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Estimation of the Environmental Impact of the phosphogypsum stockpile in the Schistos waste site (Piraeus, Greece) using a combination of laboratory techniques and GIS

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Abstract

The present study was conducted in collaboration with the Environmental Association of Municipalities of Athens - Piraeus (EAMAP). The purpose of the present study was the determination of the radionuclides concentrations of the phosphogypsum deposited in the Schistos waste site (Piraeus, Greece), as well as the study of potential radiation release to the surrounding environment. Sampling was carried out in collaboration with EAMAP, using GPS, in order to record the exact location of each sampling site. Afterwards, several laboratory and analytical techniques were employed to characterize the phosphogypsum and soil samples collected from the deposit and the surrounding environment. These techniques included powder-XRD, XRF, SEM-EDS and γ -ray spectrometry using a HPGe detector. In addition, laboratory experiments, such as TCLP procedure and leaching experiments using rainwater from the Attica region, were conducted.

Finally, the experimental results obtained from the γ -ray spectrometry were distributed in maps created using GIS (Geographic Information Systems). The resulted maps showed the radionuclides distribution in our studied area and the potential hazard. The distribution indicated the existence of an area, in which the radionuclides, more specifically the most imporant ²²⁶Ra, show elevated concentrations. This can be attributed to the fact that phosphogypsum is exposed at the time in the studied area.

Key words: phosphogypsum, ²²⁶Ra, radioactivity distribution, GIS maps

<u>Περίληψη</u>

Η παρούσα διπλωματική εργασία πραγματοποιήθηκε σε συνεργασία με τον Περιβαλλοντικό Σύνδεσμο Δήμων Αθηνών - Πειραιώς (ΠΕΣΥΔΑΠ), που διαχειρίζεται την απόθεση της φωσφογύψου στο Σγιστό. Σκοπός της παρούσας εργασίας ήταν ο προσδιορισμός των συγκεντρώσεων των ραδιονουκλιδίων που περιέχονται στην φωσφογύψο που έχει αποτεθεί στον αποκατεστημένο ΧΑΔΑ Σχιστού, καθώς επίσης και η μελέτη ενδεχόμενης διαφυγής ραδιενέργειας στο περιβάλλον. Αρχικά, πραγματοποιήθηκε δειγματοληψία με χρήση GPS, δειγμάτων φωσφογύψου, δειγμάτων εδάφους από την γύρω περιοχή και δειγμάτων εδάφους από το κάλυμμα της απόθεσης. Στη συνέγεια, έγινε εφαρμογή πλήθους εργαστηριακών και αναλυτικών τεχνικών με σκοπό τον προσδιορισμό της συγκέντρωσης του ²²⁶Ra στα συλλεγμένα δείγματα, αλλά και τη μελέτη της ενδεχόμενης διαφυγής του στο περιβάλλον. Εφαρμόστηκαν αναλυτικές μέθοδοι όπως powder-XRD, XRF, SEM-EDS και φασματοσκοπία ακτίνων γ. Τέλος, εφαρμόστηκαν εργαστηριακές τεχνικές, όπως η μέθοδος της TCLP αλλά και τεστ έκπλυσης με νερό βροχής. Αφότου, έγινε προσδιορισμός των συγκεντρώσεων ραδιενέργειας στον αποκατεστημένο ΧΑΔΑ Σχιστού, δημιουργήθηκαν ψηφιακοί χάρτες της περιοχής, με χρήση Γεωγραφικών Συστημάτων Πληροφοριών (GIS), ούτως, ώστε να απεικονιστεί η κατανομή των συγκεντρώσεων στην περιοχή μελέτης. Από τα αποτελέσματα γίνεται εύκολα κατανοητό ότι οι τιμές της ραδιενέργειας εμφανίζονται αυξημένες στην περιοχή της απόθεσης που έχει αποκαλυφθεί και εμφανίζεται εκτεθειμένη η φωσφογύψος.

Λέξεις κλειδιά: φωσφογύψος, ²²⁶Ra, κατανομή ραδιενέργειας, Χάρτες GIS

1.Introduction

1.1 Phosphogypsum in general

Phosphogypsum (PG) is the main by-product generated during the wet-process manufacture of phosphoric acid by treating phosphate rock (raw material) with sulphuric acid according to the following reaction: (Fukuma et al., 2000; Haridasan et al.,2002; Abdel-Aal, 2004; Papastefanou et al., 2006; Perez-Lopez et al., 2007; Bituh et al., 2009; Silva et al., 2010; Al Hwaiti et al., 2010; Villalobos et al., 2010; Zielinsko et al., 2011; Chauhan et al., 2013)

$Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 + 20H_2O \rightarrow 6H_3PO_4 + 10CaSO_4 \cdot 2H_2O + 2HF$ (1)

