Sequential extraction for the leachability evaluation of phosphate fertilizers

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ABSTRACT

Reducing or oxidizing conditions or pH changes may enable a fraction of naturally occurring radionuclides present in phosphate fertilizers to eventually be released to the environment.
Knowledge of the leachability of some components of these samples is important to estimate what, if any, contribution is made to the food chain and other water dependent pathways such as drinking water and ground water.
A sequential extraction method consisting of five selective leachings was selected to simulate extreme environmental conditions and a wide range of pH that may occur in time at a site with residual radioactive contamination.

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1. Introduction

It is well known that phosphate fertilizers (P-fertilizers) are essential in agriculture in that they supply nutrients to the farming fields. A constituent of these fertilizers is phosphorus, which is obtained from the treatment of phosphate rocks. By processing phosphate rock to fertilizer, the radioactivity of the ore is transferred to the product and to waste products [1].

The most common P-fertilizers are triple superphosphate (TSP), single superphosphate (SSP), monoammonium phosphate (MAP) and diammonium phosphate (DAP). In the chemical wet process, phosphate rocks (PR) are treated with sulfuric acid, generating in addition to phosphoric acid (PA), a by-product called phosphogypsum (PG) (mostly calcium sulphate). This process can be summarized in the following chemical equation:

$$Ca_{10}F_2(PO_4)_6 + 10H_2SO_4 + 10H_2O \rightarrow 10CaSO_4 \cdot 2H_2O + 6H_3PO_4 + 2HF$$
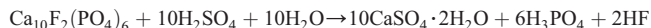
The phosphoric acid produced reacts with phosphate rock in excess giving a final product, monocalcium phosphate (SSP). In the production of TSP, phosphoric acid reacts with apatite.

The chemical fertilizers with ammonium, monoammonium phosphate (MAP) and diammonium phosphate (DAP), are obtained by reacting PA with different amounts of NH_3 [2,3].

The radioactive broad equilibrium that normally exists inside each series (^{238}U and ^{232}Th) in the phosphatic rock is broken during processing and they are partitioned depending on their solubility into phosphoric acid or phosphogypsum: approximately 80% of the radium originally present in the ore is concentrated in the phosphogypsum. In contrast, most of the uranium is extracted with phosphoric acid and enters the final products; consequently, uranium concentrations in P-fertilizers are typically 50% higher than in the original ore. Uranium content of fertilizers can vary according to their phosphate content. Thorium behaviour is dependent upon the chemical reaction and is uniformly distributed in the two reaction products [4,5]. The ^{232}Th series has only a minor contribution to the radioactivity in phosphate compared with the uranium series. In addition, fertilizers contain the naturally occurring ^{40}K [6].

Radionuclides together with some other heavy metals are the primary toxic pollutants for the P-fertilizers. In fact these are dispersed in significant amounts via P-fertilizers. Several long-term field studies showed that surface soils, which received regular P fertilization contained higher uranium concentrations than unfertilized soils; therefore, it is necessary to pay attention to the use of fertilizers in agriculture and its environmental impact. Particularly, the knowledge of the leachability of some component of the P-fertilizers is important to estimate what, if any, contribution is made to food chain and other water dependent pathways such as drinking water and ground water. For the purpose of environment health risk assessment, it is necessary to know how much radioisotopes are available for each of these exposure pathways to humans. The mobility of radioisotopes present in P-fertilizers depends strongly on soil conditions such as the pH, soil moisture, mineralogy and texture [7]. Transient flow conditions in the soil (infiltration, evapotranspiration, and moisture redistribution) furthermore can influence

specific geochemical conditions in the soil (e.g. pH and solid phase reactivity), and thus also affect the mobility of aqueous elements [8].

One experimental approach commonly used to identify the mobility of a given radionuclide in a specific sample is the use of selective sequential extraction procedures. In these techniques, several chemical extractants are sequentially applied to the sample, so the leachability of the radionuclides can be evaluated in each chemical treatment. Many of the techniques used are based on modified sequential extraction protocols. Of these, Tessier's method has been the most widely used both for heavy metals and radio-nuclides [9]. This approach involves successive leaching of the sample using increasingly aggressive treatments, and then each leachate is analyzed for the radionuclide to determine its partitioning. This sequential extraction protocol consists of five operationally-defined fractions which will be further described [9–11].

