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Evaluating radiation risks and resource opportunities associated with phosphogypsum in the Philippines

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Abstract

Phosphogypsum (PG) accumulates during wet-phosphoric acid production for fertilizers. In the Philippines, PG is partly (40%) utilized to produce gypsum walls and cement. This work assesses the radiological risks and resource opportunities associated with PG stacks in the Philippines. The conducted in situ radiometric survey measured the activity concentrations of ^{40}K, ^{238}U, and ^{232}Th at 270 locations. Besides, another 120 surface samples were collected. Pure PG exceeds the recommended radiation limits, but simple dilution with conventional materials can make PG available as an inexpensive secondary raw material for construction. PG further contains relevant concentrations of rare earths and Y (195 ppm).

Keywords Phosphogypsum · Radiological risk assessment · Heavy metals · Rare earth elements (REEs) · Circular economy · Secondary resources

Introduction

More than three quarters of phosphate fertilizers produced globally are produced from phosphate rock (PR) using phosphoric acid (PA) as an intermediate product, leaving 4–6 t low-radioactive phosphogypsum (PG) per t P_2O_5 produced, as relevant and potentially hazardous by-product/waste behind [1, 2]. About 85% of the 5.6–7.0 billion t PG produced globally over the lifetime of the phosphate industry are disposed of in stacks in more than 50 countries worldwide. 3–4 billion t are accessible for recovery worldwide [3] while some fresh 100–280 million t PG are added to existing stacks every year [4–6]. The relatively low radioactivity concentrations (0.2–3 Bq/g for ^{226}Ra) present in most PG does not allow using the material under most national regulations today [7]. The complete purification of PG from Ra is challenging as the Ra is chemically very similar to Ca making separation from the PG matrix complicated, inefficient, and thus costly, mitigating the direct use of PG as an otherwise inexpensive building material or soil amendment [8]. Besides Ra, PG contains considerable amounts of heavy- and light rare earth elements (REEs) associated with the processed phosphate ores [9].

During PA production nearly 80% of ^{226}Ra and 60–90% of the REEs transfer to the PG [10–14] while nearly 86% of ^{238}U and 70% of ^{232}Th transfer to the PA [5, 15]. The occurrence of radionuclides in PG can be traced to the abundance of Ca in the PR that can substitute radionuclides with similar ionic radius such as U and Th [16, 17]. ^{226}Ra that is a decay product of ^{238}U is the major source of radioactivity among the different radionuclides found in PG [18]. ^{226}Ra further decays to the dense radioactive noble gas ^{222}Rn that is accountable for much of the hazards associated with ^{226}Ra [19, 20]. Numerous studies have also reported elevated concentrations of heavy metals [21, 22] and REEs [23, 24] in PG.

Hakkar et al. [25] estimated that REEs associated with PR production from Morocco alone could substitute some 7–15% of the global REE demand while mitigating adverse

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environmental effects [26] associated with traditional REE mining. Recovering REEs during PR processing could further provide additional supply security to non-REE mining countries [27, 28]. REEs recovery from PG is an active field of research today [29, 30] and even led to nearly a dozen pilot plant operations that have been reviewed by Al Khaledi et al. [31] and Wu et al. [32]. In addition, Ramirez et al. [33] recently reviewed the economic potential of REEs associated with PG in the Philippines.

There are currently an estimated 10.1 million t PG in tailing ponds in the Philippines that have been accumulated in fertilizer production since 1984. Remarkably, the Philippines do not mine phosphate ores and very different sedimentary PR from China, Egypt, Israel, Jordan, Peru, Tunisia, the USA, and Vietnam as well as igneous PR from Russia and South Africa have been imported and processed over the years. Igneous and sedimentary PR show very different concentrations of accompanying trace elements such as REEs that can reach concentrations of 2% in igneous PR while the concentrations are usually lower in sedimentary PR and uranium that can show concentrations of 0.02% in sedimentary PR but are usually below 0.005% in igneous PR. Nearly 40% of the currently produced PG is already used in cement production and as soil conditioner in the Philippines today. Despite several works detailing the occurrence of radionuclides in Philippine PG [24, 34], knowledge of potential risks associated with the use of the Philippine PG as additives in construction materials is not well-understood yet. This mitigates further unobjectionable utilization of PG as an inexpensive secondary resource.

