The Application of Phosphogypsum in Agriculture

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Summary

Phosphogypsum (PG) is a by-product of phosphoric acid production and according to the Waste Management Strategy of the Republic of Croatia for 2007 - 2015 (Official Gazette 85/07, 126/10, 31/11, 46/15) it is classified under the waste code 06 09 01. Phosphogypsum has a significant impact on the environment by its effects, admixtures (impurities) and amount. One of its possible applications is in agriculture. Many positive effects on soil and plants were noted, but there is also a growing concern regarding the effect of residues of heavy metals and natural radioactivity of radionuclides. In order to obtain a better understanding of this subject, this study provides a general overview of the available literature regarding the application of phosphogypsum in agriculture.

Key words

phosphogypsum, fertilizers, environmental impact

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Introduction

Phosphoric acid that is nowadays primarily used in the production of complex NP (MAP, DAP) and NPK fertilizers is obtained by a method wherein along with the phosphoric acid there are also by-products of calcium sulfate dihydrate (phosphogypsum), and hydrogen fluoride. The process takes place in the reactor where the ground phosphate ore or raw phosphate (fluorapatite) decomposes with concentrated sulfuric acid at a temperature of 75-80°C and with 26-30% P_2O_5 in the meadow, under this circumstance calcium sulphate dihydrate – phosphogypsum is produced. The chemical formula of that reaction is as follows:

$$Ca_{10}(PO_4)_6F_2 + 10\,H_2SO_4 + 20\,H_2O \leftrightarrow 6\,H_3PO_4 + \underbrace{10\,CaSO_4 \cdot 2\,H_2O}_{\text{phosphogypsum}} + 2HF$$

During the technological process of vacuum filtration the separation of weak phosphoric acid and phosphogypsum (PG) occurs, phosphogypsum (PG) is then transported either by dried (belt conveyors) or wet (hydraulic piping) method and disposed at a specifically regulated landfills. For each ton of phosphoric acid, 4-6 tons of phosphogypsum are produced in this process (Leaković et al., 2012; Papastefanou et al., 2006; IAEA, 2013). The current annual production of phosphogypsum in the world is 160 million tons, of which 40 million tons is produced in the USA. The production is constantly increasing, and it is expected to reach 200-250 million tons in the next decade (IAEA, 2013). Given the large quantities that are produced, and having in mind that only 14% is used in the construction industry, it is necessary to dispose the surpluses (Taybi et al., 2009). There are two main waste disposal methods: a) construction of landfills above the ground where it can settle (> 50%); and b) permanent disposal of the material in water resources (28%). Although the composition of phosphogypsum is dominated by calcium sulfate, more than 50 different impurities were also identified (Rajković, 2003). The diversity and the number of impurities present depend on geological origin of phosphate ore, processing method, disposal method, landfill age and location and possible contamination in the production process (Arman et al., 1990). Radionuclides are a special type of impurities that do not significantly affect the quality of phosphogypsum, but significantly affect the environment. It is known that phosphate ores have increased natural radioactivity (Naturally Occurring Radioactive Material - NORM). In the process of phosphate mineral fertilizers production, about 86% of natural ^{238}U from phosphate ore is extracted to phosphoric acid, while 80%-90% of ^{226}Ra is extracted to phosphogypsum, replacing Ca in chemical structure (Sahu et al., 2014). A small percentage of uranium may end up in phosphogypsum in the following ways (IAEA, 2013): (I) through unreacted raw phosphate which after filtration ends in a mixture of phosphogypsum, (II) substitution of U^{4+} in the crystal lattice of phosphogypsum, (III) phosphoric acid residues in phosphogypsum after filtration, (IV) UO_2HPO_4 adsorption on the surface of phosphogypsum.

