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SYMPOSIUM ON PROSPECTS OF THE USE OF FERTILIZERS WITH A VIEW TO RAISING
SOIL FERTILITY AND YIELDS AND OF PROTECTING THE HUMAN ENVIRONMENT

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TRENDS IN FERTILIZER FORMULATION AND USE

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INTRODUCTION

Recent developments in fertilizer production and use have been amply discussed in various international meetings in the past decade (Araten (1968), Dinauer (1968), Saalbach (1970), Smilde (1972), Sutton (1972)), and no attempt is made here to review these data.

The present paper is focussing on some more general aspects of fertilizer formulation and use, such as nutrient concentration, efficiency in handling and application, noxious side-effects etc.

1. GENERAL ASPECTS OF FERTILIZERS

In choosing between fertilizers, the modern farmer should consider the following characteristics:

1. Nutrient concentration, i.e. the price per unit of nutrient.
2. Efficiency in meeting the crops' nutrient requirements under various soil and climatic conditions, keeping losses by leaching, volatilization, runoff and fixation at a minimum.
3. Ease of storage, handling and distribution.
4. Presence of accompanying constituents, e.g. chloride, sulphur, sodium and possible acidifying effects.

Concentration

Costs of marketing, shipping, storage and distribution may constitute up to 80 per cent of the fertilizer price if low-analysis materials are used (Araten, 1968). Therefore, there is a marked tendency towards the production of high-analysis materials, with the United States as the leading country (long transport lines). This holds true for both straight (simple) and compound (mixed) fertilizers, the

total nutrient concentration of the latter having doubled in the past 25 years. In most developed countries the use of compound fertilizers has greatly increased, to cut labour costs.

Efficiency

Fertilizer efficiency is affected by the time and method of application. Autumn and winter application of water-soluble materials under conditions conducive to leaching and volatilization of the nitrogen component, or immobilization of the phosphorus component should be avoided. By contrast, water-insoluble materials, like some phosphates and lime, may be applied in autumn and winter, especially if granulated.

In cereal growing, there is considerable advantage in splitting high nitrogen rates into a seedbed application and a later top-dressing. For instance, the following rates, based on the stock of mineral nitrogen in the soil by the end of February, are recommended in The Netherlands (Table 1). On the other hand,

Table 1
Nitrogen Fertilizer Rates (kg N.ha⁻¹), as Based on the Stock
of Mineral Nitrogen in the Soil by the End of February

Crop	Seedbed application	Top-dressing		
		N-stock in soil (kg.ha ⁻¹)		
		<170	170-200	>200
Winter wheat	140 - soil N	60	30	0
Spring wheat, oats, winter barley	120 - soil N	50	30	0
Spring barley	120 - soil N	0	0	0

cereals may dispense with phosphate and potash, provided a compensation is given to more responsive crops in the rotation, usually potatoes.

For row crops like potatoes, maize, and beans, placing the fertilizer in a band, preferably 5 cm to the side and 2.5 cm under the

seed, has definite advantages over broadcasting, especially so when soil fertility is low and fertilizers are expensive. However, the striking effects obtained for potatoes in the U.K. (Cooke, 1972) are not confirmed by Dutch experimental results. Placing substantial amounts of nitrogen and potassium (compound) fertilizer should be discouraged altogether because of possible damage to young seedlings.

Broadcast fertilizer should normally be ploughed down to a depth where the soil is likely to remain moist, i.e. just under the seedbed. Top-dressing is often at a disadvantage, even for mobile nutrients like nitrogen when subject to volatilization, and is not commonly practised for arable crops other than cereals.

Top-dressing is, of course, common practice on grassland. For early production, nitrogen should be applied as soon as grass starts growing, i.e. in Western Europe when accumulated daily temperatures after 1 January reach a value of about 200⁰C (Jagtenberg, 1970). Further nitrogen dressings are to be adjusted to grass use and growth rate, the larger amounts being applied in early summer and following cutting, the lesser ones in late summer and after grazing (Van Burg, 1968). On intensive grassland holdings importing concentrated feeds and recycling plant nutrients via the animal faeces, there is virtually no need for phosphate and potash fertilizer.

