. P. Hignett, *Farm Chem.* 1963, no. 1, 34 – 35.
315. *Winnacker-Küchler*, 4th ed., **2** pp. 334 – 378.
316. J. Jung, *Proc. Int. Congr. Phosphorus Compd., 3rd*, 1983, 463 – 495.
317. "Granular Fertilizers," supplement to *Phosphorus Potassium* **1985**.
318. V. Sauchelli, *Chemistry and Technology of Fertilizers, ACS Monograph Series*, Reinhold

Publishing Corporation, New York; Chapman & Hall Ltd., London 1960, p. 280.
319. A. T. Brook, "Developments in Granulation Techniques," paper read before the Fertiliser Society of London, 1957.
320. O. Bognati, L. Buriani, I. Innamorati, Proc. ISMA Tech./Agric. Conf., 1967.
321. T. E. Powell, *Proc. Technol. Intern.* **18** (1973) 271 –278.
322. *Nitrogen* 1981, no 131, 39 – 41.
323. *Nitrogen* 1975, no. 95, 31 – 36.
324. *World Guide to Fertilizer Process and Constructors*, 6th ed., The British Sulphur Corp., London 1979, pp. 138 – 139.
325. *Nitrogen* **175** (1988) 32 – 40.
326. O. E. Skauli: "Pan Granulation of Ammonium Nitrate and Urea," (Symposium on New Fertilizer Technology) ACS National Meeting, 168th, 1974.
327. J. P. Bruynseels: "Fluid Bed Granulation of Ammonium Nitrate and Calcium Ammonium Nitrate," *Proc. of the Fertiliser Society* 1985, no. 235.
328. J. P. Bruynseels, *Hydrocarbon Process.* **60** (1981) no. 9, 203 – 208.
329. *H. B. Ries, Aufbereit. Tech.* **18** (1977) 633 – 640.
330. *Nitrogen* **193** (1990) 22 – 26.
331. Private communication.
332. R. S. Meline, I. W. McCamy, J. L. Graham, T. S. Sloan *J. Agr. Food Chem.* **16** (1968) 235 – 240.
333. *Nitrogen* **177** (1989) 21 – 24.
334. J. W. McCamy, M. M. Norton, *Farm Chem.* **140** (1977) no. 2, 61 – 68, 70.
335. *New Developments in Fertilizer Technology, 11th Demonstration*, Tennessee Valley Authority, Muscle Shoals, Ala., 1976, pp. 33 – 35.
336. *Nitrogen* 1975 no. 98, 37 – 39.
337. L. M. Nunnely, F. T. Carney: "Melt Granulation of Urea by the Falling-Curtain Process," ACS National Meeting, 182th, 1981.
338. W. Pietsch, *Aufbereit. Tech.* **12** (1971) 684 – 690.
339. C. Debayeux in [340] , p. 8.1 – 8.5.
340. V. Bizzotto, IFA Technical Conference 5 – 8 Nov. 1984, Paris, p. 7.1 – 7.14 (Reprints).
341. *New Developments in Fertilizer Technology, 8th Demonstration*, Tennessee Valley Authority, Muscle Shoals, Ala., 1970, pp. 41 – 47.
342. G. C. Hicks, J. M. Stinson, *Ind. Eng. Chem. Proc. Des. Dev.* **14** (1975) 269 – 276.
343. A. S. Maartensdijk: "Direct Production of Granulated Superphosphates and PK-Compounds," *New Dev. Phosphate Fert. Technol. Proc. Tech. Conf. ISMA Ltd., 1976* (1977).
344. G. H. Wesenberg: "Concentrated Superphosphate: Manufacturing Process" in [312]
345. F. P. Achorn, D. G. Salladay: "Granulation Using the Pipe-Cross Reactor" in [312]
346. J. A. Benes, A. Hemm: "Modern Process Design in Compound Fertilizer Plants", *Seminar of Trends and Developments in the Fertiliser Industry,* 1985.
347. G. C. Hicks: "Review of the Production of Monoammonium Phosphate" in [312]
348. G. H. Wesenberg: "Diammonium Phosphate Plants and Process" in [312]
349. J. Steen, E. A. Aasum, T. Heggeboe: "The Norsk Hydro Nitrophosphate Process" in [312]
350. *Phosphorus Potassium* 1975, no. 76, 48 – 54.
351. I. W. McCamy, G. C. Hicks, *Proc. Annu. Meet. Fert. Ind. Round Table*, 26th, 1976, 168 – 176.
352. G. C. Hicks, I. W. McCamy, B. R. Parker, M. M. Norton; "Basis for Selection of Granulators at TVA," paper presented at the *Proc. Annu. Meet. Fert. Ind. Round Table*, 28th, 1978.
353. H. Stahl, *Aufbereit. Tech.* **21** (1980) 525 – 533.
354. G. Heiseler, D. Baier, D. Juling, W. Kretschmer, *Chem. Tech. (Leipzig)* **25** (1973) 410 – 414.
355. L. Diehl, K. F. Kummer, H. Oertel: "Nitrophosphates with Variable Water Solubility: Preparation and Properties," paper read before the Fertiliser Society of London, 1986.
356. M. Autti, M. Loikkanen, P. Suppanen: "Economic and Technical Aspects in some Differential NPK-Processes," *New Dev. Phosphate Fert. Technol. Proc. Tech. Conf. ISMA Ltd,* 1976 (1977).
357. H. B. Ries, *Aufbereit. Tech.* **16** (1975) 17 – 26.
358. I. S. E. Martin, F. J. Harris in [310], pp. 253 – 270.
359. J. Kotlarevsky, J. Cariou in [310], pp. 245 – 252.
360. M. Kuwabara, S. Hayamizu, A. Hatakeyama in [310] pp. 125 – 147.
361. J. L. Medbery, F. T. Nielsson, *Ind. Eng. Chem. Prod. Res. Dev.* **22** (1983) 291 – 296.
362. B. Dencs, Z. Ormós, *Int. Symp. Agglomeration, 3rd, 1981*, G 2 – G 15.
363. A. Maroglou: "Fluidized Bed Granulation," Ph. D. Thesis, University of Birmingham 1985.