The research focused on the investigation and the evaluation of the maximum amount of leachable radionuclides present in P-fertilizers as ^{238}U, ^{210}Pb and ^{210}Po which are highly toxic radionuclides; in fact, ^{238}U, ^{210}Pb have long half-lives so they can persist in the environment whereas the persistence of ^{210}Po does not depend from a long half-life (it has only 138.4 days) but because of the presence of the precursor ^{210}Pb (22.3 years). Moreover the solubility of these radionuclides allows them (particularly polonium and in part lead) to cross the gastrointestinal tract barrier of animals and people.

2. Experimental

2.1. Samples

Analysis was carried out on three P-fertilizer samples purchased in stores of central Italy where the local farmers normally buy these products.

Sample 1 is a complex fertilizer (NP) with 32% of P as P_2O_5 and 8% of N. It can be classified as an organic mineral fertilizer as it contains 7.5% of C. It is a concentrated perphosphate or double perphosphate coming from the treatment of phosphoric rock by H_3PO_4 and H_2SO_4 (it presents also 8% of S as SO_3, residue of this treatment). Sample 1 consists of a mixture of calcium phosphates of different solubilities: 26% of $Ca(H_2PO_4)_2$ (soluble in water), 28% of $CaHPO_4$ (soluble in citric acid) and 4% of $Ca_2(PO_4)_2$ (soluble in mineral acid).

Sample 2 can be classified as a superphosphate (TSP) with 52% of P as P_2O_5. It consists of a mixture of calcium phosphates of different solubilities: 42% of $Ca(H_2PO_4)_2$ and 51% of $CaHPO_4$.

Sample 3 can be classified as a diammonium phosphate (DAP). It contains 46% of P as P_2O_5 and 18% of N. This fertilizer, in addition to diammonium phosphate, a very soluble salt, presents a high content of insoluble compounds.

2.2. Determination of ^{238}U, ^{210}Pb and ^{210}Po total concentration

A complete dissolution of the samples is necessary so that the total quantity of ^{238}U, ^{210}Pb and ^{210}Po contained can be compared to the amount of these radionuclides dissolved in the leachant. For this aim it is necessary to treat the sample with a mix of concentrated HCl and HNO_3.

Samples 1 and 2 were divided in two subsamples (1/A and 1/B, 2/A and 2/B), sample 3, as the most abundant, was divided in three subsamples (3/A, 3/B and 3/C).

2.3. Sequential extraction techniques

The sequential extraction protocol consists of five operationally-defined fractions. Extreme conditions were necessary to evaluate the maximum leaching potential for uranium, ^{210}Pb and ^{210}Po [12,13]. These sequential leachings were performed twice on the original sample (10 g) by using the experimental conditions shown in Table 1. Separation of aqueous and solid phases was performed by centrifu-

Table 1
Sequential extraction procedure according to the Tessier method.

Fraction	Extraction reagent (200 mL)	Temperature (°C)	Time (h)
1	0.4 mol L^{-1} H_2O/$MgCl_2$ pH 6.5	25°	1
2	1 mol L^{-1} NH_4Ac/25% HAc pH 4	25°	2
3	0.04 mol L^{-1} NH_2OH HCl/25% HAc pH 2	25°	5
4	30% H_2O_2/0.02 mol L^{-1} HNO_3 pH 2	85	5
5	8 mol L^{-1} HNO_3	25°	1

gation followed by filtration of the supernatant solution using 0.45 μm Millipore filters. A 15:1 reagent to sample ratio (mL extractant/g sample) was adopted for these experiments.

Each filtrate resulting from the leaching experiments was evapo-rated to near dryness and the residue was mineralized with some concentrated HCl and dissolved in 1 M HCl. The final solution was transferred into a 200 mL volumetric flask and different volumes were analyzed for the uranium isotopes, ^{210}Po and ^{210}Pb as described in "Radioanalytical methods".

Sequential extraction procedure can present some problems, such as incomplete selectivity of the extractants, radionuclide re-adsorp-tion and redistribution during the extraction process [11], but, despite its drawbacks, is often used to determine leachability.

To test the reproducibility of the sequential extraction technique, the sample was subdivided in two parts and the sequential extraction procedure was carried out two times, then, for every fraction, the average value of the results obtained in the two sequences was calculated.