Phosphogypsum activity in soil

Physical properties

According to Beretka (1990), in arid areas in Australia, on basic soils, 3-5 t/ha of phosphogypsum of 10-12% humidity is applied, and it is plowed at 15 cm depth. The procedure is repeated every 3-5 years. The improvement of surface soil structure and better water capacity is noted, soil management is easier and faster, and there is less damage to the equipment. Phosphogypsum enhances the cation exchange of Na^+ and Ca^{2+} in clay soils, and thus contributes to density, increased porosity and formation of stable soil structure (Orlov et al., 1989). Agassi et al. (1985) reported that the application of phosphogypsum (5 t/ha) reduced runoff in loess by 70-85% compared with the control. Vyshpolskya et al. (2010) conducted a two-year experiment on the plots of cotton on heavy clay with organic matter content of 1%, and by applying phosphogypsum they increased the efficiency of irrigation and improved water retention around the root system.

Chemical properties

Acidic soils

Positive effects of phosphogypsum in reclamation of acidic soils are generally attributed to the reduction of mobile aluminum concentration (Noble et al., 1988; Alva and Sumner, 1989; Frenkel et al., 1989; Alva et al., 1990; Mullins and Mitchell, 1990; Rechcigl et al., 1993). Mesić (2001) conducted experiments on dystric luvic semigley soil with two doses of phosphogypsum applied (12.5 t/ha and 25 t/ha), and found that phosphogypsum generally had a modest effect on the improvement of soil acidity and it caused a reduction of mobile aluminum content in soil during the four-year research.

Alva et al. (1990) investigated the effect of phosphogypsum on mobile aluminum content in subarable layer for three different types of soil. They have saturated the soil in the laboratory with deionized water and an aqueous solution with phosphogypsum concentration of 2 g/L. Saturating the soil with phosphogypsum solution caused a reduction of mobile aluminum by 40%, 21% and 7%. Higher values were observed in soils with dominant kaolinite component, and the lowest value was observed in soil with the highest concentration of smectite. The authors concluded that the amelioration effect of phosphogypsum is conditioned by the increase of surface charge of soil particles due to the presence of SO_4^{2-} ions, as well as the reduction of exchangeable aluminum content. Amelioration effects of phosphogypsum are stronger in soils with predominant variable charge in relation to soils with higher content of permanent charge of clay minerals.

Blum et al. (2012) studied the irrigation (purified wastewater) of soil that was treated with phosphogypsum and they warned that Ca easily leached. They also recommended the application of phosphogypsum in small amounts several times. The combination of phosphogypsum and lime and/or silicates improves surface and subsurface chemical properties of soil 12 months after application. The composite increased the concentration of K^+, Ca^{2+}, Mg^{2+}, $N\text{-}NO_3^-$, $S\text{-}SO_4^{2-}$ in subsurface layer (Crusciol, 2016). Van der Watt et al. (1990) conducted a study on kaolinite type of clay (South Africa). All plots (20x10 3m) were treated with 20 kg of P in the form of superphosphate before they were divided into control and plots with increased amounts of phosphogypsum and mulch. Phosphogypsum with 0.36% of P was used. They found that within two years with the application of 2 t/ha of phosphogypsum, conductivity and available phosphorus were increased. Mays et al. (1986) used phosphogypsum (0.23 mg Cd kg, 925 Bq/kg ^{226}Ra) at 0.22 and 112 t/ha doses in corn-wheat-soybean crop rotation, and the results showed an increase of ^{226}Ra from 34.8 Bq/kg (control) to 73.3 Bq/kg (112 t/ha PG) in 0-15 cm layer, while there were no consequences at greater depths. These values are below the limits of toxicity according to National Council of Radiation Protection and Measurement (NCRPM, (1984). The values determined by research conducted by Mullins et al. (1990), Papastefanou et al. (2006) and Rechcigl et al. (1992) were also below the permitted limits.

Alkaline soils

Nayak et al. (2011) conducted a research in India on agricultural soil without vegetation, with the addition of 5-20% phosphogypsum and they found that with the increasing amounts of phosphogypsum applied, pH was reduced from 7.9 in control to 5.1 in treatment with 20% phosphogypsum.

