Phosphogypsum: P Fertilizer By-Product and Soil Amendment

By Valery Kalinitchenko and Vladimir Nosov

Phosphogypsum (PG) is a reaction product from the making phosphoric acid by treating phosphate ore (apatite) with sulfuric acid according to the following reaction:

$$Ca_5(PO_4)_3F + 5\ H_2SO_4 + 10\ H_2O \rightarrow$$
$$3\ H_3PO_4 + 5\ (CaSO_4 + 5\ (CaSO_4\ \cdot 2\ H_2O) + HF$$

Annual world production of PG has been estimated at 300 million (M) t (Yang et al., 2009), but only a small percentage [4% according to Recheigl and Alcordo (1994)] finds use by either agriculture or industry. The remainder is either disposed of in the ocean or stockpiled near production facilities.

PG is considered a low-cost source and one of the most effective amendments for problematic soils including those affected by general salinity, high Na (sodic or solonetzic), and soil compaction (Belyuchenko et al., 2010). Russia is significantly impacted by sodic and saline soils, which occupied 20% of its agricultural land area in 2007 (The Nature of Russia…, 2016). This article discusses a range of ameliorative and nutritive uses for PG in specific Russian cropping systems, but these issues are common elsewhere and the examples of PG use presented here are transferable to other settings through adaptive management.

Phosphogypsum Research

Amelioration of sodic soils requires the replacement of Na adsorbed on the cation exchange complex of the poorly structured, illuvial soil horizon, with Ca. Rates of PG ameliorants are generally calculated based on the amount of Ca required to displace equivalent quantities to Na adsorbed on the soil exchange. The addition of various mineral and organic substances like composts can strengthen the ameliorative effect of PG (Belyuchenko et al., 2010). Acidic ameliorants are most preferable for saline solonetz soils with high concentrations of exchangeable Na. Granulation of PG may be considered to achieve a more effective application (Granular Gypsum, 2016). An advanced reclamation scheme for sodic soils includes rototilling to the depth of up to 60 cm and a simultaneous PG application into the appropriate soil layer (Kalinichenko, 2010). Such a technology has the highest ameliorative effect because of the placement of PG directly into a sodic horizon rather than simply spreading it on the surface.

Long-term field research on solonetzic soil in southern Russia found a single application of PG at 11 t/ha produced 15 to 25% yield increases for various crops over 30 years (Sukovatov, 2009). Chernozem soils in the south often become alkaline or compacted over time and their amelioration also becomes necessary. Mischenko et al. (2009) reported that PG application to a compacted chernozem a (10 to 40 t/ha with tillage of the 30 to 60 cm soil layer) increased sunflower and maize grain yields by 16 and 23%, respec-

Chestnut solonetz soil profile. Photo courtesy of Dr. L.P. Iljina, Southern Scientific Center of Russian Academy of Sciences, Rostov-on-Don.

SUMMARY

This review outlines the use of phosphogypsum, a by-product from the phosphate fertilizer industry, in Russia including its ameliorative roles for Na-affected and compacted soils; its value as a multi-nutrient fertilizer; in composting with various organic wastes to produce organo-mineral fertilizers; and in remediation of oil-contaminated soil.

KEYWORDS:

phosphogypsum; soil amelioration; soil fertility; crop productivity.

ABBREVIATIONS AND NOTES:

N = nitrogen; P = phosphorus; S = sulfur; SO_4^{2-} = sulfate; Ca = calcium; Cu = copper; Na = sodium; Ni = nickel; Zn = zinc; F- = fluoride; Pb = lead; Cd = cadmium; Sr = strontium; MAP = monoammonium phosphate; FYM = farmyard manure.

