

# Mineral Fertilizers

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Soil is a strategic resource and a vital part of the environment, being the main source of agricultural products. The human race receives about 95% of food products in the form of crops from cultivated land. The main task of land users is to preserve and increase soil fertility and then increase the productivity of agrocenoses and protect agroecosystems from pollution. The optimal physiological development of plants is ensured by adequate nutrition, primarily mineral nutrition. In the majority of soils, mineral salts are present in sufficient quantities. If not, their need for minerals can be fulfilled with mineral fertilizers.

productivity

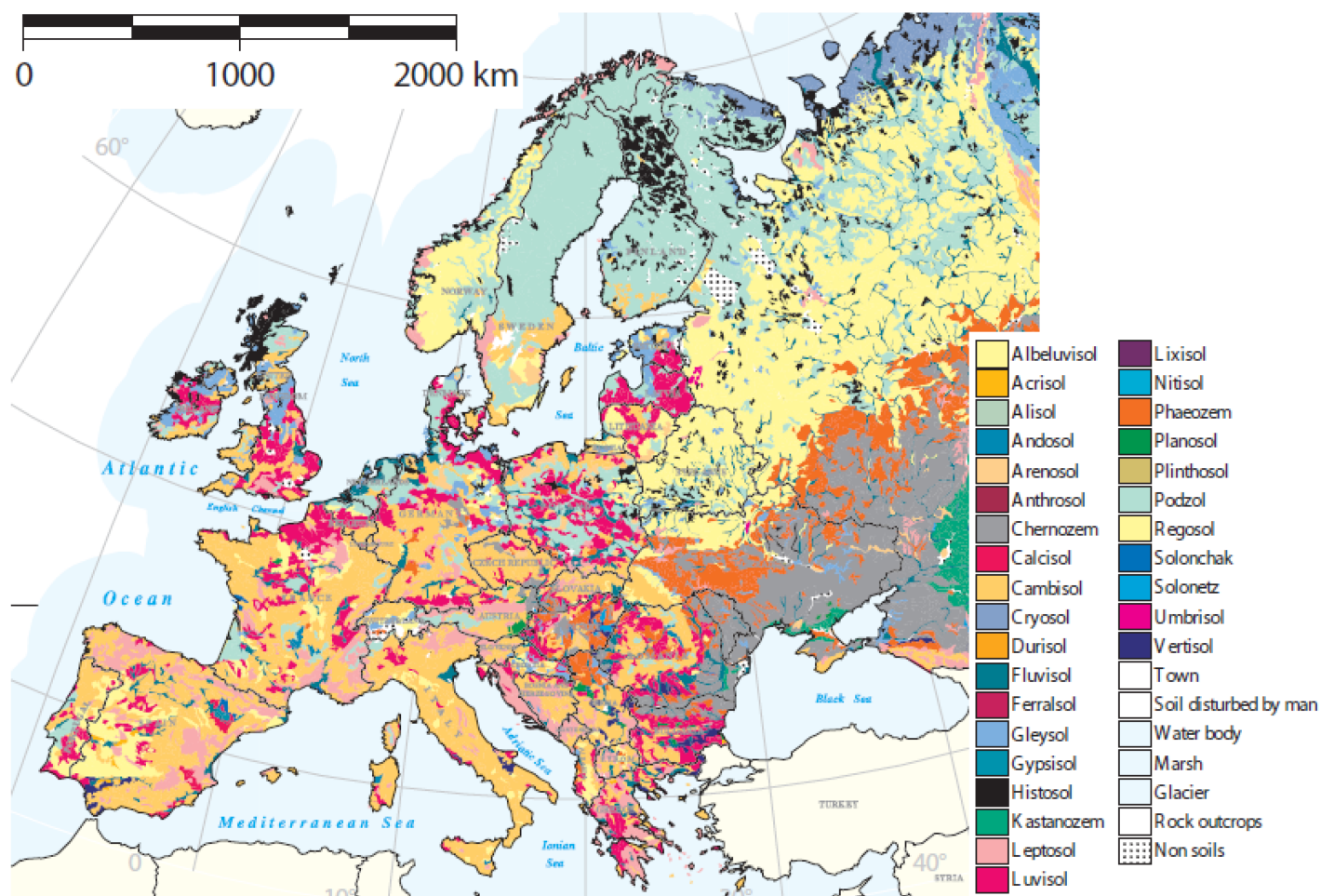
soils

Retisols

## 1. Introduction

Soil is a strategic resource and a vital part of the environment, being the main source of agricultural products. The human race receives about 95% of food products in the form of crops from cultivated land <sup>[1]</sup>. At the present stage, there is a quickly developing relative decrease in the productive land resources on the planet and their replacement by depleted territories (deserts, badlands, ravines, built-up and flooded lands, etc.). These trends, combined with modern crises (migration of the population, disruption of fertilizer supplies, and high susceptibility of agriculture to climate change) increase food security risks <sup>[2]</sup>. This problem is of global importance since the prospects for sustainable development of all countries on the world that are involved in the processes of food production and consumption depend on its solution <sup>[3]</sup>.

The relative decrease in soil area is not accompanied by a proportional or faster increase in the average global yield of agricultural crops grown for food, raw materials and livestock feed. The problem is complicated by the uneven distribution of soil resources suitable for use in agriculture throughout the continents and a steady increase in population <sup>[4]</sup>. In this regard, the use of cryolitic soils for agricultural purposes is particularly relevant for the solution of these issues. Various Retisols prevailing in the soil cover of the cryolitic zone (**Figure 1**) are low-fertility and in the case of insufficient application of fertilizers and ameliorants are subject to degradation; humus and nutrients reserves decrease, and physical-chemical and other soil properties deteriorate <sup>[5]</sup>.