This study aims to assess the potential risks associated with the radionuclides and heavy metals in Philippine PG through a combination of an in situ ground radiometric survey and chemical analysis. The study is expected to provide important baseline information for the creation of policies related to upcycling and further utilization of PG in the Philippines and elsewhere. Such practice holds the promise of minimizing the environmental and economic risks associated with PG stacking in a region prone to typhoons.

Materials and methods

Description of the PG ponds

There are a total of eight PG ponds with no distinct boundaries at the main fertilizer plant in the Philippines that are shown in Fig. 1. A total of 270 data points in a 25 m × 25 m grid on the surface of the tailing ponds were assessed for ^{40}K, ^{238}U, and ^{232}Th using Bismuth Germanate Oxide (BGO) portable gamma spectroscopy. In addition, 120 surface PG samples were analyzed for heavy metals and REEs using atomic emission spectroscopy. The results of the survey and chemical analysis were compared to literature data of various PG stacks and international regulatory limits.

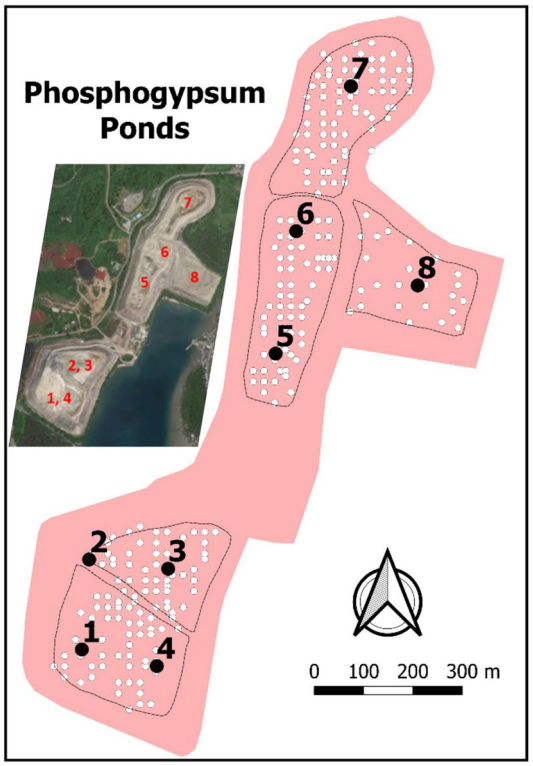

Fig. 1 Distribution map and aerial view of the investigated PG ponds with the location of the 270 radiometric data points

In situ ground radiometric survey

An in situ radiometric survey of naturally occurring radionuclides ^{40}K, ^{232}U, and ^{238}Th was carried out on the surface of the ponds using portable gamma ray spectrometers (Radiation Solutions RS 230) equipped with 103 cm^3 BGO detectors. K was measured through the detection of 1,461 keV gamma rays emitted by its isotope ^{40}K, U was measured through the detection of 1,765 keV gamma rays of ^{214}Bi, a decay product of ^{238}U, and Th was measured through the detection of 2615 keV gamma rays of ^{208}Tl, a decay product of ^{232}Th. The measured concentrations assume radioactive equilibrium in the U and Th decay series. The reliability of the spectrometer was pre-validated using a set of 1 m × 1 m × 30 cm concrete standard calibration pads: one background pad and three pads salted with known concentrations of ^{40}K, ^{238}U, and ^{232}Th, prior to the field measurements. A total of 270 measurements using a 25 m × 25 m grid space on the ponds surface (Fig. 1) were taken for activity concentrations of ^{40}K, ^{232}U, and ^{238}Th using three measurement trials each time.

Surface sample collection, preparation, and analysis

PG samples were also collected from the 270 measurement locations during two fieldtrips in September 2018 and June 2019. Approximately 2 kg of PG were collected per sample from the upper 0.2 m of the ponds and then stored in plastic bags. The collected samples were then dried in an oven at 60 °C for 24 h.

The concentrations of the REEs (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y) and seven heavy metals (As, Cd, Cr, Cu, Ni, Pb, and Zn) in the 120 PG samples were determined using inductively coupled plasma mass spectrometry (ICP-MS) on an Agilent 7700 and inductively coupled plasma optical emission spectrometry (ICP-OES) on an Agilent 5100. The samples were digested using a combination of analytical grade HCl, HNO_3, HF and $HClO_4$.The detection limits for REEs ranged from 0.05 to 0.1 mg kg^{-1} and that of heavy metals from 0.05 to 2 mg kg^{-1} respectively. A blank solution and certified reference materials (OREAS 501c, 600, 623 90, and 44P) were analyzed for analytical control and validation.