2.4. Radioanalytical methods

The natural radioisotope (uranium isotopes, ^{210}Po and ^{210}Pb) determination was carried out by the following techniques.

2.4.1. Uranium

Activity concentration of isotopes alpha emitters of uranium was determined by alpha spectrometry after separation from the matrix [14,15]. This technique requires lengthy preparation and source counting; however, it does have the advantage of being inexpensive, highly sensitive and specific, while providing complete information on concentration and isotopic ratios of ^{238}U, ^{235}U and ^{234}U.

Radiochemical separation of uranium was performed by extrac-tion chromatography. A known activity of ^{236}U as the yield internal standard was added to the solution coming from the sample leaching; then the solution was evaporated and the residue dissolved with 2 M HNO_3. The nitric solution was passed through a column of microporous polyethylene supporting tri-n-octylphosphine oxide (TOPO) and conditioned with 2 M HNO_3. TOPO is a selective extractant in nitric medium for tetravalent and hexavalent actinides (Th, U, Pu, and Np). Thorium was eliminated by column washing with 1 M HCl, then uranium was eluted by 1 M $(NH_4)_2CO_3$ which forms strong uranilcarbonate complexes. First the elution solutions were evaporated, dried and mineralised; then the residue was dissolved in conc. H_2SO_4 and transferred into an electrolytic cell. Uranium was electroplated from ammonium sulphate solution at pH 4; the measurements of uranium alpha isotopes were carried out using an alpha spectrometry system with silicon detectors (Canberra, USA) counting the source for 86,000 s. The mean counting efficiency was $31.7 \pm 3.1\%$. and the background was approximately 2×10^{-6} s^{-1} in the energy region of interest. The mean chemical yield of uranium resulted $66.6 \pm 9.0\%$. The minimum detectable concentration was found to be for ^{238}U 0.1 Bq kg^{-1}.

2.4.2. [210]Polonium

[210]Po was determined by alpha spectrometry because it emits only alpha particles at 5.407 MeV. It is not possible to use the gamma emission of other members of [238]U series because a secular equilibrium for all members of the series cannot be assumed [15,16].

Polonium was deposited at 85–90 °C and pH 1.5–2.0 in a silver disk, placed in a syringe and immersed in continuously for 4 h into a 200 mL of 1 M HCl solution containing 10 mL of 20% hydroxyl-amine hydrochloride and 10 mL of 25% sodium citrate. The silver disk was measured by α-spectrometry. No preliminary separation was required and essentially quantitative recoveries were obtained by using standard [209]Po tracer. The mean chemical yield resulted 72.9±11.5. The minimum detectable concentration was found to be for polonium 0.1 Bq kg^{-1}.

2.4.3. [210]Lead

It is possible to determine indirectly ^{210}Pb by measuring the α or β emissions of its daughters [210]Po or [210]Bi, respectively [16,17]. In this study an indirect method to determine ^{210}Pb was used based on a chemical separation of [210]Bi by reversed phase partition chromatography with a column of microporous polyethylene supporting tri-octyl phosphine oxide (TOPO) and a [210]Bi precipitation as Bi_2S_3, This source was counted with a low background β-detector, repeating the counting during two weeks in order to verify the [210]Bi decay ($T\frac{1}{2} = 5.02$ d).

The 1 M HCl solution coming from the sample leachate was boiled for 5 min with 2 g hydrazine sulphate to reduce iron to Fe(II) and passed through a column of microporous polyethylene-TOPO conditioned with 1 M HCl. After washing with 3 M HCl, bismuth was eluted with 8 M HNO_3. The solution was evaporated to dryness to eliminate HNO_3 and the residue dissolved in 1 M HCl, then 4% thioacetamide was added and cooled to precipitate Bi as Bi_2S_3; filtration was carried out with 0.1 µm Millipore filters with a diameter of 20 mm. The source was counted with a low background beta counter. The purity of [210]Bi source was checked following the [210]Bi decay during two weeks [18]. The mean chemical yield resulted 85.0 ± 5.0%. The minimum detectable concentration was found to be for ^{210}Pb was 1.00 Bq kg^{-1}.