364. S. Mortensen, S. Hoomand, *Chem. Eng. Prog.* **79** (1983) no. 4, pp. 37 – 42.
365. S. Mortensen, A. Kristiansen, *Int. Symp. Agglomeration, 3rd, 1981*, F 77 – F 90.
366. H. B. Ries, *Aufbereit., Tech.* **11** (1970) 262 – 280.
367. I. S. Mangat in [310] pp. 148 – 161.
368. J. L Hawksley in [310] pp. 110 – 124.
369. P. J. Sherrington, *Can. J. Chem. Eng.* **47** (1969) June, 308 – 316.
370. A. I. More (ed): *Fert. Nitrogen: Proc. Br. Sulphur Corp. Int. Conf. Fert. Technol., 4th, 1981*.
371. Y F. Berguin in [310] pp. 296 – 303.
372. P. J. Sherrington, R. Oliver: *Granulation*, Hlyden& Sons Ltd., London p. 172.
373. O. Uemaki, K. B. Mathur, *Ind. Eng. Chem. Process Des. Dev.* **15** (1976) 504 – 508.
374. F. E. Steenwinkel, J. W. Hoogendonk: "The Prilling of Compound Fertilisers," paper read before The Fertiliser Society (1969).
375. *Nitrogen* 1980, no. 127, 45.
376. P. J. van den Berg, G. Hallie: "New Developments in Granulation Techniques," *Proc. Fert. Soc.* 1960, no. 59.
377. *"Supra Today*," 1977, p. 23.
378. R. P. Ruskan, *Chem. Eng. (N. Y.)* **83** (1976) June 7, 114 – 118.
379. I. R. Schoemaker, I. A. C. M. Smit, "Criteria for a Choice between various Granulation and Prilling Technologies for Fertilisers," paper read before the Fertiliser Society of London (1981).
380. R. G. Lee, M. M. Norton, H. G. Graham, *Proc. Annu. Meet. Fert. Ind. Round Table*, 24th, 1974, 79.
381. R. G. Lee, R. S. Meline, R. D. Young, *Ind. Eng. Chem. Process. Des. Dev.* **11** (1972) 90 – 94.
382. C. J. Pratt, *Br. Chem. Eng.* **14** (1969) 185 – 188.
383. H. B. Ries, *Int. Symp. Agglomeration, 3rd*, 1981, F 34 – F 59.
384. H. Rumpf, *Chem. Ing. Tech.* **30** (1958) 329 – 336.
385. G. Nöltner, *Int. Symp. Agglomeration, 3rd, 1981*, F 16 – F 33xs.
386. H. Schubert, E. Heidenreich, F. Liepe, Th. Neeße, *Mechanische Verfahrenstechnik II*, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1979, p. 204.
387. G. Heinze: "Verfahrenstechniken des Agglomerierens," Seminar of the VDI-Bildungswerk, Stuttgart-Vaihingen 1984.
388. J. Eimers: "Granuliertechniken bei der Düngemittelherstellung," paper presented at the congress AGRICHEM 81, Bratislava 1981.
389. H. B. Ries, *Aufbereit. Tech.* **11** (1970) 147 – 153.
390. H. B. Ries, *Aufbereit. Tech.* **11** (1970) 615 – 621.
391. H. B. Ries, *Aufbereit. Tech.* **11** (1970) 744 – 753.
392. *New Developments in Fertilizer Technology, 13th Demonstration*, Tennessee Valley Autority, Muscle Shoals, Ala., 1980, pp. 75 – 79.
393. R. J. Milborne, D. W. Philip, "Adapting a Pipe Reactor to a Blunger for NPK Production," paper read before the Fertiliser Society of London, 1986.
394. W. Pietsch, *Aufbereit. Tech.* **7** (1966) no. 4, 177 – 191.
395. G. Heinze, *Chem. Tech. Heidelberg* **15** (1986) no. 6, 16, 18, 21.
396. R. H. Perry, C. H. Chilton: *Chemical Engineers' Handbook*, 5th ed., McGraw-Hill, New York 1973 pp. 57 – 65.
397. J. O. Hardesty, *Chem. Eng. Prog.* **51** (1955) 291 – 295.
398. F. T. Nielsson: "Granulation" in [312]
399. Ch. Davis, R. S. Meline, H. G. Graham, *Chem. Eng. Prog.* **64** (1968) no. 5, 75 – 82.
400. *Farm Chemicals Handbook*, 1986, p. B 35.
401. R. D. Young, G. C. Hicks, C. H. Davis, *J. Agric. Food Chem.* **10** (1962) , no. 1, 68 – 72.
402. F. G. Membrillera, J. L. Toral, F. Codina in [310], pp. 162 – 173.
403. "The Cros Fertilizer Granulation Process", *Phosphorus Potassium* **1977,** no. 87, 33 – 36.
404. *Phosphorus Potassium* 1986, no. 144, 27 – 33.
405. J. W. Baynham: "The SAI-R Process for the Manufacture of Compound Fertilisers containing Ammonium Nitrate and Diammonium Phosphate", *Proc. ISMA Tech. Conf. 1965*.
406. *Nitrogen* 1970, no. 64, 25 – 26.
407. E. Pelitti, J. C. Reynolds in [310], pp. 95 – 109.
408. R. M. Reed, J. C. Reynolds, *Chem. Eng. Prog.* **69** (1973) no. 2, 62 – 66.
409. E. Vogel, *Nitrogen*, 1986, no. 161, 28 – 31.
410. *Nitrogen* 1987, no. 166, 39.
411. K. Sommer, W. Herrmann, *Chem. Ing. Tech.* **50** (1978) 518 – 524.
412. F. D. Young, T. W. McCamy, *Can. J. Chem. Eng.* **45** (1967) 50 – 56.
413. H. Klatt, *Zem. Kalk Gips* **11** (1958) no. 4, 144 – 154.