**Figure 1.** Soil map of Europe (Albeluvisols of the former editions of WRB are included in the concept of Retisols).

Retisols cover an estimated 320 million ha in Europe, North Asia and Central Asia, with minor occurrences in North America. Retisols are concentrated in two regions, each having a particular set of climate conditions: (1) the continental regions that had permafrost in the Pleistocene of northeastern Europe, northwestern Asia and southern Canada, which constitute by far the largest areas of Retisols; (2) the loess, cover-sand areas and old alluvial areas in moist temperate regions, such as France, central Belgium, the southeast of the Netherlands and the west of Germany [6].

The main task of land users is to preserve and increase soil fertility and then increase the productivity of agrocenoses and protect agroecosystems from pollution. The optimal physiological development of plants is ensured by adequate nutrition, primarily mineral nutrition. In the majority of soils, mineral salts are present in sufficient quantities. If not, their need for minerals can be fulfilled with mineral fertilizers.

## 2. Mineral Fertilizers

### 2.1. Nitrogen Fertilizers

The use of nitrogen fertilizers for agricultural crops in naturally low-fertility soils, including Eutric Albic Retisols, is among the main conditions necessary for increasing the productivity and sustainability of agriculture in the non-Chernozem zone. A high long-lasting effect of this strong optimization means of the plant production process can be attained only under the condition of a balanced level of plant root nutrition via fertilizers and under the creation of favorable conditions for the effective utilization of applied nitrogen by crops. Applying nitrogen to soil in an amount exceeding the need of crops, especially against recommendations on the regular use of nitrogen fertilizers in crop rotation, can lead to a number of undesirable environmental consequences, among which the following should be highlighted: increased migration of nitrates along the soil profile creating a risk of contamination of natural waters, excessive mineralization of humus leading to its unproductive losses, violation of the balance of natural nitrogen cycles in the soil and its acidification [7]. All of these make it necessary to create a nitrogen balance-ensuring system using the soil and plant diagnostic methods to determine the need of crops in fertilizers.