3. Results and discussion

Table 2 shows the total concentration of [238]U, ^{210}Pb and [210]Po for the analyzed samples. The ^{210}Pb and [210]Po concentration are sufficiently similar to indicate the presence of radioactive equilibrium between the two radionuclides but not with [238]U. In fact, the radioactive equilibrium that normally exists between the radionuclides of the series [238]U in the phosphatic rock is broken during processing of P-fertilizer production and they are partitioned depending on their solubility into phosphoric acid (U) or phosphogypsum (Ra, Pb and Po).

Table 3 reports, for all samples, the [238]U, ^{210}Pb and [210]Po activity concentration (Bq kg^{-1}) mean obtained by repeating the extraction procedure twice in the five fractions.

Fig. 1 shows, for the three samples, the percent fractionation obtained for [238]U, ^{210}Pb and [210]Po by the ratio between the mean concentration of every fraction and the total concentration of [238]U, ^{210}Pb and [210]Po. The residue (fraction 6) was obtained by subtracting the sum of the five fractions from the radionuclide total concentration.

As far as uranium is concerned, its leachability is high (87%, 44% and 94% in fractions 1–4, for sample 1, 2 and 3 respectively) therefore reducing or oxidizing conditions or pH changes may introduce an important fraction of this very toxic radionuclide into the environment.

[210]Pb was found almost totally in the fraction 5 (74%, 100% and 86% resulted in 8 M HNO_3 for samples 1, 2 and 3 respectively) indicating

Table 2
[238]U, ^{210}Pb and [210]Po total activity concentration (Bq kg^{-1}) in three P-fertilizer samples.

Sample	[238]U	[210]Pb	[210]Po
1/A	1447 ± 145	376.7 ± 56.5	369.3 ± 55.3
1/B	1440 ± 144	342.9 ± 51.4	245.5 ± 36.8
Mean	1444	359.8	307.4
2/A	2714 ± 271	13.94 ± 2.79	13.06 ± 2.61
2/B	2200 ± 220	15.30 ± 3.06	16.52 ± 3.30
Mean	2457 ± 246	14.62	14.79
3/A	2539 ± 254	385.7 ± 57.8	251.2 ± 37.7
3/B	2349 ± 235	285.6 ± 42.8	354.0 ± 53.1
3/C	2700 ± 270	401.0 ± 60.2	167.0 ± 25.0
Mean	2529	357.4	257.4

Table 3
[238]U, ^{210}Pb and [210]Po activity concentration (Bq kg^{-1}) mean for all samples.

Fraction	Radionuclide								
	Sample 1			Sample 2			Sample 3		
	[238]U	[210]Pb	[210]Po	[238]U	[210]Pb	[210]Po	[238]U	[210]Pb	[210]Po
1	246.42	<1.00	35.0	560.5	<1.00	1.16	108.3	<1.00	4.50
2	784.63	59.82	60.0	264.4	<1.00	1.92	907.1	50.83	189.8
3	145.59	<1.00	3.71	120.5	<1.00	0.93	927.8	<1.00	22.15
4	137.21	<1.00	2.25	135.7	<1.00	0.47	727.9	10.36	2.54
5	188.28	265.7	174.0	636.1	15.86	2.83	174.3	361.44	111.8

association to a mineral phases (es.: phosphate) soluble only at conditions of high acidity.

[210]Po presents a solubility higher than ^{210}Pb but lower than [238]U; 67%, 70% and 34% of this radionuclide was found in fractions 5 and 6 for samples 1, 2 and 3 respectively.

The low availability of ^{210}Pb and [238]U present in these samples leads to the conclusion that their presence in the environment is not dangerous for ingestion pathway, but only for inhalation of the particulated materials.

4. Conclusions

The leaching potential of uranium, ^{210}Pb and [210]Po is an important factor for risk assessment calculations involving environment treated by P-fertilizers.

As far as uranium is concerned, its leachability is very high: the mean value for the three different samples was 75% in fractions 1–4, therefore reducing or oxidizing conditions or pH changes may enable a fraction of these very toxic radionuclides to eventually be released to the environment.

[210]Pb was found almost totally in fraction 5 (8 M HNO_3) indicating that it is associated with the mineral phases (e.g.: phosphate) soluble only at conditions of high acidity. In any case, the results obtained show that the solubility of [210]Po is higher than ^{210}Pb but lower than uranium. The low availability of lead and polonium present in P-fertilizers leads to the conclusion that their presence in the environment is not dangerous for the ingestion pathway, but only for inhalation of the particulate materials.