414. Tennessee Corp., US 769 058, 1985.
415. J. W. McCamy, M. M. Norton in [310], pp. 68 – 94.
416. St. Ruberg, *Aufbereit.-Tech.* **28** (1987) 75 – 81.
417. H. B. Ries, *Tech. Mitt.* **77** (1984) 583 – 589.
418. H. B. Ries, *Maschinenmarkt* **92** (1986) 25 – 28.
419. H. Stahl: "Press-Agglomeration," seminar of the VDI-Bildungswerk, Stuttgart-Vaihingen 1984.
420. S. Maier in [310], pp. 283 – 295.
421. A. Seixas, J. D. Ribeiro in [340] p. 11.1 – 11.21.
422. H. Rieschel, *Aufber. Tech.* **11** (1970) 133 – 146.
423. A. Tassin, Chr. Fayard, *Inform. Chem.* **269** (1986) no. 1, 127 – 131.
424. P. Heroien, C. Fayard, *Proc. Inst. Briquet. Agglom. Bienn. Conf.* **22** (1991) 173 – 185.
425. W. Herrmann: *Das Verdichten von Pulvern zwischen zwei Walzen*, Verlag Chemie, Weinheim, Germany 1973.
426. W. Herrmann, K. Sommer, *Int. Symp. Agglomeration, 3rd*, 1981, F2 – F15.
427. W. Herrmann, *Chem. Ing. Tech.* **51** (1979) 277 – 282.
428. G. J. Thorne, J. D. C. Hemsley, H. Hudson, *Chem. Process. (London)* **19** (1973) no. 1, 17 – 18.
429. I. Podilchuck, W. T. Charlton, M. D. Pask: *Modern Approach to the Design of Granular Fertilizer Plants*, Fisons Ltd., Fertilizer Division, 1975.
430. H. Vernède, *Nitrogen* 1969, no. 60, 29 – 33.
431. Sahut-Conreur, *Verfahrenstechn.* 1987, no. 5, 8, 10, 12.
432. G. Hoffmeister: *"Physical Properities of Fertilizers & Methods for Measuring Them"*, TVA Bulletin Y 147, 1979.
433. L. Jäger, P. Hegner, *Fert. Technol.* **1** (1985) 191 – 221.
434. K. Niendorf, W. Teige, *Chem. Tech. (Leipzig)* **26** (1974) 771 – 774.
435. M. Brübach, A. Göhlich, *Verfahrenstechnik* **7** (1973) 268 – 272.
436. P. Runge, *Chem. Tech. (Leipzig)* **28** (1976) 163 – 165.
437. J. Silverberg, *Proc. Ann. Meet. Fert. Ind. Round Table 16th* 1966, 81.
438. D. C. Thompson: "Fertiliser Caking and its Prevention," *Proc. Fert. Soc.* 1972, no. 125.
439. O. Kjöhl, A. Munthe-Kaas: "Study of the Mechanism of Caking in some Nitrophosphate Fertilizers," Proc. ISMA Tech. Conf., 1970.
440. G. C. Lowrison: *Fertilizer Technology*, Ellis Horwood Limited, Chichester, 1989, p. 406.
441. P. A. Mackay, K. S. Sharples: "The Use of Special Oils and Coatings to Prevent Caking of Fertilizers," *Proc. Fert. Soc.* 1985, no. 239.
442. *Nitrogen* 1986, no. 164, 33 – 34.
443. *Nitrogen* 1990, no. 187, 20 – 27.
444. *Nitrogen* 1987, no. 166, 19.
445. E. Alto, P. Suppanen: "Dust Control in NPK Production," *Proc*, ISMA Tech. Conf. 1974.
446. J. Baretincic: "Environmental Regulations," in [312]
447. J. E. Seymour, in [310], pp. 174 – 180.
448. *Bulk Blend Quality Control Manual*, The Fertilizer Institute, Washington, D.C., 1975.
449. L. G. Croysdale, W. E. Samuels, J. A. Wagner, *Chem. Eng. Prog.* **61** (1965) 72 – 77.
450. G. Hoffmeister, "Bulk Blending," in [312]
451. L. Taylor, "Latest Technology and Methods Used for Bulk Blending and Fertilizer Storage in the United States," paper read before the Fertiliser Society of London, 1987.
452. H. W. Frizen: "Verfahrensketten für feste und flüssige Mehrnährstoffdünger in den USA," Dissertation, Universität Bonn, 1974.
453. K. H. Ullrich, *Vereinigte Landwarenkaufleute* 1979, no. 3.
454. Official Bulletin of the European Community, 20th ed., No. L213 from 22 August 1977, 77/535/EEC: Guidelines of the commission from 22 June 1977 on the approximation of the laws of the member states concerning sampling and methods of analysis of fertilizers. The Guidelines are extended and modified in: Bulletin L265 from 12.09.89, 89/519/EEC for Ca., Mg, Na and S; and Bulletin L113 from 07.05.93, 93/1/EEC for trace elements B, Co, Cu, Fe, Mn, Mo, Zn.
455. Methodenbuch, Band II: Die Untersuchung von Düngemitteln, [Book of Methods. Vol. II: The Analysis of Fertilizers] Verband Deutscher Landwirtschaftlicher Untersuchungs- und Forschungsanstalten (LUFA) [Association of German Agricultural Research Institutes] LUFA-Verlag, Darmstadt, 1995.
456. ISO (International Organization for Standardization).
457. Official Methods of Analysis of AOAC International, 16th ed, 3rd rev., AOAC International, Gaithersburg, Maryland, USA, 1997.

General References

458. B. Wermingshausen: *Kunststoffe im Landbau*, Kohlhammer-Verlag, Stuttgart-Berlin-Köln-Mainz 1985.

459. H. Baumann: *Plastoponik, Schaumkunststoffe in der Agrarwirtschaft*, Dr. Alfred Hüthig Verlag, Heidelberg 1967.
460. A. Kullmann: *Synthetische Bodenverbesserungsmittel*, VEB Deutscher Landwirtschaftsverlag, Berlin 1972.
461. M. G. Voronkov, G. I. Zelchan, E. Lukevitz in K. Ruhlmann (ed.): *Silizium und Leben, Biochemie, Toxikologie und Pharmakologie des Si*, Akademie-Verlag, Berlin 1975.