According to Vyshpolsky et al. (2010) by using phosphogypsum in irrigated areas, the effects of excess Mg^{2+} in soil, which are negative regarding soil structure and ultimately plant growth and yield, are mitigated.

Phosphogypsum and gypsum are excellent substitutes for carbocalk and other liming materials only in neutralizing the excess of aluminum in acid soils or sodium in alkaline soils (Vukadinović et al., 2016).

The effect of phosphogypsum on plants

According to Butorac (1999) yield is a part of natural produce and the reason why certain cultures are grown, with certain quality and quantity it has an economic value. The application of phosphogypsum as a fertilizer, in doses of 100-600 kg/ha, contributed to a significant increase in yield in 50 types of crops (Hilton, 2006). Mesić (2001) conducted experiments on dystric luvic semigley soil with the application of two different doses (12.5 t/ha and 25 t/ha), and found a relatively small increase in yield in corn and winter wheat production (10% -15% higher than control). Bašić et al. (1990) studied the effect of liming with several materials (soft limestone, hard limestone, dolomite and phosphogypsum) on crop yields in maize - winter wheat -rapeseed crop rotation. Studies were conducted on semigley dystric brown soil. The application of phosphogypsum had a pronounced positive effect on corn yield, but not on winter wheat yield. Da Costa et al. (2015) conducted a study on acid soils of Brazil in soybeans-oats-sorghum crop rotation, with the application of 2 t/ha of phosphogypsum. Soybeans and oats yield was not statistically different from control, whereas the application of phosphogypsum resulted in several times higher yield of grain sorghum as compared to control, but it was economically negligible (250 kg/ha). Dimitrijević et al. (2010) conducted an experiment with different varieties of wheat on solonetz, with the application of phosphogypsum as a reclamation agent in the amount of 25 t/ha and 50 t/ha, and they found average yield of 5.17 t/ha (25 t/ha PG) and 3.81 t/ha (50 t/ha PG). Vyshpolskya et al. (2010) conducted a two-year experiment on heavy clay, with 1% of organic matter, with the application of 3.3 t/ha PG and 8 t/ha PG on the area covered with cotton, and in the second year of the experiment in treatment with 3.3 t/ha PG they recorded the highest yield (2.2 t/ha) as compared to control (1.2 t/ha). Also, plant density was significantly higher (162 000 plants/ha) than control (139 000 plants/ha).

Macro and micro-nutrients are essential for plant growth and development. Soratto et al. (2008) studied cultivation of rice and beans on kaolinite type of soil with no-tillage, and they noted that the application of phosphogypsum in rice cultivation had positive effects on the amount of S in leaf and yield, and when combined with lime, the content of Zn in leaf was significantly lower. Also, with the application of phosphogypsum they recorded bean leaf an increase of S and Ca, and a decrease of Mg content. Elloumi et al. (2015) studied sunflower under controlled greenhouse conditions and the application of phosphogypsum in value of 5% of the weight of the soil. They found a significant reduction of shoot length (17%), while there was no change in roots. With the application of 5% phosphogypsum, an increase of K and Na concentration and a decrease of Ca concentration were recorded in leaf. There was also an increase of Ca and Na, and a decrease of K and Mg concentration in root.

