



Radiological investigation of phosphate fertilizers: Leaching studies



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ABSTRACT

The raw materials of the phosphate fertilizer industry are the various apatite minerals. Some of these have high levels of natural radionuclides, and thus phosphate fertilizers contain significant amounts of U-238, K-40 and Ra-226. These can leach out of the fertilizers used in large quantities for resupplying essential nutrients in the soil and can then enter the food chain through plants, thereby increasing the internal dose of the affected population.

In the current study, the radiological risk of eight commercially available phosphate fertilizers (superphosphate, NPK, PK) and their leaching behaviours were investigated using different techniques (gamma and alpha spectrometry), and the dose contributions of using these fertilizers were estimated. To characterize the leaching behaviour, two leaching procedures were applied and compared –the MSZ 21470-50 (Hungarian standard) and the Tessier five-step sequential extraction method.

Based on the evaluation of the gamma-spectra, it is found that the level of Th-232 in the samples was low ($\max. 7 \pm 6 \text{ Bq kg}^{-1}$), the average Ra-226 activity concentration was $309 \pm 39 \text{ Bq kg}^{-1}$ (min. $10 \pm 8 \text{ Bq kg}^{-1}$, max. $570 \pm 46 \text{ Bq kg}^{-1}$), while the K-40 concentrations (average $3139 \pm 188 \text{ Bq kg}^{-1}$, min. $51 \pm 36 \text{ Bq kg}^{-1}$) could be as high as $7057 \pm 427 \text{ Bq kg}^{-1}$. The high K-40 can be explained by reference to the composition of the investigated fertilizers (NPK, PK). U concentrations were between 15 and 361 Bq kg^{-1} , with the average of 254 Bq kg^{-1} , measured using alpha spectrometry. The good correlation between P_2O_5 content and radioactivity reported previously is not found in our data.

The leaching studies reveal that the mobility of the fertilizer's uranium content is greatly influenced by the parameters of the leaching methods. The availability of U to water ranged between 3 and 28 m/m%, while the Lakanen-Erviö solution mobilized between 10 and 100% of the U content.

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1. Introduction

Given the ongoing requirement for increased food production, the use of phosphate fertilizers is necessary for today's intensive agriculture to achieve high yields. To maintain annual production in agriculture, fields must be cared for and provided with the necessary macro- and micronutrients needed for the particular crop we hope to harvest. To resupply the basic nutrients in soil, nitrogen (N), phosphate (P_2O_5) and potash (K_2O) fertilizers are used in large quantities, sometimes (and especially in rapidly developing countries) leading to their overuse (Mueller et al., 2012).

According to a report by the International Fertilizer Industry Association (IFA), the world's nutrient demand was expected to reach 188 Mt nutrients (N 114.3 Mt, P_2O_5 42.6 Mt, K_2O 31.0 Mt) by

2018/2019, with an average expected annual growth of 1.8% (Heffer and Prud'homme 2014).

Before the industrial revolution, various materials naturally and renewably produced by agriculture and human habitation were used as fertilizers, such as animal manure, crushed animal bones, fish and their remains, human and bird wastes, city waste and ash. With increased food demand, however, these renewable resources proved to be insufficient and a more concentrated, higher quantity source was required. Thus, people turned to mining natural ore deposits and harnessing unique opportunities like the harvesting of guano (piled up bird or bat manure) (Cordell et al., 2009; Van Vuuren et al., 2010).

While N compounds such as saltpetre (KNO_3) were mined, better methods needed to be invented. Since the beginning of the 20th century, the Haber-Bosch synthesis has provided an N source for fertilizer production using a process of N_2 fixation from air. Novel methods attempt either to improve the existing technology or to create a more efficient nitrogen fixation process (Cherkasov

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et al., 2015). There was a production potential of 152.77 million metric tonnes of N in 2014, and it is predicted that the increase in production capacity will remain ahead of consumption expansion in the near future (Heffer and Prud'homme 2014).

K₂O was traditionally provided by the ash remaining after burning wood, but with the increase of demand production turned to natural salt deposits, salt lakes and brines. Current estimates of known, high-quality reserves of potassium ore range from nine to 20 billion tonnes of K₂O, which are expected to last at least 350 years at current consumption rates; other sources (150 billion tonnes) extend this estimation much further.

Potassium chloride (muriate of potash, MOP) is the main chemical form (95%) of K in potassium fertilizers used in agriculture, due to its high K content (60%), low price, good availability and ease of integration into fertilizer production (Johnston, 2003).

In the case of phosphorus, close to 46.71 million tonnes of P₂O₅ equivalent was mined in 2014, according to the IFA, with increasing yearly demand and slowly dwindling resources. However, recently, some new deposits have been emerging in Africa and Asia, increasing the expected phosphate rock supply to 258 million tonnes in 2018 (Heffer and Prud'homme 2014).

Phosphate rock is the main source of phosphate for the fertilizer industry. The P₂O₅ content varies between 25% and 37%, the higher grades being more desirable. Amongst the existing sources, the leading role is undeniably taken by sedimentary marine deposits (approximately 75%), followed by igneous and weathered deposits (15–20%), while biogenic resources only account for 1–2% of production. Primary phosphate minerals include fluorapatite (Ca₁₀(PO₄)₆F₂), hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂), carbonate-hydroxyapatites (Ca₁₀(PO₄, CO₃)₆(OH)), and francolite (Ca_{10-x-y}Na_xMg_y(PO₄)_{6-z}(CO₃)_zF_{0-4z}F₂₂). The phosphate ores can contain various toxic elements such as fluor (F), cadmium (Cd), arsenic (As), mercury (Hg), chromium (Cr) and lead (Pb), along with radionuclides such as U-238, Ra-226, Th-232, Pb-210, Po-210 (Gupta et al., 2014).