The phenomenon of an increasing plant nitrogen nutrition level partly improves their resistance to moisture deficiency occurs because nitrogen plays an important role in water regime regulation. In drought conditions, nitrogen is often a more limiting factor than moisture is, and crops grown in soils with a low availability of this nutrient suffer more from drought than those in soils with a high level of assimilable nitrogen do. As shown by many researchers, in the case of insufficient moisture, nitrogen consumption by plants is limited due to a decrease in the amount of its available compounds, primarily nitrates, in the soil since the nitrification process proceeds poorly under unfavorable moisture conditions [8]. Therefore, application of nitrogen fertilizers, optimizing the nitrogen nutrition of plants, has a positive effect on the water regime in case of moisture deficiency. This is because nitrogen-fertilized plants form a root system with a high absorption capacity which allows a more efficient use of the subsurface moisture reserve. Noting that the use of soil moisture is closely related to the plant nitrogen nutrition level, many authors [9] emphasize that nitrogen fertilizers, stimulating the active growth of aboveground biomass, can contribute to the depletion of soil moisture reserves even before the period of their maximum consumption. In this regard, taking a decision on the optimal application dose of nitrogen, it is recommended to balance it with the available soil moisture reserves. There is an opinion [10] that in order to avoid early consumption of moisture and to increase the productivity of its use by crops, the application of nitrogen fertilizer in split portions should be practiced.

The stationary field experiments on poorly and medium-cultivated Eutric Albic Retisols have allowed the dependence of the effectiveness of the nitrogen fertilizer on the crop's phosphorus and potassium supply [11]. The crop rotation includes six fields sown with grain crops rotating by 66% and potato and clover rotating by 17% each. Along with the enrichment of phosphorus-potassium background, the yield increments from nitrogen fertilizer increased. The yield increases in the second rotation were lower than those in the first field rotation which seems to be associated with the improvement of the soil nitrogen regime under the influence of regular liming and cultivation of clover in the crop rotation [12].

## 2.2. Phosphorus Fertilizers

Phosphorus is among the most important elements of plant nutrition, the availability of which is considered to be one of the main indicators of soil cultivation. Therefore, the creation of an optimal phosphate level in the soil, ensuring the formation of high and stable yields of agricultural crops, is one of the priorities of modern agriculture [13]. The role of phosphorus in plant nutrition is determined primarily by the participation of its compounds in the conversion of solar energy into chemical energy of macro-energy bonds during photosynthesis, as well as in the synthesis of carbohydrates, proteins, fats and nucleic acids. Under normal conditions, the phosphate ion of the soil solution is rapidly absorbed by the root. It can be assumed that in the root most of the inorganic phosphates are already included in organic compounds [14].

Phosphates are present in the soil in the form of mineral and organic compounds. Among the minerals containing phosphorus, iron and aluminum phosphates predominate in Eutric Albic Retisols, including strengite, variscite, crandallite, augelite, etc. [15].

Phosphates can also be absorbed by soil colloids. The sorption bond of phosphates with the soil absorbing complex increases with a decrease in pH; therefore, the availability of absorbed phosphates to plants decreases with the acidification of Eutric Albic Retisol [16].

The severity of the phosphorus problem in agriculture in the non-Chernozem zone of Russia is aggravated by the fact that this element is mostly concentrated in agricultural end products to be unilaterally excluded with harvests from nature's cycle [17]. To increase the yield of agricultural crops in conditions of high phosphorus deficiency, it is particularly interesting to determine the optimal level of phosphorus availability for different soil types. The establishment of optimal phosphate levels for the main field crops in the six-field crop rotation in various zones of the country, as well as the estimation of the cost of fertilizers to achieve them, will allow access to the needs of agriculture by phosphorus fertilizers. The availability of phosphorus in the soil is the main indicator of its fertility, which determines (up to a certain limit) the yield level of all agricultural crops [18].