Radiation hazard indices

Around 40% of the PG produced by the fertilizer plant is currently utilized as additives for cement production and as soil conditioner. To assess the risks associated with K, U, and Th in the PG, several radiological risk assessments were performed that are commonly used to assess the potential public exposure and usability of materials with elevated radionuclide concentrations in construction. Specifically, these were the radium equivalent activity (Ra_{eq}), the gamma specific activity index (I_γ), the external hazard index (H_{ex}), the internal hazard index (H_{in}), the absorbed gamma dose rate (D_{air}), and the annual effective dose equivalent (AEDE).

Radium equivalent activity (Ra_{eq})

The radiological hazards associated with the radionuclides in PG was assessed using the activity concentrations of ^{40}K, ^{238}U, and ^{232}Th and the Ra_{eq} (1).

$$Ra_{eq}\left(Bq\ kg^{-1}\right) = A_U + 1.43A_{Th} + 0.077A_K < 370 \quad (1)$$

A_U, A_{Th}, and A_K are the activity concentrations in Bq kg^{-1} of ^{238}U, ^{232}Th, and ^{40}K. A Ra_{eq} of 370 Bq kg^{-1} is equivalent to the allowable annual dose rate for the general public [35].

Gamma hazard index (I_γ)

The external gamma radiation from the decay of radionuclides is also a major hazard. To assess whether the PG meets the regulatory standards for gamma radiation, we determined the I_γ according to (2).

$$I_\gamma = \frac{A_U}{300} + \frac{A_{Th}}{200} + \frac{A_K}{3000} \quad (2)$$

I_γ values of ≥ 6 correspond to an annual gamma dose rate of 1 mSv y^{-1} [35].

External (H_{ex}) and Internal (H_{in}) hazard indices

The estimation of gamma ray exposure of an individual is done using the H_{ex}. An internal hazard through ingestion and inhalation of radon and other radionuclides is also a major concern. The estimation of gamma radiation exposure through the aforementioned exposure pathways is possible using the H_{ex} and H_{in} that were determined using (3) and (4), respectively.

$$H_{ex} = \frac{A_U}{370} + \frac{A_{Th}}{259} + \frac{A_K}{4810} \leq 1 \quad (3)$$

$$H_{in} = \frac{A_U}{185} + \frac{A_{Th}}{259} + \frac{A_K}{4810} \leq 1 \quad (4)$$

H_{ex} and H_{in} should be less than 1 or the unity which is equivalent to an external dose rate of 1.5 mGy y^{-1} [35].

Absorbed gamma dose rate (D_{air})

The D_{air} is used to measure the amount of radiation from the radionuclides that an individual receives at a given time. It is calculated using (5).

$$D\ (nGy\ h^{-1}) = 0.462\ A_U + 0.604\ A_{Th} + 0.0417\ A_K \quad (5)$$

The D_{air} of the PG ranges from 47.1 to 805.2 nGy h^{-1} with a mean of 315.3 nGy h^{-1}. The mean D_{air} exceeds the world average D_{air} of 59 nGy h^{-1} [35].

Annual effective dose equivalent (AEDE)

The AEDE is the estimated dose received by an individual over the course of a year. The AEDE of an individual exposed outside to the relevant radionuclides is provided in (6),

$$AEDE\ (Sv\ h^{-1}) = D\ (nGy\ h^{-1}) \times 8760\ h \times 0.2 \times 0.7\ Sv\ Gy^{-1} \times 10^{-3} \quad (6)$$

where D is the dose rate (D_{air}), 8760 h is the number of hours in a year, 0.2 is the outdoor occupancy factor, and 0.7 Sv Gy^{-1} is the conversion coefficient from absorbed dose in air to effective dose received by adults. The mean AEDE of the PG is 386.7 μSv y^{-1} which exceeds the world average AEDE of 70 μSv y^{-1} [35].

Heavy metal risk indices

PG contains a number of heavy metals. Due to the absence of heavy metal risk indices for industrial waste by-products existing indices that are frequently used to assess heavy metal pollution in soils and sediments are used in this work. Specifically, the single pollution index (SPI), the pollution load index (PLI), and the potential ecological risk index (PERI) were considered.