Specific References

462. H. Prün, *Rasen Turf Gazon* **17** (1986) no. 1, 120 – 127.
463. B. Werminghausen, *Chemie und Technik in der Landwirtschaft* 1962, 359 – 360.
464. H. Knobloch, *Wasser und Boden* **12** (1964) 403 – 405.
465. F. Penningsfeld, *Das Gartenamt* **28** (1979) 1 – 4.
466. J. Günther, *Gb + Gw*, Gärtnerbörse und Gartenwelt, 81 (1981) no. 31, 714 – 716.
467. B. Werminghausen, private communication, 1987.
468. B. Werminghausen, *Mitt. Landbau* 1964, no. 4, 1 – 8.
469. BASF, DE 1 245 205, 1962 (F. Stastny, J. Jung)
470. H. Will, paper presented at the meeting of the Gesellschaft für industriellen Pflanzenbau, Wien 1975.
471. H. Knobloch, *Wasser Boden* **18** (1960) 415 – 418.
472. H. Knobloch, *Z. Kulturtech. Flurbereinig.* **8** (1967) 54 – 59.
473. E. Zinck, R. Krötz, *Umweltmagazin* 1980, no. 3, 38 – 40.
474. E. Zinck, DE 2 742 606, 1977.
475. H. Rasp, *Z. Pflanzenernähr. Bodenk.* **133** (1972) no. 1/2, 111 – 123.
476. H. Rasp, *Mitteilungen Deutsche Bodenkundl. Gesellschaft* **15** (1972) 181 – 183.
477. W. Tepe, private communication based on an internal report (1976).
478. S. Maier, *Landwirtsch. Forsch. Sonderh.* **18** (1970) 14 – 20.
479. B. Werminghausen, *Acta Hortic.* **26** (1972) 159 – 164.
480. A. Buchner, J. Jung, P. Weisser, H. Will, *Landwirtsch. Forsch.* **22** (1969) no. 2, 94 – 99.
481. J. F. Kitchens, R. E. Casner, G. S. Edwards, W. E. Harward III, B. J. Macri, EPA 560/2–76–009, ARC 49–5681, Springfield, Va., 1976, pp. 1 – 200.
482. W. Skirde, *Z. Vegetationstechnik* **5** (1982) 1 – 6.
483. L. Unterstenhöfer, *Kunststoffe* **57** (1967) no. 11, 850 – 855.
484. F. Doehler, DE 839 944, 1948.
485. P. di Dio, paper presented at the Congress Chemistry in Agriculture, 2nd., Pressburg/Bratislawa 1972.
486. *Guide to Evaluating Sands and Amendments Used for High Trafficked Turfgrass*, University of California, Agricultural Extension, AXT no. 113 1970.
487. W. Ganssmann, *Phosphorsäure* **22** (1962) 223 – 241.
488. E. Seifert, Mitteilungen Leichtweiss-Institut Technische Universität Braunschweig, **1970,** nos. 25 and 27.
489. T. Niedermaier, *Landwirtsch. Forsch.* **32** (1979) no. 1/2, 129 – 137.
490. H. Gebhardt, *Mitteilungen Deutsche Bodenkundl. Gesellschaft* **15** (1972) 225 – 245.
491. W. Büring, *Das Gartenamt* **23** (1974) no. 5, 258 – 281.
492. K. Wiede, Dissertation, Bonn 1976.
493. W. Büring, *Rasen und Rasengräser.* 1969, no. 6, 78 – 83.
494. B. Walter, E. Petermann, *Weinberg und Keller* **21** (1974) no. 12, 513 – 532.
495. A. H. Sayegh, A. M. Osman, B. Hattar, M. Barasiri, M. Chaudri, M. Nimeh, *Agrochimica*, **26** (1982) no. 1, 22 – 30.
496. H. H. Becher, R. Woytek, *Z. Kulturtech. Flurbereinig.* **25** (1984) 46 – 53.
497. E. Schulze, unpublished reports of the Institut für Pflanzenbau, Universität Bonn, 1970 – 1977.
498. W. Büring, *Das Gartenamt* **31** (1982) 659 – 667.
499. A. Okuda, E. Takahashi, *Nippon Dojo Hiryogaku Zasshi* **32** (1961) 533.
500. L. H. P. Jones, K. A. Handreck, *Adv. Agron.* **19** (1967) no. 19, 107 – 149.
501. J. Vlamis, D. E. Williams, *Plant Soil* **27** (1967) 131.
502. H. Rasp, *Landwirtsch. Forsch. Sonderh.* **35** (1978) 394 – 411.
503. W. Friedmeann, W. Pesch, private communication (1979).
504. H. O. Leh, *Gesunde Pflanze* **38** (1986) no. 6, 246 – 256.
505. Henkel, DE 2 208 917, 1972 (E. Seifert, H. von Freyhold).
506. Guano-Werke, DE 2 612 888, 1976 (J. Bochem, G. Eisenhauer).
507. J. Cronjaeger, A. Hardt, H. Bernard, *Gesunde Pflanze* **45** (1993) 7.

508. M. Kretschmer, K. Schaller, K. Wiegand, *Landwirtsch. Forsch.* **35** (1982) , no. 1 – 2, 66 – 76.
509. H. Prün, Landwirtsch. Forsch. *Sonderh.* **30** (1973) 288 – 296.
510. B. Meyer, *Mitteilungen Deutsche Bodenkundl. Gesellschaft* **15** (1972) 253 – 258.
511. F. Callebaut, D. Gabriels, M. D. Boodt, *Med. Fac. Landbouwwet., Rijksuniv. Gent* **49** (1984) no. 1, 53 – 61.
512. E. McGuire, R. N. Carrow, J. Troll, *Agron. J.* **70** (1978) 317 – 348.
513. M. J. Carrol, A. M. Petrovic, *Proceed. Int. Turfgrass Research Conference, 5th*, Avignon 1985, pp. 381 –389.
514. L. M. Rivière, S. Charpentier, B. Valat, *Rev. Horic.* **267** (1986) 43 – 49.
515. H. Prün, paper presented before the Deutsche Rasengesellschaft, Heidelberg 1984.
516. F. Masuda, *CEER Chem. Econ. Eng. Rev.* **15** (1983) no. 11, 19 – 22.
517. R. L. Flannery, W. J. Busscher, *Comm. Soil Sci. Plant Anal.* **13** (1982) no. 2, 103 – 111.
518. *Kirk-Othmer* 4th ed., vol. **22.**
519. C. A. York, N. A. Baldwin, *J. Sports Turf Res. Inst.* **68.**
520. C. A. York, N. A. Baldwin, *International Turfgrass Society Research Journal* **7** (1993).
521. Gefahrstoffverordnung vom 26.08.1986 (letzte Anpassung 06.98) ergänzt durch technische Regeln (TRGS511), Carl Heymann-Verlag, Köln.
522. M. Brübach: “Der Einfluß der Korngröße, der Granulatfestigkeit und der Reibung auf die Verteilung von Dünger- und Pflanzenschutzgranulaten,” Dissertation, Berlin 1973.
523. A. Buchner, H. Sturm: *Gezielter düngen*, DLG-Verlag, Frankfurt 1985.
524. K. Rühle, “Die Verteilgenauigkeit pneumatischer Mineraldüngerstreuer,” *KTBL-Schrift* no. 198, Darmstadt-Kranichstein 1975.
525. W. Werner, H. W. Olfs, K. Auerswald, K. Isermann: “Stickstoff- und Phosphoreintrag in Oberflächengewässer über diffuse Quellen,” in A. Hamm (ed.): *Studie über die Wirkungen und Qualitätsziele von Nährstoffen in Fließgewässern*, Academia Verl., St. Augustin 1991, pp. 665 – 764.
526. W. Werner, H. P. Wodsack: “Stickstoff und Phosphoreintrag in die Fließgewässer Deutschlands unter besonderer Berücksichtigung des Eintragsgeschehens im Lockergesteinsbereich der ehemaligen DDR,” *Agrarspektrum*, vol. **22**, DLG-Verl., Frankfurt 1994.
527. O. Strebel: “Untersuchungen zur Grundwasserbelastung bei land- und forstwirtschaftlicher Bodennutzung von Sandböden im Raum Hannover,” *Z. Kulturtech. Flurbereinig.* **18** (1977) 310 – 312.
528. P. Obermann: “Hydrochemische/hydromechanische Untersuchungen zum Stoffgehalt von Grundwasser bei landwirtschaftlicher Nutzung,” *Bot. Mitt. Dtsch. Gewässerkd.* **42** (1981) 1 – 217.
529. P. Obermann: “Die Belastung des Grundwassers aus landwirtschaftlicher Nutzung nach heutigem Kenntnisstand,” in H. Nieder (ed.): *Nitrat im Grundwasser. Herkunft, Wirkungen, Vermeidung,* Verlag Chemie, Weinheim 1985, pp. 53 – 64.
530. P. Obermann, G. Einars, H. Zakosek, G. Schollmayer: *Hydrogeologische/bodenkundliche Untersuchungen im Bereich des Schüttensteiner Waldes bei Bocholt/Westfalen, 1st interim report to the Bundesministerium für Ernährung, Landwirtschaft und Forsten (Ministry of Nutrition, Agriculture, and Forestry): Beitrag der Landwirtschaft zur Verminderung der Nitratbelastung des Grundwassers*, **parts B2 und E**, 1985.
531. P. Obermann, W. Leuchs, G. Einars, H. Zakosek, G. Schollmayer, S. Schulte-Kellinghaus, H. Zepp: *Hydrogeologische/bodenkundliche Untersuchungen im Bereich des Schüttensteiner Waldes bei Bocholt/Westfalen*, final report, 1986.
532. P. Obermann, W. Leuchs: *Chemische Genese eines pleistozären Porengrundwasserleiters bei Bocholt/Westfalen, final report*, 1987.
533. *LWA Nordrhein-Westfalen: Grundwasserbericht 85,* Landesamt für Wasser- und Abfallwirtschaft Nordrhein-Westfalen, Düsseldorf 1985.
534. U. Rohmann: “Landwirtschaftliche und aufbereitungstechnische Maßnahmen zur Lösung des Nitratproblems,” DVGW-Schriftenr. no. 46 (1985) 105 – 123.
535. K. Isermann: “Vertikale Verteilung von Nitrat- und Denitrifikationsparametern bis in 10 m Bodentiefe bei unterschiedlicher Landbewirtschaftung,” *Herbsttagung Limburgerhof 1986.*
     K. Isermann: “Vertical Distribution of NO_3-N and Denitrification Parameters in the Soil