Granulation

Granulation of fertilizers is widely practised now, greatly improving the ease of handling and storage of hygroscopic and/or dusty products, but decreasing the initial effectiveness of water-insoluble materials. In general, coarser granules are advantageous for water-soluble and finer granules for water-insoluble materials.

Acidifying effects

All anions neither adsorbed on exchange sites nor taken up by the plant are subject to leaching from the root zone, taking along cations, whenever rainfall exceeds evapotranspiration. The resulting decrease in lime content of the soil and hence in pH, is mitigated by supplying cations (calcium, magnesium, potassium, sodium). The negative effect of the anions is reduced by processes like volatilization (nitrogenous

materials) and immobilization (phosphates). In general, nitrates and phosphates not accompanied by ammonium, and potassium salts do not acidify the soil. Ammonium (NH_4^+), although adsorbed by cation exchange sites, is readily converted to nitrate under soil conditions of pH, moisture, temperature normal for crop growth. Consequently, it acidifies the soil, particularly so when accompanied by mobile anions like nitrate, sulphate and chloride.

The present trend of substituting high-analysis for low-grade fertilizers entails a relative shortage of bases, eventually leading to soil acidification if used exclusively. The following formula (Sluijsmans, 1966) may be used to calculate the amount of lime (in kg CaO) needed to neutralize the effect of 100 kg of a compound or straight fertilizer:

$$\text{lime requirement} = - 1.0 \times \% \text{CaO} - 1.4 \times \% \text{MgO} - 0.6 \times \% \text{K}_2\text{O} - 0.9 \times \\ \text{Na}_2\text{O} + 0.4 \times \% \text{P}_2\text{O}_5 + 0.7 \times \% \text{SO}_3 + 0.8 \times \% \text{Cl} + \\ 1.0 \times \% \text{N}.$$

The formula is based on the fact that 100 kg of N, P_2O_5 , SO_3 and Cl, respectively, combine with 200, 40, 70 and 80 kg of CaO. The coefficients for MgO, K_2O and Na_2O reflect the CaO equivalences. It is assumed that the acidifying effect of nitrogen is reduced to 50% as a result of crop uptake.

2. NITROGEN FERTILIZERS

Nitrates

Nitrates are easily lost from the soil by leaching and denitrification. Denitrification is a microbiological process in which, under anaerobic conditions, nitrates (NO_3) are converted to nitrous oxide (NO_2) and gaseous nitrogen (N_2). As a consequence, nitrate fertilizers are unsuitable for temporarily or permanently water-logged soils (rice). They are at an advantage when used as a top-dressing, particularly on calcareous soils, and also in semi-arid areas where conditions favouring denitrification seldom occur and leaching losses are small. Large dressings worked into the soil just before sowing may damage germinating seedlings as a result of high salt concentrations in a dry top-soil.

Nitrate fertilizers, mainly Chilean nitrate (NaNO_3 ; 16% N and 26% Na) and potassium nitrate (KNO_3 ; 14% N and 44% K_2O), are not widely used, being rather expensive in most countries.

Ammonium forms

Ammonium salts are subject to volatilization losses as the ammonia (NH_3) component escapes, mainly occurring when surface-applied on calcareous soils. Ammonium (NH_4^+) becomes susceptible to leaching, following nitrification by soil bacteria, thus acidifying the soil. Where soil temperatures in winter are not consistently below the threshold for nitrification to occur, application of ammonium-containing fertilizers should be delayed until spring. Nitrification inhibiting chemicals have not fully overcome this problem so far.

Ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$; 21% N) has been the most common nitrogen fertilizer for decades. It is now rapidly being replaced by the more concentrated ammonium nitrate (NH_4NO_3 ; 35% N), which is either incorporated in compound fertilizers or used as a (prilled) straight fertilizer. When mixed with limestone, ammonium nitrate is safer to handle and its acidifying effect is partly or completely offset. Ammonium nitrate limestone is the leading nitrogen fertilizer in most developed countries.