According to the world's chemicalization experience, to obtain high and stable yields, it is necessary to create an optimal level of available phosphate content in the soil via a single application of high fertilizer doses or the annual use of phosphorus in quantities exceeding the removal of nutrients. In the future, the yield level and its quality are regulated via the after-effect of phosphorus fertilizers against the application of other nutrients, as well as progressive agrotechnical techniques [19]. The economic feasibility of regular application of phosphorus fertilizers in a number of years has been shown by numerous studies. The correct scientifically justified inclusion of phosphorus fertilizers into crop rotations with concentrations under those of the most responsive crop is particularly important in this process [20]. Under the condition of equal P amounts applied to soil within fertilizers in the form of phosphorous flour and superphosphate, the soil after the application of phosphorous flour contains more acid-soluble phosphorus than it does that after the application of superphosphate. Even in a case when phosphorus is applied within superphosphate in higher quantities than it is within phosphorous flour, the content of acid-soluble phosphorus is higher in the soil treated with phosphorous flour compared to that after superphosphate treatment. This is probably explained by the fact that phosphorus within phosphorous flour, in contrast to phosphorus within superphosphate, is better-retained in the composition of phosphate forms available to plants after their long-term

interaction with soil [21]. Thus, the P of water-soluble fertilizer superphosphates undergoes chemical sorption in the soil and largely transforms into compounds that are not as available to plants as the P of phosphorite is. This property of phosphorite determines its advantage over superphosphate when applying these as the main phosphorus fertilizers.

When studying the reserve application of phosphorous flour to medium-loamy Eutric Albic Retisol, phosphorous flour introduced at a dose of 140 kg P per hectare resulted in a greater increase in crop productivity for 7 years than its annual use did. The high efficiency of phosphorous flour for soils with an acidic medium reaction is beyond doubt. However, convincing materials have been accumulated, evidencing the positive effect of phosphorous flour in unusual conditions for its use, i.e., for soils with a slightly acidic, neutral and even slightly alkaline medium reaction. An example is the results of field experiments conducted in the Volgograd region, Tatarstan, Western and Eastern Siberia, and the Far East, where phosphorous flour was prepared from local phosphorous raw materials. Now, local agricultural ores are the most reliable source of improving the nutrient regime of soils and increasing the yield of agricultural crops [22]. Phosphorous flour from local deposits is the main source of phosphorus nutrition for agricultural crops and a means of reproducing soil fertility in the Russian Federation.

In the zone of mandatory soil liming (Retisols, Phaeozems, and leached and podzolized Chernozems), the solution of phosphorus problems in agriculture is associated with the use of ground (milled) phosphorites [23]. One of the most important factors of the effectiveness of phosphorites is soil acidity [24]. There are two opposing opinions about the possibility of using ground phosphorite together with liming. At the beginning of the twentieth century, ground phosphorite was assigned only a narrow field of application which included acidic soils and the ploughing of wastelands enriched with humus. In modern agriculture, with numerous repetitions of liming cycles, there are soils with different medium reaction levels to which phosphorus fertilizer should be applied.

The effectiveness between ground phosphorite and superphosphate did not significantly differ for heavy-loamy Eutric Albic Retisol with an acidic medium reaction after liming to a slightly acidic-neutral level (pH 5.2–6.4) [25]. Regular liming did not reduce the effectiveness of ground phosphorite. Phosphorite is significantly superior to superphosphate in terms of energy expense recoupment, and does not differ from superphosphate in terms of its effect on the soil phosphorus regime. Based on a series of studies, phosphorites improve soil fertility via enriching the soil with available forms of macro- and microelements. At the same time, phosphorous flour, ground raw phosphorites, can be used to increase both the soil phosphate level and the content of other nutrients. In economic terms, this will be much cheaper than using industrial mineral fertilizers will be. In addition, local raw materials are more accessible and can be used directly in the deposit area of agricultural ores after mechanical crushing.