The various phosphate rocks are well known for their elevated levels of natural radionuclides. For example, the typical activities for sedimentary phosphate rock types are between 1500 and 1700 Bq kg⁻¹ for the U-238 decay chain, often in equilibrium (Casacuberta et al., 2011).

During phosphoric acid production, some of these are removed with the phosphogypsum fraction (most of Po-210), some are evenly distributed (Ra-226), while others remain in the phosphoric acid (most of the uranium) and reach the fertilizer. The ratio can vary depending on the technology used in the production (Casacuberta et al., 2011; Olszewski et al., 2015). Since phosphate fertilizers contain excess amounts of radionuclides and heavy metals, their prolonged and extensive use can lead to gradual contamination (Schipper et al., 2011), using this kind of fertilizer could increase the internal and external radiation exposure of humans compared to the original situation.

The leaching properties of the radionuclides are very important to the calculation of the ingestion dose rate as they determine the radionuclides' mobility and thus their availability to the food chain. Plants are able to obtain the necessary macro- (primary: N, P, K, secondary: Ca, S, Mg) and micronutrients (B, Cl, Mn, Fe, Zn, Cu, Mo, Ni, etc.) from soil, yet the quantity of said elements is of great importance. If there are not enough essential elements, such as Zn, Cu, B, Cl, Mo or even Fe, plant growth will suffer (White and Zasoski, 1999). On the other hand, excess amounts of essential and non-essential metals can have a toxic effect and inhibit growth. Radionuclides behave similarly to other elements in their group and are available to plants through similar mechanisms (Gupta et al., 2014).

While some plants are capable of absorbing materials through their leaves and stem, the root zone plays a crucial role in metal

uptake. The metals bound to soil particles or in precipitated form can become available through contact with water, enzymes or organic acids produced by the roots and microbial activity in the soil. The uptake of a particular element is influenced by many factors, such as soil microorganisms, chelating agents and pH changes made by the plant, redox reactions, the transporter proteins of the plants, even the co-transportation or inhibition of other ions (Gupta et al., 2014).

The European Union, despite encouraging efforts towards the standardization of methods, such as the LEAF protocols (Kosson et al., 2014) and the harmonization of protocols for waste evaluation, still does not offer commonly accepted methods for the testing of NORM materials' leaching characteristics. A great variety of tests are reportedly used for this purpose, ranging from single-step batch extractions (Lysandrou and Pashalidis, 2008) to column tests (Nisti et al., 2015) and sequential extraction procedures (Vandenhove et al., 2014), both for regulatory and scientific purposes (Tiwari et al., 2015; Kosson et al., 2014; Hegedűs et al., 2016). The availability of the leaching tests vary greatly, the standards used in the EU have to be bought, while the US EPA standards for leaching (Kosson et al., 2014) and the scientific experimental setups are freely available. The differences and similarities of the available tests have been scrutinized many times in the past and still hold interest (Rauret, 1998; Sahuquillo et al., 2003; Kosson et al., 2014; Vandenhove et al., 2014). Since there is no commonly accepted protocol for the leaching of natural radionuclides, the already existing national protocols for the leaching of heavy metals have been evaluated.

The MSZ-21470-50:2006 Hungarian standard has been selected for this study due to its frequented use in agriculture and by the Hungarian authorities for environmental protection, while the Tessier five-step speciation method reveals information regarding which chemical forms the investigated radionuclides are bound to, and the environmental conditions under which they become mobile.

In this study, uranium was investigated to evaluate the leaching tests, given that it has toxic effect as a heavy metal and its chemical toxicity are considered more harmful to the general population than its radiological hazard (Schipper et al., 2011). It has well-documented toxicity and carcinogenesis in the lungs and kidneys, while recently absorption through the skin is also considered to be a major route of exposure. Additionally, new mechanisms for chemical carcinogenic effects have been proposed, while the UV activation of uranyl ions' DNA strand breaks and uranium-DNA adducts, and mutations can occur (George et al., 2011; Wilson et al., 2014a, 2014b). The dose assessment from ingestion has been included in UNSCEAR 2000 and 2008 reports, based on the International Atomic Energy Agency Safety Series No. 115 (1996).

In addition to the ingestion dose, the assessment of the external dose rate could be reasonable in some cases (e.g., workers). Several approaches can be used during the external dose assessment of phosphate fertilizers. One of the most common methods is to calculate the absorbed dose rates due to gamma radiations in air at 1 m above the ground surface, assuming the uniform distribution of Ra-226, Th-232 and K-40, based on guidelines provided by UNSCEAR (Shahul Hameed et al., 2014; Uosif et al., 2014; Hassan et al., 2016). Using this method means overestimating the radiological risk for the majority of the populace; it may thereby provide an upper limit of the expected excess dose per year with the conservative assumptions made before.

This study aims to assess the radiological characteristics of different types of commercially available phosphate fertilizers by using gamma-spectrometry, complemented by leaching studies of the availability of uranium species contained within them. The results are expected to be useful in the assessment of public doses

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