Single pollution index (SPI)

The SPI is a direct comparison of the metal concentration to background levels. It is calculated following (7),

$$\mathrm{SPI} = \frac{C_n}{B_n} \tag{7}$$

where C_n is the metal concentration and B_n is the background or reference concentration of the same metal. The average heavy metal concentrations in the Earth's upper continental crust was used as reference concentrations [36]. The qualitative ratings of the SPI are as following: ≤ 1 no pollution, 1–2 low level of pollution, 2–3 moderate level of pollution, 3–5 strong level of pollution, and ≥ 5 very strong level of pollution.

Pollution load index (PLI)

To assess the overall degree of heavy metal contamination in the PG, we used the PLI that combines the SPI of the individual heavy metals into a single measure according to (8) [37].

$$\mathrm{PLI} = \sqrt[n]{\mathrm{SPI}_1.\mathrm{SPI}_2.\mathrm{SPI}_3 \ldots \mathrm{SPI}_n} \tag{8}$$

A PLI < 1 signifies no heavy metal pollution, 1 is the baseline of pollution, and > 1 indicates that a material is polluted.

Potential ecological risk index (PERI)

The PERI is the most used index to assess the ecological risks of toxic metals in sediments. It measures the vulnerability of organisms to heavy metal contamination and is expressed through the potential toxicity response index (RI) (9) of various heavy metals in the considered sediments.

$$RI = \sum_{i=1}^{n} Er^i = \sum_{i=1}^{n} Tr^i \times Cf^i \tag{9}$$

Er^i is the potential ecological risk factor of the heavy metal, Tr^i is the biological toxic response factor of the heavy metal (Tr^i: Cd = 30, As = 10, Cu, Ni, Pb = 5, Cr, V = 2 and Zn = 1), and Cf^i is the contamination factor of the individual heavy metal [38]. RI is rated as < 150 low risk, 150–300 moderate risk, 300–600 considerable risk, and > 600 very high risk. The mean RI of the individual heavy metal is classified as < 40 low risk, 40–80 moderate risk, 80–160 considerable risk, 160–320 high risk, and > 320 very high risk.

Results and discussion

Radiometric survey and radiological risk assessment

The in situ radiometric survey determined the activity concentrations of ^{40}K, ^{232}Th, and ^{238}U at 270 locations in the Philippine PG ponds. The results of the activity concentrations of the radionuclides in the ponds is provided in Table 1. The relatively high standard deviation and range of activity concentrations of ^{40}K, ^{238}U, and ^{232}Th in the PG ponds indicate varying radioactive characteristics in each pond which could be attributed to the processing of more than ten different types of PR at the fertilizer plant. It was further found that the mean ^{40}K and ^{232}Th concentrations are within the world average activity concentrations in soil while the concentration of ^{238}U is 18.7 times higher than the world median activity concentration in soil reported by the United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) [35]. Uranium can be recovered as a by-product during PR processing to PA and ultimately mineral fertilizers [39]. This practice provided nearly 20% of domestically produced uranium in the United States

Table 1 Results of the activity concentrations of ^{40}K, ^{238}U, and ^{232}Th from the 270 sample locations in Philippine PG

	^{40}K (Bq kg^{-1})	^{238}U (Bq kg^{-1})	^{232}Th (Bq kg^{-1})
Mean	84.8	655.8	14.5
Standard deviation	58.9	228.3	6.7
Minimum	0.0	87.8	1.6
Maximum	328.7	1684.8	36.0
World median activity concentrations in soil [35]	400	35	30

in the late 1980s early 1990s before it became uneconomic [40] and might still be useful to increase supply security at locations that process PR with elevated uranium concentrations [41–43]. It is worth noting that if uranium is recovered, it is usually recovered from the PA so that the ^{238}U concentration in the PG remains unchanged. The elevated concentrations of ^{238}U in the Philippine PG show that innovative processes that could not only recover uranium but reduce the uranium concentration in the PG are most desirable, as they would allow the direct use of PG in construction and as soil amendment.