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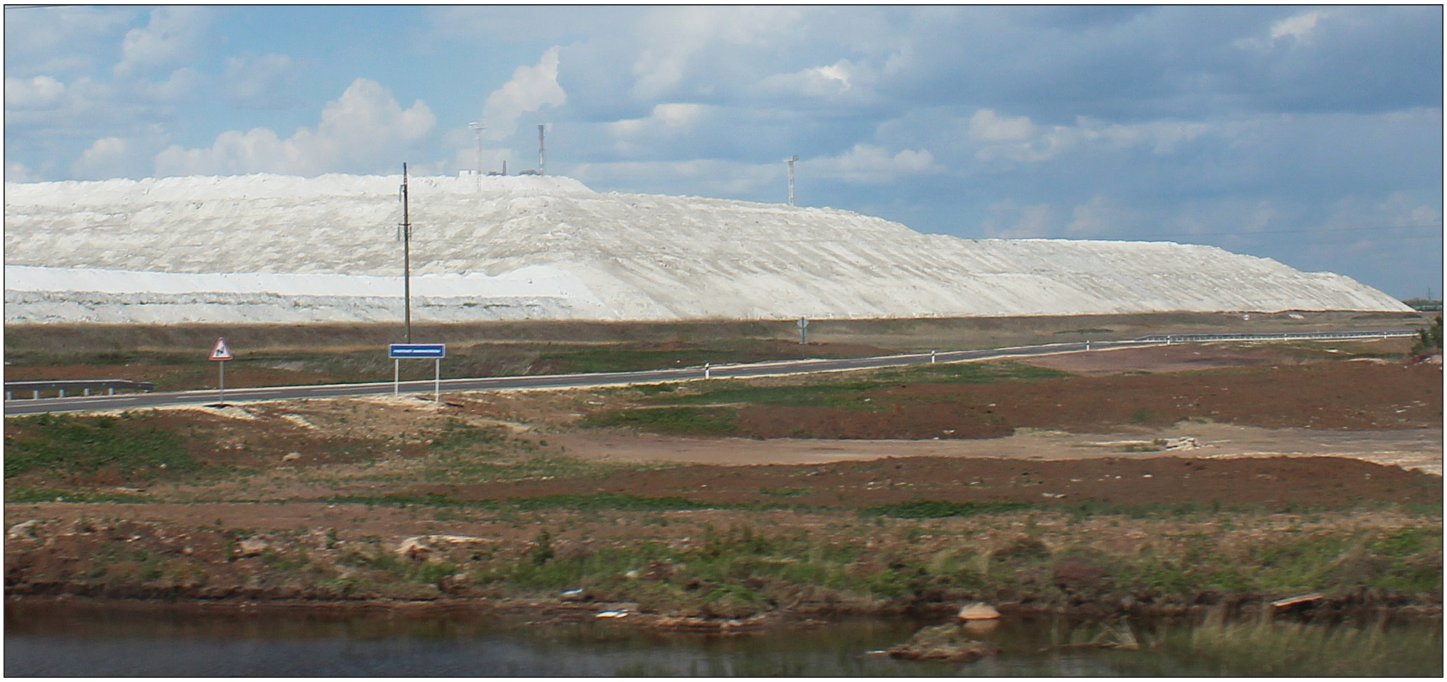

Phosphogypsum is commonly stock in large open areas a by-product from the phosphate fertilizer industry.

tively. Imgrunt (2004) found PG application at 10 t/ha to be helpful in improving an extremely compacted chernozem, with positive changes being both decreased soil clay content and bulk density. The presence of gypsum and carbonates has been found to prevent dispersion of labile soil minerals, and appears to have a stabilizing effect (Prikhodko, 2003). Special microscopic studies have shown that fine soil particles and applied organic matter are tightly fixed to colloidal PG particles, which improves soil aggregation, aeration, and water permeability (Slavgorodskaya, 2009).

The effect of PG amelioration for sodic soils developed in the presence of excess moisture, such as hydromorphic soil in southwestern Siberia appears to be more limited. Studies with PG in this region have found improvements in physical and chemical properties (Semendyaeva et al., 2015); however, the effect is generally not stable over time. A surface application of PG without incorporation into the soil can explain why exchangeable Na concentration may not change at depth (20 to 40-cm soil layer). Besides the placement of PG into the appropriate soil layer, the hydrological regime of these soils often needs to be changed to ensure a more lasting impact. However, the risk of soil salinization may even be increased after successful amelioration due to an improvement in the soil physical properties and, in turn, a decreased depth to groundwater (Semendyaeva and Elizarov, 2014).

Under irrigation, PG amelioration of sodic soils can be highly effective. Kalinichenko (1990) reported a decrease in exchangeable Na percentage from 15 to 2% in the 20 to 30-cm soil layer of a southern solonetzic soil after an application of 8 t PG/ha, which resulted in a 27% yield increase in maize silage. Yurkova (2012) demonstrated improved soil physical properties of degraded chernozems irrigated with saline water due to both PG applied at 10 to 12 t/ha and PG-based composts. Soil bulk density was decreased while soil porosity and water-stable aggregates were improved. Improvements in crop production were between 36 to 44% for various crops due to the use of PG-based composts. Martynenko (2014) studied drip irrigation with calcinated water prepared from a stock PG solution of 1.5 g/L and PG application at 1.9 and 3.0 t/ha on solonetzic soil growing onion. Bulb yields were increased by 15% compared to a control treatment irrigated without PG.

Rice-based cropping in Krasnodar Krai, Southern Russia.

Amelioration of chernozem soils degraded under rice-based cropping has been widely studied in the south. An excessive mixing with water results in cracked soil structure and increased bulk density to a level that is unfavorable for root development (Sheudzhen et al., 2013). The long-term use of sodic soils under rice-cropping systems without chemical amelioration causes solodization and secondary salinization and increases the labile fraction of soil organic matter and its loss through leaching. There is also a risk of Ca losses through leaching. The sum of exchangeable cations and the percentage of the CEC occupied by Ca can be improved with PG application. PG applied at 10 and 40 t/ha was effective in improving the physical properties of solonetzic soil, resulting in a 17 to 29% increase in rice yield (Radevich and Baranov, 2015).

Skuratov et al. (2005) reports that physical and chemical properties of southern chernozems and chestnut soils under rice-cropping have been improved through combined amelioration with both PG and FYM and a deep soil loosening. Salt concentrations in a surface layer (0 to 40 cm) of solonetzes noticeably decreased over the first year due to soil reclamation programs including PG application at 4 and 6 t/ha. Its application resulted in a 20 to 24% rice yield increase but the combination of PG and FYM was more effective, giving a 29 to 32% yield increase compared to a control treatment (Rice cropping…, 2009; Dedova et al., 2015). PG improves soil organic matter synthesis, optimizes the soil calcium carbonate equilibrium, and complexes with heavy metals (Kalinichenko et al., 2018).