Down to Greater Depths (about 10 m) under Various Soil Management/Nitrogen Fertilization," International Symposium of CIEC Agricultural Waste Management and Environmental Protection, 4th, Braunschweig 1987.

536. I. F. I. Gast, J. Taat, W. van Duijvenbooden: "Landelijk meetnet — grondwaterkwaliteit," Rijksinstituut voor volksgezondheit en milieuhygiene 2, DEEL Rapport no. 840 382002, April 1985.
537. LAWA – Länderarbeitsgemeinschaft Wasser: "Nitrat," *Bericht zur Grundwasserbeschaffenheit*, Umweltministerium Baden-Württemberg, Stuttgart 1995.
LAWA – Länderarbeitsgemeinschaft Wasser: Ergebnisse der Überwachung der Gewässer gemäß Artikel 5 Abs. 6 Satz 2 der Richtlinie 91/676/EWG. Anlage 3 der Mitteilung der Bundesrepublik Deutschland (BMU) vom 25. Oktober 1996 über die Umsetzung der Richtlinie 91/676/EWG.
538. EU Nitrate Directive 19/676.
539. Bocholter Energie und Wasserversorgung GmbH, personal communication, August 17, 1998.
540. U. Rohmann, H. Sontheimer: *Nitrat im Grundwasser. Ursachen, Bedeutung, Lösungswege*, DVGW Forschungsstelle am Engler-Bunte-Institut, Karlsruhe 1985.
541. Der Rat von Sachverständigen für Umweltfragen: *Umweltprobleme der Landwirtschaft, Sondergutachten März 1985*, Verlag W. Kohlhammer, Stuttgart-Mainz 1985.
542. D. Sauerbeck: *Funktionen, Güte und Belastbarkeit des Bodens aus agrikulturchemischer Sicht. Materialien zur Umweltforschung*, published under the auspices of the Rat von Sachverständigen für Umweltfragen, Verlag W. Kohlhammer, Stuttgart-Mainz, 1985.
543. J. Jung, J. Dressel: "Zum Stand des Nitratproblems," *Herbsttagung Limburgerhof 1981*, 1 – 7.
544. A. Vömel: "Stickstoffdüngung und Stickstoffverluste auf ackerbaulich genutzten Böden," *Landwirtsch.* no. 197 Sonderh. (1981) 205 – 222.
545. O. J. Furrer, 1986: "Einfluß von Fruchtfolge und Düngung auf den Nitrateintrag ins Grundwasser," vol 10 C, Pro Aqua-Pro Vita, Internationale Fachmesse und Fachtagungen für Umweltschutztechnik und ökologie, 10th, Basel 1986.
546. W. Burghardt, cited in H. Kuntze: "Möglichkeiten und Grenzen des Bodenschutzes durch den Landwirt — aus ackerbaulich-bodenkundlicher Sicht," *Bodenschutz — mit der Landwirtschaft*, Arbeiten der DLG **185** (1986) 33 – 35.
547. O. Strebel, J. Böttcher, W. H. M. Duynisfeld: "Einfluß von Standortbedingungen und Bodennutzung auf Nitratauswaschung und Nitratkonzentration des Grundwassers," *Landwirtsch. Forsch., Sonderh.* **37** (1984) 34 – 44.
548. O. Strebel, J. Böttcher: "Ermittlung von Ursachen und Prognosen der mittleren Nitratkonzentration im Grundwasser von Wassereinzugsgebieten," *Mitt. Dtsch. Bodenkd. Ges.* **53** (1987) 305 – 307.
549. F. Hess: "Acker- und pflanzenbauliche Strategien zum verlustfreien Stickstofftransfer beim Anbau im Organischen Landbau," *Mitt. Ges. Pflanzenbauwiss.* **3** (1990) 241 – 244.
550. I. Günther, Farm Economic Data Working Group, Assoc. of Sugar Beet Growers, personal communication, 1995.
551. M. Bach, H. G. Frede, G. Lang: "Entwicklung der Stickstoff-, Phosphor- und Kaliumbilanz der Landwirtschaft in der Bundesrepublik Deutschland," Studie der Gesellschaft f. Boden- und Gewässerschutz e.V., Wettenberg 1997.
552. H. Behrendt: "Detection of anthropogenic Trends in Time series of river rhine lead using Windows of Discharge and long-term Means," Report of the ICES/OSPAR-Workshop "Identification of statistical methods for temporal trends" Kopenhagen, 25 – 26. Sept. 1997, pp. 20 – 24.
553. Umweltbundesamt Berlin (UBA): Forschungsbericht 1994, Berlin, 1995.
554. H. G. Frede, S. Dabbert (eds.): *Handbuch zum Gewässerschutz*, Landwirtschaft. Verlagsges. ECOMED, Landberg. 1998
555. H. Carlson: "Quality Status of the North Sea," *Dtsch. Hydrogr. Z.* (1986) suppl. vol. B, no. 16.
556. E. Schwedhelm, G. Irion: "Schwermetalle und Nährelemente in den Sedimenten der deutschen Nordseewatten," CFS Cour. Forschungsinst. Senkkenberg no. 73 (1985).
557. K. G. Malle: "Wie schmutzig ist die Nordsee?" *Chem. Unserer Zeit* **21** (1987) no. 1, 9 – 16.
558. G. Müller, J. Dominik, R. Reuther, R. Malisch, E. Schulte, L. Acker: "Sedimentary Record of Environmental Pollution in the Western Baltic Sea," *Naturwissenschaften* **67** (1980) 595 – 600.