The fractionation measurements do not provide any kinetic information and cannot be interpreted in terms of time. Therefore, once chemical equilibrium is achieved, the particle size of the sample and the duration of the method of agitation will have little, if any, effect on the results. In any case the described sequential treatment provides considerably more information than simply determining the total quantity of the three radionuclides.
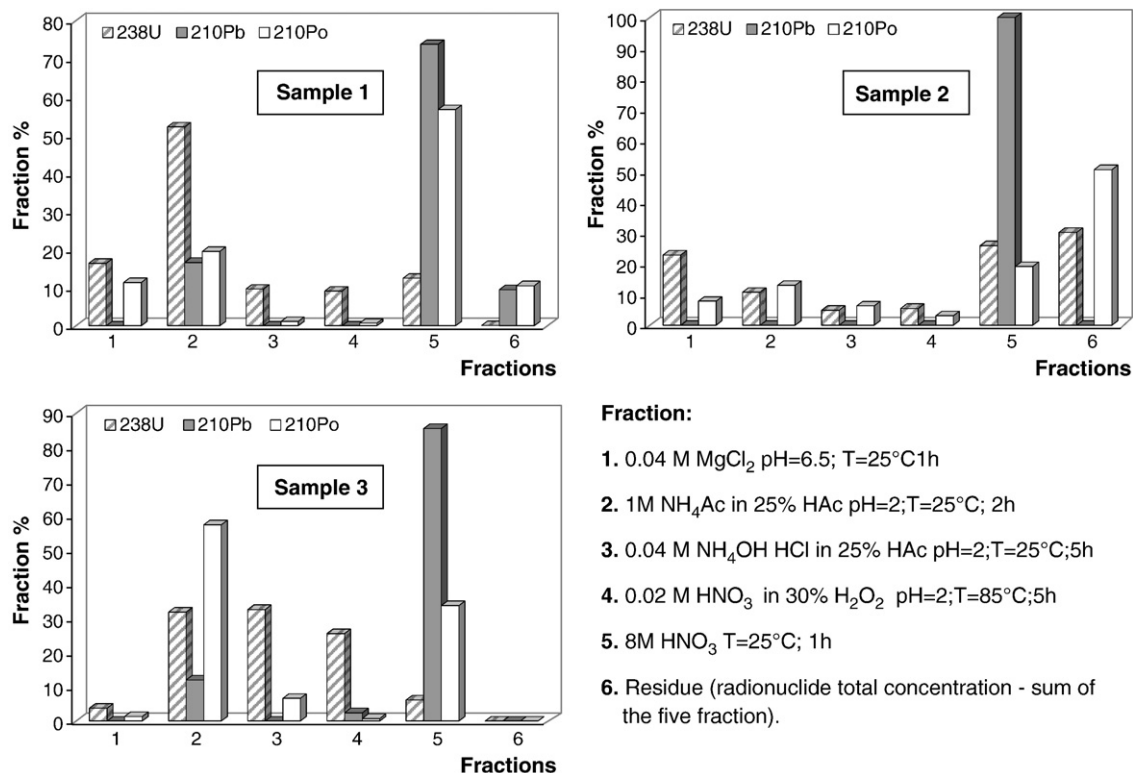
Fraction:

1. 0.04 M MgCl$_2$ pH=6.5; T=25°C1h

2. 1M NH$_4$Ac in 25% HAc pH=2;T=25°C; 2h

3. 0.04 M NH$_4$OH HCl in 25% HAc pH=2;T=25°C;5h

4. 0.02 M HNO$_3$ in 30% H$_2$O$_2$ pH=2;T=85°C;5h

5. 8M HNO$_3$ T=25°C; 1h

6. Residue (radionuclide total concentration - sum of the five fraction).

Fig. 1. Percent fractionation (ratio between the mean concentration of every fraction and the total concentration) of ^{238}U, ^{210}Pb and ^{210}Po for all samples.

The results are likely to be of interest for use in the local environmental risk assessment and in health impact estimation due to ^{238}U, ^{210}Pb and ^{210}Po present in P-fertilizers used in agricultural practices.

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