Along with major plant nutrients, mineral fertilizers often contain different admixtures in form of heavy metals, organic compounds and radioactive substances (Butorac, 1999). Abril et al. (2008) studied the cultivation of tomatoes on soils that were treated with 20-25 t/ha of phosphogypsum every 2-3 years during the past 30 years and they concluded that Cd levels in tomatoes were permitted under the EU regulation (EC 1881/2006). In their experiment Enamorado et al. (2014) used the soil that was treated with phosphogypsum at a dose of 20-25 t/ha six times during the last 40 years. Sampled soil was additionally treated with 0, 20, 60 and 200 t/ha of phosphogypsum (2.1 mg Cd/kg PG) and they found that with the maximum amount of applied phosphogypsum the accumulation of Mn, Co and Cu in shoots was stopped, as well as the accumulation of B, Cu, Sb, Cs, Ba, Tl, Th in yield. Also, concentrations of Pb in the entire plant were negligible and did not pose a problem for human and animal nutrition while the content of Cd was very close to the maximum allowed value, and a constant control of Cd is required. Roša (1998) noted geno- and cyto-toxicity of phosphogypsum after a 24-hour treatment (0.5%, 1.0%, 2.5%, 5% and 10% in the solution of water from landfills) and a 24-hour recovery (tap water) in onion bulb treated with all concentrations, where chromosomal and mitotic aberrations occurred in the cells in the tip of an onion root. Also, higher concentrations of fluoride were noted in leaves of common oak near a landfill.

The effect of fertilizers and materials mixed with phosphogypsum

Van der Watt (1990) carried out experiments with a combination of phosphogypsum and mulch, where a positive effect, that is, the reduction of crust formation could be seen through a cycle of 4-5 months (in the systems of no-tillage or minimum tillage). Crusciol et al. (2016) also conducted a research in no-tillage system and concluded that the combination of limestone, silicate and phosphogypsum improves surface and subsurface chemical structure of soil, and an increase in the concentration of K, Ca, Mg, N-NO_3^-,S-SO_4^{2-} was recorded, which has definitely improved culture conditions. Bayrakli (1990) studied the methods of ammonia volatilization from urea, and by using phosphogypsum he reduced nitrogen loss by approximately 85%. Mesić (2001) conducted an experiment where he combined eight liming materials. One of the combinations was NPK + phosphogypsum, which in winter wheat achieved better yield (53.9 dt/ha) than control (35.6 dt/ha), but when that combination was compared to simple NPK application (51.3 dt/ha) the difference was not statistically significant. The application of limestone and phosphogypsum increases the absorption of Ca in soybean and sorghum, and it also increases yield (da Costa et al., 2016).

Oates and Caldwell (1985) conducted a laboratory study of the efficiency of phosphogypsum, hydrofluorogypsum and gypsum on the neutralization of soil with the initial pH value of 4.9. They found that when phosphogypsum was stored in open-air storage areas it had adverse physical characteristics due to large particles and high water content. Unlike hydrofluorogypsum where with the application of 5x4.2 cmol (+) / kg dose the pH value of soil in vegetation pots had increased to 5.3, the application of gypsum and phosphogypsum in the same amount had not resulted with an increase of soil pH. In contrast to pH value, mobile aluminum content was reduced by 81% with hydrofluorogypsum, and by 55% with phosphogypsum. The reduction of aluminum content is explained by the formation of fluoride and aluminum complex, because the materials that were used contain substantial amounts of fluorine, 23.8 mg/g in hydrofluorogypsum, and 6.5 mg/g in phosphogypsum. Along with the reduction of aluminum content they also observed a decreased content of other cations, magnesium, sodium and manganese. During the 35 days of vegetation in pots, according to plant height and weight, soybeans reacted positively to the application of hydrofluorogypsum, and after that the application of phosphogypsum.

Alva and Sumner (1989) investigated the effect of solutions of different aluminum and phosphogypsum content on soybean root development. In the control treatment consisting of solution without mobile aluminum content, a relative soybean roots length of 100 was obtained, and the values of relative roots length achieved in three other treatments were also indicative. The first was a treatment without the application of aluminum, and with the application of phosphogypsum in the amount of 2 g/L, in which the aluminum concentratiotion of 16 μM and a relative root length of 86 were recorded. The following was a treatment with 40 μM of added aluminum, but without phosphogypsum where aluminum concentration of 39.5 μM and a relative root length of only 22 were measured. The third treatment included the application of 40 μM of aluminum and 2 g/L of phosphogypsum in which the concentration of aluminum in a solution of 32.5 μM and a relative soybean root length of 85 were recorded, which suggests that the application of phosphogypsum positively affects roots growth in a solution with the addition of aluminum.