559. G. Müller: "Zur Chronologie des Schadstoffeintrages in Gewässer," *Geowiss. Unserer Zeit* **1** (1983) 2 – 11.
560. P. J. Crutzen: "Atmospheric Interactions — Homogeneous Gas Reactions of C, N, and S Containing Compounds," in B. Bolin, R. B. Cook (eds.): *The Major Biochemical Cycles and their Interactions,* J. Wiley & Sons, Chichester, England 1983, pp. 65 –114.
561. T. Granli, O. C. Bøckman: "Nitrous Oxide from Agriculture," *Norwegian J. Agric. Sci.* (1994) Suppl. 12.
562. R. F. Weiss: "The Temporal and Spatial Distribution of Tropospheric Nitrous Oxide," *J. Geophys. Res. C* **86** (1981) 7185 – 7195.
563. R. J. Stevens, R. J. Laughlin, L. C. Burns, J. R. M. Arah, R. C. Hood: "Measuring the Contributions of Nitrification and Denitrification to the Flux of Nitrous Oxide from Soil," *Soil. Biol. Biochem.* **29** (1996) 139 – 151.
564. E. A. Kaiser, O. Heinemeyer: "Temporal Changes in N_2O-Losses from two arable Soils," *Plant and Soil* **181** (1996) 57 – 63.
565. F. C. Thornton, R. J. Valente: "Soil Emissions of Nitric Oxide and Nitrous Oxide from no-till Corn," *Soil Sci. Soc. Am. J.* **60** (1996) 1127 – 1133.
566. E. A. Kaiser et al., "What predicts Nitrous Oxide Emission and Denitrification N-Loss from European Soils?" *Z. Pflanzenernähr. Bodenk.* **159** (1996) 541 – 547.
567. E. A. Davidson, P. A. Matson, P. D. Brooks: "Nitrous Oxide Emissions controls and inorganic Nitrogen Dynamics in fertilized tropical agricultural Soils," *Soil Sci. Soc. Am. J.* **60** (1996) 1145 – 1152.
568. K. A. Smith, I. P. McTaggart, H. Tsuruta, K. Smith: "Emissions of N_2O and NO associated with Nitrogen Fertilization in intensive Agriculture, and the Potential for Mitigation," *Soil Use Manage.* **13** (1997) 296 – 304.
569. M. J. Eichner: "Nitrous Oxide Emissions from fertilized Soils: Summary of available Data," *J. Environ. Qual.* **19** (1990) 272 – 280.
570. A. F. Bouwman (ed.): *Soils and the Greenhouse Effect*, Wiley and Sons, New York 1990.
571. C. Henault, X. Devis, J. L. Lucas, J. C. Germon: "Influence of different agriculture Practices (type of Crop, form of N-Fertilizer) on Soil Nitrous Oxide Emission," *Biol. Fertil. Soils* **27** (1998) 299 – 306.
572. K. Isermann: "Agriculture's share in the emission of trace gases affecting the climate and some source-oriented proposals for sufficiently reducing this share", *Environm. Pollution* **83** (1994) 95 – 111.
573. K. L. Weier, J. W. Doran, J. F. Power, D. T. Walters: "Denitrification and the Dinitrogen/Nitrous Oxide Ratio as affected by Soil Water, available Carbon, and Nitrate," *Soil Sci. Soc. Am. J.* **57** (1993) 66 – 72.
574. J. C. G. Ottow, G. Benckiser, M. Kapp, G. Schwarz: "Denitrifikation — die unbekannte Größe," *DLG-Mitteilungen* **105** (1990) 8 – 10.
575. H. Flessa, W. Pfau, P. Dörsch, F. Beese: "The influence of Nitrate and Ammonium Fertilization on N_2O Release and CH_4 Uptake of a well-drained Topsoil demonstrated by a Soil Microcosm Experiment," *Z. Pflanzenernähr. Bodenk.* **159** (1996) 499 – 503.
576. H. Clayton, I. P. McTaggart, J. Parker, L. Swan: "Nitrous Oxide Emission from fertilized Grassland: a 2-Year Study of the Effects of N Fertilizer Form and environmental Conditions," *Biol. Fertil. Soil* **25** (1997) 252 – 260.
577. V. Cole et al.: "Agricultural Options for Mitigation of Greenhouse Gas Emissions," in R. T. Watson, M. C. Zinyowera, R. H. Moss (eds.): *Climate Change 1995*, Chap. 23, Cambridge University Press, Cambridge 1996, pp. 745 – 771.
578. R. Lipschultz, O. C. Zafiriou, S. C. Wofsy, M. B. McElroy, F. W. Valois, S. W. Watson: "Production of NO and N_2O by Soil Nitrifying Bacteria," *Nature* **294** (1981) 641 – 643.
579. C. A. Stutte, R. T. Weiland: "Gaseous Nitrogen Loss and Transpiration of Several Crops and Weed Species," *Crop. Sci.* **18** (1978) 887 – 889.
580. C. A. Stutte, R. T. Weiland, A. R. Blem: "Gaseous Nitrogen Loss from Soybean Foliage," *Agron. J.* **71** (1979) 95 – 97.
581. J. V. Dean, J. E. Harper: "Nitric Oxide and Nitrous Oxide Production by Soybean and Winged Bean During the In Vivo Nitrate Reductase Assay," *Plant Physiol.* **82** (1986) 718 – 723.
582. I. E. Galbally: "Factors controlling NO_x emissions from soils", *Exchange of trace gases between terrestrial ecosystems and the atmosphere*, John Wiley and Sons, New York 1989 pp. 23 – 27.
583. T. Yoneyama, A. Hashimoto, T. Totsuka: "Absorption of Atmospheric NO_2 by Plants and Soils. 4. Two Routes of Nitrogen Uptake

by Plants from Atmospheric NO_2: Direct Incorporation into Aerial Plant Parts and Uptake by Roots after Absorption into the Soil," *Soil Sci. Plant Nutr. (Tokyo)* **26** (1980) no. 1, 1 – 7.