Urea

Urea ($\text{CO}(\text{NH}_2)_2$; 46% N), because of its high nitrogen concentration, is becoming increasingly important as a relatively cheap source of nitrogen, not in the least for developing countries. Urea is readily hydrolysed to ammonium carbonate by the enzyme urease, ammonium carbonate easily decomposing to ammonia and carbon dioxide. When worked well into the soil, urea is as effective as other nitrogenous fertilizers. Substantial losses may occur, however, when surface-applied as a top-dressing, particularly in dry weather and on calcareous soils. On grassland, urea effectiveness is variable, depending on temperature and rainfall conditions. Work on urease inhibitors has shown some promising results (Matzel c.s., 1978). Urea placed close to germinating seeds may damage the seedlings as the toxic ammonia is being released.

Urea is the most common material for foliar application of small quantities of nitrogen (top-dressing), but plant tolerance (scorching) is rather low.

Liquids

The following liquids can be distinguished: high-pressure anhydrous ammonia (82% N); low pressure aqueous ammonia (21-29% N), with or without ammonium nitrate and /or urea; non-pressure ammonium nitrate/urea solutions (30-40% N).

Liquids with pressure must be injected into the soil to prevent ammonia losses and, therefore, require heavy and expensive machinery for application and transport. High application costs and other disadvantages such as soil compaction on arable land and sward damage on grassland, may offset the low price of these materials. Trends in the USA have had little impact so far on sales in Western Europe (with the exception of Denmark), accounting for only some 5 per cent of the total nitrogen fertilizer consumption.

Non-pressure solutions, to which fungicides and herbicides may be added, are easy to handle, by pumping, and to distribute evenly in the field. Application presents no special problems, but the spraying equipment is subject to corrosion.

Nitrogenous solutions, if properly incorporated into the soil, perform similar to corresponding solids. If placed close to germinating seeds, they may induce ammonia toxicity in sprouts or young seedlings.

Slow-release materials

With the present fertilizers it is difficult to meet the plant's nitrogen requirements over a long period by one single dressing. High salt concentrations in the soil, resulting from heavy dressings, easily damage crops at the seedling stage. On the other hand, leaching and denitrification may induce deficiencies. To meet these shortcomings, slowly dissolving or decomposing nitrogenous fertilizers have been manufactured as substitutes for the conventional water-soluble materials.

Various processes may be adopted to attain slow-release characteristics: chemical, by condensing urea with various aldehydes (ureaform, crotonylidene diurea, isobutylidene diurea), or developing inorganic materials of low solubility (magnesium ammonium phosphate); physical, by coating fertilizer granules (sulphur-coated urea).

In general, the nitrogen release pattern of the urea condensation products is difficult to predict, being dependent on soil temperature

moisture and pH. Sulphur-coated urea performance in ornamentals and on turf and commercial swards justifies further experimentation in arable crops. At present, however, the non-competitive price of this product precludes a more universal use, the more so as the efficiency of conventional fertilizers may still be improved by choosing proper application times and rates.

3. PHOSPHATE FERTILIZERS

Water-soluble forms

Water solubility is a main characteristic of phosphate fertilizers, affecting both time and method of application. Water-soluble phosphates should be applied shortly before sowing to ensure a quick start of the crop. A small amount of "starter" fertilizer is even profitable on soils with a sufficiently high phosphate status, to overcome relative shortages occurring at low soil temperatures in spring. Crops with shallow root systems, like potatoes, are highly responsive to water-soluble phosphate. It is also at an advantage when drilled in bands near the seed in order to reduce contact and reaction with phosphate bonding sites (adsorption, precipitation) in the soil.

Water-soluble phosphates are essentially monocalcium and ammonium phosphates. Superphosphate ($\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{CaSO}_4$; 18-22% P_2O_5) is a low-analysis phosphate fertilizer and an important source of sulphur as a plant nutrient, as opposed to concentrated (triple) superphosphate ($\text{Ca}(\text{H}_2\text{PO}_4)_2$; 46-47% P_2O_5). Ammoniation of phosphoric acid produces monoammonium phosphate (MAP: $\text{NH}_4\text{H}_2\text{PO}_4$; 11-12.5% N, 48-51% P_2O_5) and diammonium phosphate (DAP: $(\text{NH}_4)_2\text{HPO}_4$; 16-18% N, 46-48% P_2O_5). In Western Europe MAP and DAP mainly serve as ingredients for solid compound fertilizers, but in the USA, and in some developing countries as well, these materials are widely used straight. Ammonium phosphates placed too near germinating seeds may be harmful as a result of ammonia toxicity.