Rechcigl et al. (1993) compared the effect of different doses of calcite (0, 1.1, 2.2, 3.3, 4.4 and 6.6 t/ha) and phosphogypsum (2.2 and 4.4 t/ha) on acidic sandy soil with the initial pH value of 4.8. The materials were applied on surface and incorporated into the soil with a disc harrow to a depth of 7 cm. After five months, soil pH at a depth of 0-15 cm had the highest increase in the treatment with the highest dose of calcite where soil pH was 6.0. After the application of phosphogypsum, pH was reduced to 4.0 regardless of the applied amount of this material. The effect of calcite was not recorded at a depth of 15 cm, while the phosphogypsum also influenced a decrease in pH values at a depth of 15 - 75 cm, and even deeper, but did not decrease the exchangeable aluminum content. The exchangeable aluminum content at a depth of 0-15 cm decreased from the initial 27.0 mg/kg to 7.0 mg/kg when the highest dose of calcite was applied, and the saturation degree of aluminum decreased from 34.3% to only 2.3%. Due to phosphogypsum application there was a certain decrease in mobile aluminum content (21.3 mg/kg and 23.0 mg/kg) compared to control (27 mg/kg), as well as a decrease in aluminum saturation level (20.3% and 25.8%). After three years the situation has changed, so that the lower doses of calcite at a depth of 0-15 cm had an insignificant effect on soil pH value, while the effect of the highest dose of calcite was unchanged compared to the initial year. The content of exchangeable aluminum increased in all treatments, although the highest increase was recorded in treatments with phosphogypsum, and the same goes for the degree of aluminum saturation. This suggests that the amelioration effect of phosphogypsum on mobile aluminum content in field trials is short-lived. Statistically significant differences between control and treatments with phosphogypsum regarding mobile aluminum content were not recorded at greater depths either (15-30, 30-45 cm).

Frenkel et al. (1989) have applied granulated phosphogypsum to soil in order to investigate the influence of granule size on its solubility. They noted that due to the formation of aluminum phosphate coating on granule surface a slower dissolution rate of phosphogypsum granules occurs in strongly acidic conditions. When the granules were larger, the dissolving process was slower, so they concluded that if the aim of phosphogypsum application is to influence the process of removing acidity in subarable layer (due to leaching), the arable layer should be calcified so that phosphogypsum could melt down more quickly in favorable reaction conditions.

Noble et al. (1988) ascribe the reduction of aluminum toxicity after the application of gypsum to the formation of less toxic $AlSO_4^+$ ions. In their research conducted on nutrient solution with the pH of 4.2 and 4.8 they noted that gypsum had a less pronounced effect on aluminum toxicity removal at pH 4.8, and they explained that by more intensive formation of $AlSO_4^+$ at pH 4.2, and $Al(OH)^{2+}$ ions at pH 4.8.

Beretka (1990) reports positive results with the application of 3-5 t/ha of phosphogypsum every 3-5 years. After such applications of phosphogypsum the improvement of soil structure at surface layer and better water infiltration were recorded in unstable structure soils and soil management was easier and faster.

Mullins and Mitchell (1990) found a positive effect of phosphogypsum application on sulfur content in soil. Although phosphogypsum had a certain radioactivity (21 pCi ^{226}Ra) before the application to soil, an increase of radioactivity was not determined in soil or plant material of wheat.