584. R. Lensi, A. Chalamet: "Absorption de l'oxyde nitreux par les parties aeriennes du mais," *Plant Soil* **59** (1981) 91 – 98.
585. J. C. Ryden: "N_2O Exchange between a Grassland Soil and the Atmosphere," *Nature* **292** (1981) 235 –237.
586. H. H. Rogers, V. P. Aneja: "Uptake of Atmospheric Ammonia by Selected Plant Species," *Environ. Exp. Bot.* **20** (1980) 251 – 257.
587. M. J. Koziol, R. R. Whatley: *Gaseous Air Pollutants and Plant Metabolism*, Butterworths, Borough Green, Kent, England, 1984.
588. F. G. M. Roelofs, A. J. Kempers, A. L. F. M. Houdijk, J. Jansen: "The Effect of Air Borne Ammonium Sulphate on Pinus Nigra var. maritima in the Netherlands," *Plant Soil* **84** (1985) 45 – 56.
589. J. G. M. Roelofs, A. W. Boxman, H. E. G. Van Dijk: "Effects of Airbone Ammonium on Natural Vegetation and Forests," *Proceedings of the EEC Symposium*, Grenoble 1987.
590. K. Isermann: "Bodenversauerung beim natürlichen Wald- und Grasland-ökosystem von Rothamsted (England) unter dem Einfluß atmosphärischer und pedogener Protonen-Anlieferung von 1880 bis heute," a paper presented at the Kongreß der Internationalen Bodenkundlichen Gesellschaft, 13th, Hamburg 1986 and published in *AFZ, Allg. Forstzeitschr.* **1987,** pp. 379 – 381.
591. K. Isermann: "Die Rolle des Stickstoffs bei den "neuartigen" Waldschäden," paper presented at the Symposium Waldschäden am Biologischen Institut II der Universität Freiburg, 3rd, 1986.
592. L. De Temmermann, A. Ronse, K. Van den Cruys, K. Meeus-Verdinne: "Ammonia and Pine Tree Dieback in Belgium," *Proceedings of the EEC Symposium*, Grenoble 1987.
593. W. M. J. Den Boer: "Ammonia, Not only a Nutrient but also a Cause of Forest Damages," Wiss. Symposium zum Thema Waldschäden, Neue Ursachenhypothesen, Text 19, Umweltbundesamt, Berlin 1986.
594. H. Ellenberg: "Veränderungen der Flora unter dem Einfluß von Düngung und Immissionen," *Schweiz. Z. Forstwes.* **136** (1985) 19 – 39.
595. G. Büttner, N. Lamersdorf, R. Schultz, B: Ulrich: *Deposition und Verteilung chemischer Elemente in küstennahen Waldstandorten — Fallstudie Wingst; Abschlußbericht, report of the Forschungszentrum Waldökosysteme/Waldsterben, series B, vol. 1*, 1986.
596. K. Kreutzer, J. Bittersohl: "Stoffauswaschung aus Fichtenkronen (Picea abies (L.) Karst.) durch saure Beregnung," *Forstwiss. Centralbl.* **105** (1986) no. 4, 357 – 363.
597. M. Hauhs: "Die regionale Bedeutung des Nitrataustrages unter Wald für die Gewässerversauerung," DFG-Workshop Modellierung des bodeninternen Stickstoffumsatzes, Hohenheim 1987.
598. G. L. Hutchinson, F. G. Viets: "Nitrogen Enrichment of Surface Water by Adsorption of Ammonia Volatilized from Cattle Feedlots," *Science (Washington, D.C.)* **166** (1969) 514 – 515.
599. J. Gehrmann: "Derzeitiger Stand der Belastung von Waldökosystemen in Nordrhein-Westfalen durch Deposition von Luftverunreinigungen," *Forst-Holzwirt.* **42** (1987) no. 6, 141 – 145.
600. S. Mehlert: "Untersuchungen zur atmogenen Stickstoffdeposition und zur Nitratverlagerung", UFZ-Bericht 22, UFZ-Umweltforschungszentrum Leipzig-Halle GmbH, 1996.
601. L. Grünhage, H. J. Jäger, K. Freitag, K. Hanewald: "Emissionskataster Hessen — Landesweite Abschätzung der Emissionen aus biogenen und nicht gefaßten Quellen," Umweltplanung, Arbeits- und Umweltschutz, no. 184, Hessische Landesanstalt für Umwelt, Wiesbaden 1996.
602. ECETOC (ed.): "Ammonia Emissions to Air in Western Europe" Tech. Rep. No. 62, European Centre for Ecotoxicology and Toxicology of Chemicals, Brussels 1996.
603. "Gasförmige Stickstoffverbindungen aus der Landwirtschaft", Bericht für die DFG-Senatskommission zur Beurteilung von Stoffen in der Landwirtschaft, Schlußentwurf, Bonn April 1996.
604. P. A. Steudler, R. D. Bowden, J. M. Melillo, J. D. Aber: "Influence of nitrogen fertilization on methane uptake in temperate forest soils", *Nature* **341** (1989) 314 – 316.
605. S. Hansen, J. E. Maehlum, L. R. Bakken: "N_2O and CH_4 fluxes influenced by fertilization and tractor traffic", *Soil Biol. Biochem.* **259** (1993) 621 – 630.