Up to 60% of organic phosphates in Eutric Albic Retisols are in the form of inositol phosphates accumulating as iron, aluminum, calcium and magnesium phytates [26]. Along with this, some organophosphates are included in the composition of HSs of a specific nature, mainly FAs. The availability of soil organic phosphates to plants is determined by the conditions of their mineralization and is closely related to soil biological activity, particularly the activity of phosphorylase [27]. There exists a close relationship between the content of mobile phosphates in the soil, plant productivity and responsiveness to phosphorus fertilizers. The optimal level of mobile phosphates

extracted with a 0.2 M HCl solution in the soil for cereals and potato lies within 10–15 mg/100 g of soil. Similar results were obtained during the long-term stationary field experiments on heavy-loamy Eutric Albic Retisols [28].

The use of phosphate fertilizers is the main way to optimize the phosphate level of Eutric Albic Retisols. The role of fertilizers in this regard account for up to 70% optimization, with liming accounting for 15–20% [23]. The enrichment of soils with mobile phosphates was achieved through the regular use of manure and phosphorus fertilizers [29]. For such soils, the cultivation of agricultural crops is based mainly on the use of nitrogen and potassium fertilizers, and the application of phosphorus only compensates for its removal by crops and stabilizes the achieved soil phosphate level. The phenomenally long duration of the effects of phosphorus fertilizers is evidenced by the data of the Rothamsted Experimental Station [30]. The ability of plants to affect difficult-to-dissolve soil phosphates and transform them into plant-available forms is also associated with the carbon dioxide released by the roots. The root zone always has a comparatively lower pH value and so the soil phosphates adjacent to it are dissolved by acidic root secretions and absorbed by plants. This mechanism of phosphorus assimilation by plants is of considerable importance in cases when phosphate ions in the soil solution are present in an insoluble form [31].

The phosphorus deficiency dramatically reduces plant productivity. At the same time, phosphorus, unlike nitrogen, has no natural sources in soil. Phosphorus intake by plants and the restoration of its reserves in soils is possible only through the application of phosphorus-containing fertilizers. Numerous studies indicate that the regular use of fertilizers for Eutric Albic Retisols increases the total phosphorus content in the arable soil horizon, enlarges the reserves of its available compounds and improves their uptake by plants. Moreover, the phosphorus of fertilizers transforms in the soil into chemical compounds characteristic of this soil formation type. Eutric Albic Retisols with low pH values contains mainly aluminum and iron phosphates. Enrichment of the arable layer of Eutric Albic Retisols normally includes inorganic phosphorus compounds. The content of organic phosphates increases insignificantly [32]. Among the mineral phosphorus compounds, soil is dominated by aluminum, and not by iron and calcium phosphates. The stationary field experiments on medium-loamy Eutric Albic Retisols of weak and medium cultivation levels allowed a close interaction between phosphorus, nitrogen and potassium fertilizers when applied in addition to regular liming [28]. Long-term application of phosphorus fertilizers increases the utilization rate of phosphorus. These functions can be successfully performed by phosphorous flour. According to many researchers, it has the same effect as superphosphate and in the conditions of the North is even more efficient.

### 2.3. Potassium Fertilizers

Potassium performs numerous functions in plant life. By optimizing the potassium regime in the agroecosystem, improving crop cultivation technologies, it is possible to significantly affect the productivity of agrocenosis, especially in extreme conditions [33]. Potassium in soils is the main source of plant potassium nutrition. Its gross content far exceeds that of the reserves of nitrogen and phosphorus in the soil and is determined mainly by the parent rock and soil texture (granulometric composition). Sandy Eutric Albic Retisols contain 0.5–1.2% K, and loamy Eutric Albic Retisols contain 1.5–2.1% K. Potassium is found in the soil mainly in the form of primary and secondary clay materials, such as feldspar, mica, illite, vermiculite, chlorite, and montmorillonite [34]. In the practice of agricultural soil use, there is an active involvement of a non-exchangeable form of potassium in plant nutrition

which largely determines the peculiar buffering of soils with respect to potassium. According to the studies on the interaction of potassium fertilizers with soil, up to 70–90% of the introduced potassium was fixed in a non-exchangeable form [35].