Observed effects on water

In Cyprus, phosphogypsum leaching from landfill was recorded, and NaCl from seawater has accelerated the entire leaching process into the deeper layers (Lyssandrou et al., 2006). Mesić et al. (2007) applied 12 t/ha in the eight-year experiment on two occasions with annual fertilization as follows: 250 kg of N, 150kg of P and 100 kg of K. The amount of leached SO_4^{2-}-S varied between 30.4 kg/ha and 145.5 kg/ha, depending on culture, plants development stage and the intensity and amount of rainfall, but the result of leaching is primarily caused by phosphogypsum. Leached particles can easily be found in waterways, and through the food chain they can eventually reach the human body (Reijnders, 2007). According to a laboratory simulation the application of larger quantities of phosphogypsum can affect the transport of phosphorus to the surrounding water bodies, and it can lead to accelerated eutrophication (Korentajer et al., 1991). In Croatia Bituh et al. (2012) conducted a research in the area of a landfill in Kutina and according to the results obtained through the analysis of leachate samples, higher levels were not obtained. After 1998 when direct discharge of waste waters was banned in the area of Huelva, Villa et al. (2009) conducted a study on natural disintegration and decontamination of local bodies of water. They conclude that ^{226}Ra and ^{210}Pb disintegrate with a half-life period of 6 and 3.5 years, respectfully, without negative effect and that they approximate natural radioactivity in the environment but they have not yet reached it.

Other effects

Hentati et al. (2015) warned of negative effect of even the slightest addition of phosphogypsum on Water flea (*Daphnia magna*) and caterpillar (*Eisenia andrei*), with acute (immobilization) and chronic (reproduction inhibition) symptoms. They found that regardless of the presence of some heavy metals, the cause of these symptoms is extremely high concentration of Ca (at 25.6% PG the concentration of Ca is 545-650 mg/L, depending on the medium). Haridasan et al. (2001) and Heijde et al. (1988) examined the effect on diet of fish from bodies of water near the phosphogypsum landfill and their results (18μSv and 20-25μSv) indicated insignificant effect of radiation through food chain. Fluoride concentrations in phosphogypsum often have a wide range, depending on the origin of phosphate ore. The concern with fluoride is the possible development of fluorosis (a bone and tooth disorder) in grazing animals from consuming plants with high concentrations of fluoride (Richardson, 1993). The use of phosphogypsum in composting is interesting, and Yang et al. (2015) applied 10% of phosphogypsum and recorded a reduction of CH_4 (by 85.8%) and NH_3 (by 23.5%), but also a slight increase of N_2O (by 3.2%). Greenhouse gas emissions were reduced by 17.4%.

Legislative framework

Phosphogypsum is a by-product of phosphoric acid production and according to the Waste Management Strategy of the Republic of Croatia for the period 2007 - 2015 (Official Gazette "Narodne novine" 85/07, 126/10, 31/11, 46/15) it is classified under the waste code 06 09 01. Due to the natural origin, but also its radioactivity that is increased by technological processes, phosphogypsum is classified into the NORM category. Phosphogypsum also contains harmful heavy metals and fluorides, it has a low level of radioactivity and therefore it is subject to constant monitoring of the environmental quality in landfill areas in accordance with the Environmental Protection Act (Official Gazette "Narodne novine" 80/13, 153/13, 78/15), the Ordinance on the methods and conditions of waste disposal, categories and operational requirements for waste landfills (Official Gazette "Narodne novine" 114/15) and the Ordinance on monitoring radioactivity in the environment (Official Gazette "Narodne novine" 121/13). In order to use phosphogypsum in agriculture in the Republic of Croatia, it is necessary to reclassify it into the category of by-products that can only be done after a detailed research in realistic environmental conditions that would also include its effect on all aspects of the environment.

Conclusion

Based on the above it can be concluded that the application of phosphogypsum in agriculture is a very complex issue. The issue of phosphogypsum waste landfills primarily poses an environmental problem. It is known that more than 85% of phosphogypsum ends up in landfills and water. Its disposal is not only a scientific problem, but an economic and a political problem as well. Solving this problem prompted many researches of commercial application of phosphogypsum, one of which is fertilization. According to the aforementioned studies, positive effects of phosphogypsum to soil, water and plants are prevailing. But a small number of studies pointing out possible problems evidently show that every state should conduct their own research corresponding with their agricultural regions and agroecosystems.

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