To assess the risks of utilizing PG in industrial applications, several radiological risk assessments commonly used to assess the safety of materials with radionuclides for construction were performed. The statistics of the radiological risk assessments are summarized in Table 2. The Ra_{eq} of the PG ranged from 101.9 to 1742.3 Bq kg^{-1} with a mean of 683.1 Bq kg^{-1}, which exceeded the allowable Ra_{eq} of 370 Bq kg^{-1} equivalent of the allowable annual dose rate for the general public [35]. On the other hand, it was found that the mean I_γ of 2.3 was less than the allowable maximum value of 6. $I_\gamma \leq 6$ corresponds to an annual dose rate of 0.3 mSv y^{-1}. The I_γ of the PG ranged from 0.3 to 5.8 which is within the safe limits for gamma radiation [35]. In addition to I_γ meeting the regulatory standards, it is also important to understand how the gamma radiation affects an individual. The mean (range) of the H_{ex} and the H_{in} of the PG were 1.8 (0.3–4.7) and 3.6 (0.5–9.3), respectively. These are considerably higher than the unity of 1. The mean values of the D_{air} and the AEDE of the PG were 315.3 nGy h^{-1} and 386.7 μSv y^{-1} and ranged from 47.1–805.2 nGy h^{-1} and 57.7–987.5 μSv y^{-1} respectively. Both the D_{air} and the AEDE exceeded the world median activity concentration in soil reported by the UNSCEAR [35].

The results of the radiological assessments consistently indicate that the ^{40}K, ^{238}U, and ^{232}Th concentrations in Philippine PG exceed the allowable safety limits for industrial use. It is important to note that in the application of PG as raw material in cement production and as replacement for natural gypsum in the Philippines, only a small fraction is being added to significantly lower the radiological hazards, to avoid unreasonable public exposure and to not compromise the mechanical stability of the final product. For instance, in Portland cement production, 5–10% PG can be added to cement clinker producing a mixture that still shows promising results in terms of setting time, flow, and compressive strength behavior [44]. In the manufacturing of fired clay bricks, 30% PG can be added with the resulting material still satisfying the standard requirements [45]. Other remedial measures to limit radiation public exposure in these applications is to simply dilute or mix batches of relatively high and low radioactive PG [46].

Table 2 Results of the radiological risk assessments from the 270 sample locations in Philippine PG

	Ra_{eq} (Bq kg^{-1})	I_γ	H_{ex}	H_{in}	D_{air} (nGy h^{-1})	AEDE (μSv y^{-1})
Mean	683.1	2.3	1.8	3.6	315.3	386.7
Standard deviation	235.0	0.8	0.6	1.3	108.6	133.2
Minimum	101.9	0.3	0.3	0.5	47.1	57.7
Maximum	1742.3	5.8	4.7	9.3	805.2	987.5
World median activity concentrations in soil [35]	370	6	1	1	59	70

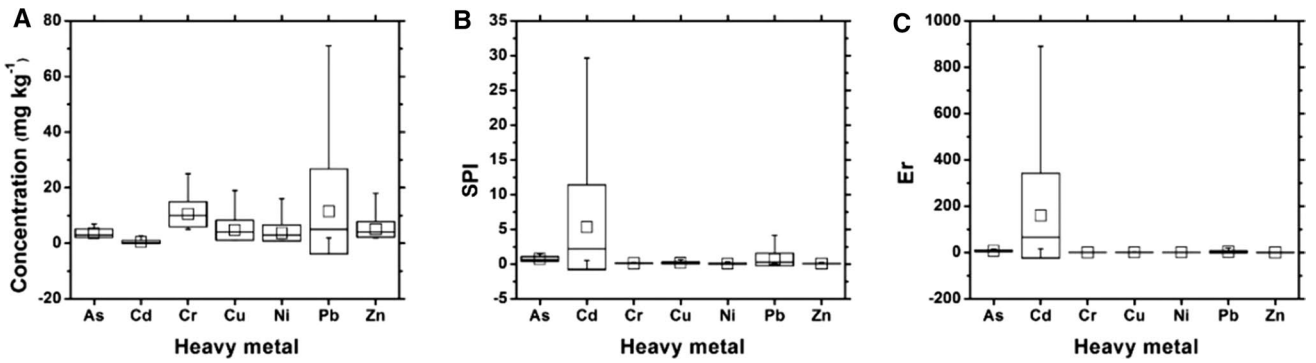

Fig. 2 The statistics of the **a** heavy metal concentration, **b** SPI, and **c** Er showing the mean (□), standard deviation (box), and the range (whiskers)

Heavy metal risk assessment

A total of 120 surface PG samples were analyzed for heavy metals using ICP-OES. The analysis revealed concentrations of As (2 mg/kg), Cd (0.05 mg/kg), Cr (5 mg/kg), Cu (1 mg/kg), Ni (1 mg/kg), Pb (1 mg/kg), and Zn (1 mg/kg) that were often below the detection limit of 1 mg/kg. A summary of statistics of heavy metals measured within the detection range is shown in Fig. 2a. Among these heavy metals it was found that Pb was the most relevant with mean concentrations of 11 mg/kg and a range from 2–71 mg/kg.