The ability of potassium to exchange absorption increases along with an increasing content of a highly disperse fine-soil fraction, mainly that of silty particles. Exchangeable potassium is absorbed on the surface of negatively charged colloidal particles. Potassium is not as firmly retained in the exchange positions of organic matter as it is in those of clay minerals [36]. According to the studies conducted in sandy-loam and heavy-loam Eutric Albic Retisols, the use of potassium fertilizers noticeably increases the content of exchangeable potassium in the arable layer only against the background of a triple dose of potassium (220 kg/ha) applied in addition to a nitrogen–phosphorus fertilizer [37].

After the application of a triple dose of potassium fertilizer, the potential greatly reduced which, according to the existing gradations, corresponds to the optimal provision of the soil with potassium. The content of easily exchangeable potassium, determined via the curves of the potential soil buffering capacity in relation to potassium, against the background of a triple dose of potassium fertilizer significantly increased only in sandy loam and not in heavy loam. The latter, as the authors suggest, is related to the ability of heavy loam to firmly retain the introduced potassium due to the high content of fine fractions in its texture [38].

Along with the regular use of potassium fertilizers for Eutric Albic Retisols of various textures at doses of 50–75 kg/ha, only sandy loam was identified for a noticeable migration of potassium down to a depth of 100 cm. In heavy loam, potassium moved no deeper than 40 cm, and in medium loam, it moved 60 cm down the soil profile [39]. The mobility degree of exchangeable potassium decreased along with the soil texture change to heavy variants [40]. The prominent absorption of potassium by clay minerals in soils of a heavy physical texture causes its poor downward movement along the soil profile; the exception for this is light soil from which potassium can be washed out. Consequently, it is possible to apply potassium fertilizers for most soil types, including Retisols, beginning in autumn, without fear of large potassium losses with leaching. However, based on the results of the long-term stationary experiment, potassium moves into the underlying horizons in amounts of 12–19 kg/ha per year [41]. The studies conducted in the same field experiment revealed the accumulation of mobile potassium in the meter-thick soil layer under crops after 62 years of fertilizer application. There is also information about more significant amounts of potassium leaching from the soil. From the arable layer of cultivated Eutric Albic Retisol bare fallow, up to 128.6 kg/ha K per year migrated to the underlying horizons. Losses due to leaching under annual and perennial grasses were significantly lower and amounted to 22–30 kg/ha annually [42].

To characterize the potassium availability in Eutric Albic Retisols, the most frequently used value is the content of exchangeable soil potassium. Summarizing the field experiment results on grain crops demonstrates that the grain yield increases as the content of mobile potassium (according to Kirsanov) also increases by up to 14–20 mg/100 g of soil [43]. Based on the data of experiments with fertilizers, there exists a close dependence of potato productivity and its responsiveness to potassium fertilizer on the content of exchangeable potassium in the soil. An increase in the content of exchangeable soil potassium from 3.1 to 28.6 mg/100 g of soil was accompanied by an increase in

the yield of potato tubers from 12.8 to 27.3 t/ha against the NP (nitrogen and phosphorus fertilizers) background, whereas the increase in yield after the application of potassium fertilizers decreased from 32 to 7% [44]. Similar data were obtained in studies on other crops of a field crop rotation. When growing flax, barley, lupine and winter rye in Eutric Albic Retisols, the yield of these crops increased with an increase in the content of exchangeable soil potassium to 15–20 mg/100 g. Any further increase in this indicator no longer led to an increase in crop rotation productivity [45].

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