Phosphogypsum as a Nutrient Source

PG is especially effective as a multi-nutrient fertilizer (i.e., source of P, Ca, S, and micronutrients) in the rice-cropping systems in the south (Baibekov et al., 2012). Constant nutrient removal from crop harvest and nutrient losses in rice field outflows and infiltrated waters cause a considerable decline in soil exchangeable Ca, available S, and micronutrients. According to Sheudzhen and Bondareva (2015), a single t of PG may also supply the following rates (kg/ha) of nutrients: Ca = 265, S = 215, P_2O_5 = 20, and SiO_2 = 9.8. Rice field experiments conducted by Sheudzhen and Bondareva (2015) on meadow soil found soil N, P, and K balances and nutrient uptake to be similar for treatments receiving $N_{120}P_{80}K_{60}$ and $N_{120}K_{60}$ + 4 t PG/ha. Rice yield was even somewhat higher with PG as the source of P instead of MAP. The above-mentioned rate of PG has been considered to be optimal under these environments. Application of PG as a source of P to leached chernozem at 4 t/ha also resulted in a significant soybean and maize yield increase over a control treatment (Sheudzhen et al., 2013). Crop response to this P source was higher compared to common fertilization practices ($N_{20}P_{40}K_{20}$). Dobrydnev et al. (2014) found the optimal rate of PG for winter wheat grown on leached chernozem to be 2 t/ha.

PG has recently been studied as a multi-nutrient fertilizer in a potato-based cropping system on coarse-textured, soddy-podzolic soil (Fedotova et al., 2017). The best treatment amounted to 1.5 t PG/ha plus NPK fertilizer.

Microbiological studies indicate that PG application results in increasing numbers of soil microorganisms utilizing organic N and assimilating mineral N (Ponomareva and Belyuchenko, 2005). A low pH of nonneutralized PG favors the making of composts with biosolids, FYM, poultry manure, wood chips, distiller's grains, defecation lime, diatomite, biochar, wastes of food processing industry, and other organic wastes (Belyuchenko, 2016a; 2016b). High quality and environmentally friendly organo-mineral fertilizers can be produced using such methods. Addition of PG could improve the quality of composts by shortening time to maturity, decreasing mineralization of organic matter, reducing N losses through ammonia volatilization, enhancing microbial activity, and decreasing the number of parasitic worms.

Application of PG could provide an opportunity to remediate oil-contaminated soils. Remediation of agricultural lands exposed to moderate oil contamination (i.e., oil concentrations up to 15 to 16 L/m^2), may be done without removing the surface soil layer by applying PG and organic fertilizers (Kolesnikov et al., 2011). PG can activate processes involved in the decomposition of oil products, increase water evaporation from contaminated substrates by 3 to 4 times, and shorten the remediation period for oil-contaminated soils (Belyuchenko et al., 2008; Kalinina and Melnik, 2009).

A combined application of rock phosphate and PG has been proposed for non-chernozemic, podzolized, and leached chernozems to convert slowly available P of rock phosphate to plant-available forms (Tsurikov, 1977; Phillipova, 2006). Sulfuric acid formed after PG reaction with acid soils having high concentrations of H^+ ions may be helpful to dissolve apatite minerals. A noticeable positive effect of PG on grain yield of cereal crops grown on soddy-podzolic soils and chernozems in the forest-steppe zone has been found when it was mixed with liming materials (Recommendations …, 1977).

Phosphogypsum may contains various trace elements, depending on the chemical composition of the phosphate rock. The accumulation of trace elements in the soil should be monitored, depending on the purity of the phosphate ore. However in Russia, numerous studies did not reveal the accumulation of heavy metals (Cu, Zn, Pb, Ni, Cd, and Sr) and F^- in soils and cereal grains in quantities higher than maximum allowable concentrations after PG application

(Loktionov et al., 2015; Batukaev et al., 2017; Fedotova et al. 2017). Similarly, the concentrations of various radionuclides in PG will range widely depending on the rock used in producing soluble phosphate. The PG may become enriched with radionuclides, especially $_{238}$U and $_{232}$Th. When PG is used properly, these elements should not pose a problem.

Phosphogypsum is widely used in parts of the world to amend subsoil acidity, such as in Brazil (Prochnow et al., 2016). In soils with excessive exchangeable aluminum (Al), application of PG facilitates movement of Ca into the subsoil and neutralization of soluble Al. The PG application results in greater root growth and crop yields in these soils. The amount of PG required to amend acid soils for improved crop growth depends on the clay content of the soil and the subsoil chemical properties.

Conclusion

The utilization of by-product PG from the phosphate fertilizer industry contributes to the sustainable use of P resources. Available technologies have allowed PG applications to improve soil properties and crop productivity in a diverse range of crop production environments with problematic soils. **BC**

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