The latest product, ammonium polyphosphate (APP; 15% N, 62% P_2O_5), made by ammoniation of "superphosphoric" acid, contains ammonium orthophosphates (H_3PO_4), pyrophosphates ($\text{H}_4\text{P}_2\text{O}_7$) and smaller amounts

of higher condensed phosphates ($H_5P_3O_{10}$). It is an important constituent of liquid compound fertilizers and an effective carrier of micro-nutrient metals (by chelation).

Citric acid- and ammonium citrate-soluble forms

Citric acid-soluble phosphates of low water-solubility should be broadcast, and mixed properly with the soil well before sowing to obtain maximum effectiveness. They are best used in long-season crops, when immediate action of phosphate is less important, and on (slightly) acid soils.

Dicalcium phosphate ($CaHPO_4 \cdot 2H_2O$; 40% P_2O_5) as a fine, evenly distributed powder, to maximize contact with the soil, may perform like water-soluble phosphates. When granulated, used straight or as a constituent of compound fertilizers, the rate of phosphate release may be too slow to satisfy crops that need a quick start.

Basic or Thomas slag (10-22% P_2O_5) is a by-product of the steel industry. For the material to be most effective it should be finely ground and contain at least 80% of its phosphate in a citric acid-soluble form (Cooke, 1972). Recently, small granules of basic slag, with or without added potassium salts, have been manufactured, greatly improving the ease of spreading. The small granules are reported to easily decompose in moist soils. Apart from supplying phosphate, basic slag is an effective liming material (35% CaO). The availability to plants of the main other constituents, magnesium, and manganese, is rather limited.

The most promising water-insoluble phosphate fertilizer has been found to be Rhenania-phosphate ($CaNaPO_4 \cdot Ca_2SiO_4$; 28-30% ammonium citrate-soluble P_2O_5), obtained by sintering rock phosphate with sodium carbonate and silica. Apart from phosphate it contains 40% CaO, 17% Na_2O and 9% SiO_2 . Rhenania-phosphate combines the quick action of water-soluble phosphates with a prolonged resistance to immobilization and may, therefore, be used on a wide range of soils (Fig. 1, after Schmitt (1969)). On P-fixing latosols, Rhenania-phosphate proved clearly superior to superphosphate (Werner, 1975). The silica contained in Rhenania-phosphate probably plays an important part in competing with phosphorus for bonding sites.

Raw forms

Rock phosphates, i.e. the untreated raw phosphate minerals, are totally insoluble in water, and there is no proper chemical test to assess their agricultural value. The degree of dissolution in 2% formic acid may be used as a rough distinction between "soft" and "hard" types. Only when finely ground, and under moist acid (pH <5.5) soil conditions conducive to rapid weathering, rock phosphates prove effective fertilizers. In the humid tropics they are widely used for perennial crops, e.g. Christmas Island Rock Phosphate in oil palm, rubber etc. On strongly P-fixing tropical soils rock phosphates, as slow-acting fertilizers, have certain advantages over water-soluble phosphates that are rapidly immobilized.

4. POTASH FERTILIZERS

Almost all potash fertilizers are water-soluble and equally effective in supplying potassium. Their overall effect, however, depends on the accompanying ions, i.e. magnesium, sodium, and chloride.

Chlorides

Potassium chloride (muriate of potash), the most common fertilizer, consists of a mixture of sodium and potassium chloride. The lower grade mixtures (KCl - 20% K₂O and KCl - 40% K₂O), containing substantial amounts of sodium and chloride relative to potassium (Table 2), are only suitable for crops benefiting from sodium and tolerant of chloride (sugar beets). They are not recommended for crops like potatoes and tobacco, chloride adversely affecting tuber (starch content) and leaf (burning) quality, respectively.

Table 2

Grades of Potassium Chloride, Contents as Percentages.