The SPI of the individual heavy metals is shown in Fig. 2b. The mean SPI indicates that there is no heavy metal pollution associated with As (0.76), Cr (0.11), Cu (0.17), Ni (0.08), Pb (0.67), and Zn (0.08) but there is a very strong level of pollution with respect to Cd (5.31). On the other hand, however, the synergistic effects of the heavy metals measured using the PLI with a mean of 0.29 ($<<1$) signifies no overall heavy metal contamination in the PG. Moreover, there is an overall low ecological risk associated with the heavy metals in PG as indicated by the mean RI (145.9). The mean Er of the individual heavy metals (Fig. 2c) shows that As (7.6), Cr (0.2), Cu (0.8), Ni (0.4), Pb (3.4) and Zn (0.1) present low risks while Cd (159.4) presents considerable risk. It is worth noting that mobility of these elements, particularly Cd (1%), is very low, thus, preventing significant amount of it leaching from the PG ponds to the groundwater and to the surrounding environment [47].

The results of the heavy metal risk assessments consistently indicate that there is generally a low contamination and ecological risk associated with the heavy metals found in PG in the Philippines.

Critical metal assessment

The 120 PG samples were also analyzed for valuable critical metals, particularly REEs using ICP-MS. Previous studies about REEs in PG reported enriched concentrations [23, 48–52] that may justify REE recovery. Table 3 summarizes the REE concentrations of the surface PG samples along with the previously published REE concentrations from trenches in the ponds recently published by Ramirez et al. (2021). The REE concentrations measured in the Philippines are further compared with REE concentrations of PG stacks in various other countries. Among the major REEs, the compositional abundance is Ce (26.3%) > La (20.9%) > Nd (17.9%) > Y (12.7%). Previous analysis of the economic potential of the REEs in the PG ponds [33] estimated the presence of 2,678 t rare earth oxides (REOs). For reference, the world's REO mine production is currently 240,000 t per year [53]. Although there are available technologies to extract the REEs from PG, doing so in the Philippines seems to be particularly unpromising as a result of the comparatively low REEs content when compared to other PG stacks as was done in Table 3. The PG taken into account in Table 3 is all derived from processing sedimentary PR that shows much lower average REE concentrations than those found in igneous PR. It is likely that the Philippines will continue processing predominantly sedimentary PR that presently accounts for more than 80% of global phosphate rock production, and all the PR processed in the Philippines in recent years.

Table 3 Average REE concentrations in PG from various origins

REE	This study	Philippines	Canada	Florida	Florida	Morocco	Spain	Togo	Tunisia
Reference		[33]	[23]	[50]	[52]	[25]	[51]	[18]	[49]
La	40.7	43.8	58	72.6	36.38	38	62	41	35.86
Ce	51.1	65.7	55	87.8	63.84	21	36	54.8	49.99
Pr	8.29	9.25	6	6.7	5.01	8	11	9.5	8.9
Nd	34.9	40.5	46	43.2	45.13	28	48	41.4	52.63
Sm	7	7.7	22	2	0	6	9.2	7.7	7.14
Eu	1.6	1.7	3	2.1	1.4	1	1.8	1.8	1.68
Gd	8	9	10	6	6.87	9	12	9.1	7.2
Tb	1.06	1.09	1	6.6	0.14	1	1.8	1.3	1.1
Dy	7.2	7.6	8	8.4	6.41	8	13	7.3	6.62
Ho	1.5	1.5	2	4.7	0.91	2	3	1.54	1.32
Er	4.4	4.4	8	6	4.35	5	8.9	4.4	3.89
Tm	0.5	0.5	–	1.1	2.26	1	1.1	0.6	0.47
Yb	3.3	3	6	7.6	2.02	4	7.2	2.7	3.31
Lu	0.45	0.45	1	0.61	0	1	1	0.32	0.34
Y	24.7	69.7	116	79.5	43.36	81	129	80	44.48
Σ REE + Y	194.69	266.15	342	334.91	218.08	213	345	263.46	224.93

Conclusions and recommendations

Heavy metal concentrations in Philippine PG are an exceedingly low risk and REE concentrations will most likely not allow for economic recovery. ^{40}K, ^{238}U, and ^{232}Th associated with PG measured at 270 locations exceeded the recommended safe limits for direct use and simple dilution with non-radioactive material is suggested here to fully utilize the PG stacks in the Philippines and thus eliminate risks associated with PG stacking.

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