606. B. W. Hütsch, C. P. Webster, D. S. Powlson: "Long-term effects of nitrogen fertilization on methane oxidation in soil of the Broadbalk Wheat Experiment", *Soil Biol. Biochem.* **25** (1993) 1307 – 1315.
607. K. F. Bronson, A. R. Mosier: "Suppression of methane oxidation in aerobic soil nitrogen inhibitors and urease inhibitors", *Biol. Fertil. Soils* **17** (1994) 68 – 84.
608. C. Bédard, R. Knowles: "Physiology, biochemistry and specific inhibitors of CH_4, NH_4^+ and CO oxidation by methanotrophs and nitrifier," *Microbiol. Rev.* **53** (1989) 68 – 94.
609. K. Mengel, E. A. Kirkby: *Principles of Plant Nutrition*, International Potash Institute, Worblaufen-Bern 1982.
610. G. Pfützer, C. Pfaff: "Einfluß der Düngung und Belichtung auf die Vitaminbildung in der Pflanze," *Umschau (1897)* **39** (1935) 917.
611. C. Pfaff, G. Pfützer: "über den Einfluß der Ernährung auf den Carotin- und Ascorbinsäuregehalt verschiedener Futterpflanzen,“ *Z. Angew. Chem.* **50** (1937) 179.
612. G. A. Rodgers, A. Penny, F. V. Widdowson, M. V. Hewitt: "Tests of Nitrification and of Urease Inhibitors, when Applied with Either Solid or Aqueous Urea, on Grass Grown on a Light Sandy Soil," *J. Agric. Sci.* **108** (1987) 109 – 117.
613. R. Prakasa, K. Puttanna: "Nitrification and Ammonia Volatilisation Losses from Urea and Dicyandiamide-treated Urea in a Sandy Loam Soil," *Plant Soil* **97** (1987) 201 – 206.
614. H. Bernhard: *Phosphor: Wege und Verbleib in der Bundesrepublik Deutschland. Probleme des Umweltschutzes und der Rohstoffversorgung*, Verlag Chemie, Weinheim-New York 1978.
615. A. Hamm: "Wie und woher kommen die Nährstoffe in die Flüsse?" in J. L. Lozan, H. Kausch (eds.): *Warnsignale aus Flüssen und Ästuaren, Wissenschaftliche Fakten*, Verl. Paul Parey, Berlin – Hamburg 1996 pp. 105 – 110.
616. A. Breeuwsma, J. G. A. Reijerink, O. F. Schoumans: Fosfaatverzadigde gronden in het oostelijk, central en zuidelijk zandgebied, Report 68, Staring Centrum, Wageningen 1990.
617. U. Pihl, W. Werner: "Erhebungsuntersuchungen zu Phosphatgehalten, Phosphatsorptionskapazität und relativer Phosphatsättigung der Böden in veredlungsstarken Gebieten Nordrhein-Westfalens als Prognosekriterien des potentiellen Phosphataustrags in Drain- und Grundwasser," Forschungsber. 64, Lehr- und Forschungsschwerpunkt "Umweltverträgliche und standortgerechte Landwirtschaft", Landwirtschaftliche Fakultät, Universität Bonn, Bonn 1998.
618. Th. Diez, K. Bucksteeg: "P-fluxes in a Watershead Area with Intensive Agriculture and Eutrophication of a Lake," paper presented at the Int. Symposium of CIEC Agricultural Waste Management and Environmental Protection, 4th, Braunschweig-Voelkenrode 1987.
619. W. Werner: "Implementation and efficiency of countermeasures against diffuse nitrogen and phosphorus inputs into surface waters from agriculture", in E. Romstad, J. Simonsen, A. Vatn (eds.): *Controlling mineral emissions in European agriculture*, CAB International, Oxon – New York 1997 , pp. 73 – 88.
620. Industrieverband Agrar e.V., personal communication, 1997.
621. K. Isermann: "Einfluß der Phosphatdüngung auf den Cadmiumgehalt des Bodens, ermittelt anhand zahlreicher Dauerversuche in Westeuropa," *Landwirtsch. Forsch. Sonderh.* **39** (1982) 283 – 301.
622. B. Machelett, W. Podlesak, J. Garz: "Zur Wirkung des Cadmiumgehalts im Düngerphosphat auf die Cadmiumkonzentration in Boden und Pflanze in einem langjährigen Phosphatdüngungsversuch," *Arch. Acker-Pflanzenbau Bodenkd.* **28** (1984) no. 4, 247 – 251.
623. J. J. Mortvedt: "Cadmium Levels in Soils and Plant Tissues from Long Term Soil Fertility Experiments in the United States," *Congr. Int. Soc. Soil Science, 13th*, vol. **3**, Hamburg 1986.
624. W. Werner, C. Brenk: "Entwicklung eines integrierten Nährstoffkonzeptes als Basis eines umweltverträglichen, flächendeckenden Recyclings kommunaler Abfälle in Nordrhein-Westfalen und regionalisierte Bilanzierung der Schwermetallflüsse", Forschungsber. 48, Landwirtschaftliche Fakultät Universität Bonn, Bonn 1997.

General References

625. *FAO Fertilizer Yearbook* , Food and Agricultural Organization of the United Nations, Rome.
626. *FAO Production Yearbook* , Food and Agricultural Organization of the United Nations, Rome.

Specific References

627. Q. Paris: “The von Liebig-Hypothesis,” *Am. J. Agric. Econ*, **74** (1992) 4, 1019 – 1028.
628. E. von Boguslawski: *Ackerbau, Grundlagen der Pflanzenproduktion*, Frankfurt/M. 1981.
629. K. Baeumer: “Düngung”, in R. Diercks, R. Heitefuss (eds.): *Integrierter Landbau*, 2nd ed., München 1994 pp. 88 – 110.
630. E. O. Heady, J. L. Dillon: *Agricultural Production Functions*, Ames, Iowa 1961.
631. F. Kuhlmann: *Betriebslehre der Agrar- und Ernährungswirtschaft*, 2nd ed., Frankfurt/M. 2003.
632. *World Fertilizer Consumption Statistics April 1998* IFA International Fertilizer Industry Association,
1998.
FAOSTAT Database results Internet http://www.FAO.org
633. FAO: *The Sixth World Food Survey*, Food and Agricultural Organisation of the United Nations, Rome 1996.
634. P. Prinstrup-Anderson et al.: *The World Food Situation: Recent Developments*, Emerging Issues and Long Term Prospects, IFPRI, Washington 1997.
635. FAO: *Dimension of Need, An Atlas of Food and Agriculture*, Food and Agricultural Organisation of the United Nations, Rome 1995.
636. G. Harris: *“An Analysis of Global Fertilizer Application Rates for Major Crops*,” International Fertilizer Development Centre (IFDC), Muscle Shoals 1998.
637. FAO: *Fertilizer Yearbook*, vol. **46**, Food and Agricultural Organisation of the United Nations, Rome 1996.
638. IFA: *“Fertilizer Demand Forecast*,” International Fertilizer Industry Association, Paris 1998.
639. FAO: *Fertilizer Outlook*, Food and Agricultural Organisation of the United Nations, Rome 1996
640. J. Debruck, G. Fischbeck, W. Kampe: *Getreidebau aktuell*, 7th ed., Frankfurt/M. 1983.
641. F. Kuhlmann: “Zum 50. Todestag von Friedrich Aereboe: Einige Gedanken zu seiner Intensitätslehre,” *Agrarwirtschaft* **41** (1992) 222 – 230.
642. F. Kuhlmann, K. F. Frick: “Produktionstheoretische Betrachtungen über das “Gesetz des Minimums”, und das “Gesetz vom abnehmenden Ertragszuwachs”,” *Berichte über Landwirtschaft* **73** (1995) 591 – 623.
643. K. F. Frick: “Analyse und Entwicklung von Standardproduktionsfunktionstypen in der pflanzlichen Produktion,” *Sonderheft der Agrarwirtschaft*, vol. **153**, Holm 1997.