	KCl	NaCl	K ₂ O	Na ₂ O	Cl
KCl-20	31.5	56.8	20.9	30.1	50
KCl-40	64.4	32.7	40.0	17.3	50
KCl-60	96.0	3.5	60.2	1.9	48

High analysis potassium chloride (KCl -60% K_2O) is the more universal potash fertilizer nowadays. Although it contains less chloride per unit of potash than the lower grade materials, there is some advantage in applying it in autumn or winter to enable the chloride to be leached from the rooting zone. Losses of potassium, though only occurring on very sandy soils, have to be compensated for.

Non-chlorides

Some farmers prefer non-chloride potash fertilizers, like potassium sulphate (K_2SO_4 ; 50% K_2O) or potassium magnesium sulphate ($K_2SO_4 \cdot MgSO_4$; 25-36% K_2O , 8-14% MgO), to potassium chloride. Potassium nitrate (p.5) is only used in horticulture. For arable crops, with the notable exception of tobacco, it may be argued whether the preference for non-chloride fertilizers is justified. As to the magnesium component, cheaper sources than potassium magnesium sulphate, e.g. ammonium nitrate magnesium limestone (23% MgO) and kieserite ($MgSO_4 \cdot H_2O$; 27% MgO), are usually available. An alternative is Epsom Salt ($MgSO_4 \cdot 7 H_2O$; 16% MgO), used in acute cases as a foliar spray.

Potassium metaphosphate (KPO_3 ; 58% P_2O_5 , 37% K_2O), as a new non-chloride, slow-acting potassium fertilizer, is worth mentioning. It is almost insoluble in water, slowly releasing its nutrients upon hydrolysis, which protects potassium from leaching and also prevents damage to germinating seeds. It is mainly used in ornamental (container-grown) crops.

5. COMPOUND FERTILIZERS

Solids

Compound fertilizers contain two or all three major plant nutrients nitrogen, phosphorus and potassium. Some are obtained by simply mixing straight fertilizers mechanically, according to the farmer's orders. Outside the USA this "bulk blending" is not widely practised, however. Farm mixing should be discouraged because of nutrient losses and risks involved in injudicious handling. More general, compound fertilizers are chemically manufactured, each granule having the same chemical composition.

In making compound fertilizers, there is a marked trend of substituting high-analysis materials (ammonium nitrate, urea, mono- and diammonium phosphates, high-grade potassium salts) for low-grade products (ammonium nitrate limestone, normal superphosphate, crude potash salts). It is emphasized again (p.4) that frequent use of compound fertilizers low in bases like calcium and magnesium leads to soil acidification.

In the author's opinion the water-soluble nitrogen contained in compound fertilizers is only compatible with water-soluble phosphate. This is because all (water-soluble) nitrogenous fertilizers are to be given shortly before sowing, and water-insoluble phosphate incorporated in them would act too slowly. Along similar lines it can be reasoned that chloride-susceptible crops respond best to low-chloride compound fertilizers.

Liquids

Liquid mixed fertilizers are not widely used as yet, except in the USA where consumption comprises about 12% of the total fertilizer tonnage. They are mainly made from ammonium polyphosphate, urea/ammonium nitrate and potassium chloride solutions. The advantages of liquid fertilizers have already been outlined on p.6. On the other hand, liquid mixtures are more expensive and less concentrated than corresponding solids (30% versus 50%). Moreover, they are corrosive and need special equipment for distribution and storage. Recently, "suspension" fertilizers have been introduced consisting of saturated solutions stabilized by the addition of clay. They are more concentrated than liquid mixtures but less easy to handle.

6. LIMING MATERIALS

Common liming materials are: ground limestone or chalk (CaCO_3 ; 50% CaO) and ground magnesium (dolomitic) limestone, a mixture of calcium and magnesium carbonate, containing 5 to 20 per cent MgO. On sandy soils, that need regular liming, dolomitic limestone is the most appropriate material to prevent magnesium deficiency. Limestone is more convenient in handling than burnt or quick lime (CaO-85%) and hydrated or slaked lime

(Ca(OH)₂; 70% CaO). It should be finely ground to ensure quick action, for instance for acid-sensitive crops given corrective dressings. For maintenance dressings, when quick action is not necessary, granulated products may be used. They are easier to spread than powdery materials and do not drift in wind.

7. MICRONUTRIENT FERTILIZERS

It is often claimed that exclusive use of high-analysis fertilizers entails potential deficiencies of micronutrients, sulphur and sodium. In the author's opinion there is insufficient evidence to sustain this view, at least for the densely populated, industrialized areas in Western Europe where industrial emission (sulphur) and increasing use of animal and domestic wastes preclude large-scale deficiencies. The benefit of maintenance dressings of micronutrients, often advertised as a special advantage of multinutrient compound fertilizers, may be questioned, also with a view to pollution of the environment. Of course, micronutrient deficiencies, if found to occur, should be controlled, but only by application of the nutrient in question.

Application of micronutrients alone, either by foliar spray or soil dressing, is time-consuming if other fertilizers are to be given separately. Moreover, even distribution of soil-applied materials is often a problem as the amounts used are small. For these reasons incorporation in nitrogen (-containing) fertilizers presents definite advantages. Possible carriers are: ammonium nitrate (copper), ammonium polyphosphate (zinc and iron), monoammonium phosphate (manganese) and various nitrogenous solutions. In Western Europe experience with these materials is scarce, and conventional (straight) micronutrient fertilizers are still widely being used.

SUMMARY AND CONCLUSIONS

Trends in fertilizer formulation and use were discussed.

The marked tendency of substituting high-analysis for low-analysis materials in manufacturing fertilizers is likely to continue. It is

also expected that the use of compound fertilizers will further expand at the expense of straight fertilizers and that liquid fertilizers will gain in popularity.

Further research on fertilizers resistant to leaching, volatilization and immobilization is needed.

The efficiency of conventional fertilizers may still be improved by choosing the right time and method of application and selecting the proper fertilizer to suit soil type, crop and climatic conditions.

Exclusive use of high-analysis (compound) fertilizers entails lime losses that should be compensated for but tend to be neglected.

Indiscriminate use of multinutrient (micronutrients-containing) compound fertilizers seems wasteful, and hazardous from the viewpoint of environmental protection.

Recent developments in micronutrient carriers in the USA warrant more extensive application of such materials in Western Europe.

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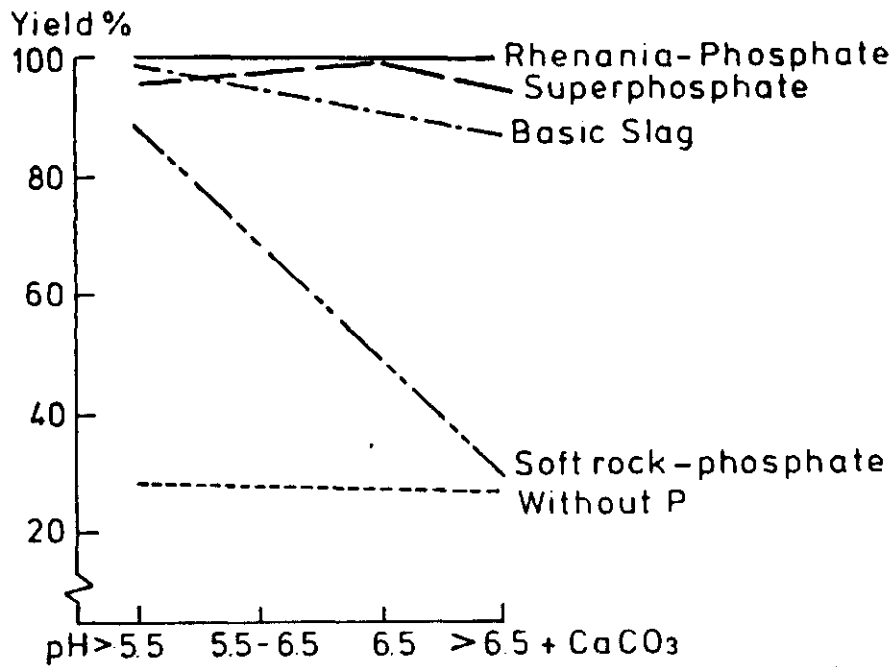


Figure 1. Effectiveness of Various Phosphate Fertilizers as Affected by Soil pH (after Schmitt, 1969)