Wet processing causes the selective separation and concentration of naturally occurring radium (Ra), uranium (U) and thorium (Th). 80% of ²²⁶Ra is concentrated in PG while nearly 86% of U and 70% of Th end up in the phosphoric acid. (Taybi et al., 2009) PG is a powdery material that has little or no plasticity, and is mainly composed by dihydrated calcium sulfate (CaSO₄·2H₂O) and fluorosilicate (Na₂SiF₆) (Berish, 1990; Kacimi et al., 2006), but it also contains impurities, such as H₃PO₄, Ca(H₂PO₄)₂·H₂O, CaHPO₄·2H₂O + Ca₃(PO₄)₂, residual acids, fluorides (NaF, Na₂SiF₆, Na₃AlF₆, Na₃FeF₆, CaF₂), sulphate ions, trace elements (Cd, Cr, Cu and Zn), organic matter as aliphatic compounds of carbonic acids, amines, ketones adhered to the surface of gypsum crystals (Rutherford et al., 1996). Its mineralogical composition is fluorapatite $[Ca_{10}F_2(PO_4)_6:CaCO_3]$, goethite, quartz (dominated), with minor amounts of Al-phosphates, anatase, magnetite, monazite, barite, cadmium and nickel. Phosphogypsum's chemical composition differs depending on the source of the main product. Main components are CaO, sulphates (expressed as SO₃), SiO₂, Al₂O₃, Fe₂O₃, P₂O₅ and trace metal content, such as arsenic, silver, cadmium, barium, chromium, lead, mercury and selenium. It also has high content in Ag, Au, Cd, Se, Sr, some light REE and Y (Carbonell -Barnachina et al., 2002, Oliveira and Imbernon, 1998). From a morphological point of view the particle size range between 0,250 and 0,045 mm in diameter (May and Sweeney, 1984), depending on the source of the phosphate rock and the reactor conditions (Becker, 1989).

According to the Environmental Protection Agency (EPA) five (5) tons of phosphogypsum are produced per ton of phosphoric acid produced. Globally, phosphogypsum production is about 100 – 250 Mt/year (Yang et al., 2009; Parreira et al., 2003). The USEPA has classified phosphogypsum as a "*Technologically Enhanced Naturally Occurring Radioactive Material*" (TENORM). Up to 15% of PG is used to make building materials, as a soil amedment and as a set controller in the manufacture of Portland cement, but its uses have been banned in most countries. (Tayibi et al., 2009)



Figure 1: Flow chart indicating the sulphuric acid phosphorous extraction process.

Phosphogypsum is removed by the filtration step in the phosphoric production process and is slurried in process wastewater onto one or more impoundments located, usually, nearby the production sites, known as gypsum stacks. In the impoundments, the solids are allowed to settle and the process water is recycled to the plant in order to be reused. Dried phosphogypsum is used to build up the dike that forms the impoundment, and then it is returned to active service. In this manner, the stack increases in height and accumulates additional phosphogypsum.

In general, the specific activities of natural ²³⁸U series radionuclides in phosphate fertilizers, depending on their levels in the used raw phosphate ore material. Radioactivity levels in phosphate ores are varied according to their geological origin (sedimentary, volcanic or biological origin) where ²³⁸U and its decay products tend to be elevated in phosphate deposits of sedimentary origin due to the accumulation of dissolved uranium, in the form of uranyl complex, in the sea water during the geological formation of the phosphate rocks. A typical concentration of ²³⁸U in sedimentary phosphate deposit is 1500 Bq/Kg (UNSCEAR 1993; Khalifa and El – Arabi, 2005).

Several studies have been conducted worldwide, such as in Syria, where the radiological impact of phosphogypsum stockpiles in the surrounding ecosystem was determined. It was found that the mean activity of ²²⁶Ra in phosphogypsum was 318 Bq/Kg. (Al Attar et al., 2011). In Portugal, two factories have been producing phosphate fertilizer for about 50 years.

In one factory, phosphorite from Syria and Tunisia was mainly used, ²²⁶Ra concentrations in the gypsum were at about 600 Bq/Kg, and levels for ²¹⁰ Po and ²¹⁰Pb were similar. The second factory used mainly phosphorites from Morocco, which gave increased radionuclide concentrations at about 1000 Bq/Kg for the same radionuclides. (Carvalho, Nuclear and Technological Institute Department of Radiological and Nuclear Safety, IAEA-CN-87/61)

In Huelva (SW Iberian Peninsula), Spain, about 3 million tons of phosphogypsum are generated annually and stored in a stack containing 100Mt over salt marshes of an estuary formed by the confluence of the Tinto and Odiel rivers, less than 1 Km away from the city center (Seville, SW Spain). The phosphate rock which is processed in the fertilizer plant, comes from Morocco. Studies indicated that the phosphogypsum displays higher relative and absolute concentrations of heavy metals contained in the mobile fraction than phosphate rock, most of these metals are bounded to organic matter, unlike phosphate rock, that does not contain metals associated to this fraction and whereas the U of phosphate rock is associated to the bioavailable fraction, phosphogypsum contains high U concentrations bound to the bioavailable fraction, hence being a threat for the environment. (Perez–Lopez et al., 2007)



Figure 2: The case of phosphogypsum in Huelva, Spain (Perez-Lopez et al., 2007).

1.2 Phosphogypsum in Greece and the case of the Schistos waste site

Studies in Greece, more specifically in Societe Industries Chimiques du Nord de la Grece SA (SICNG) operating in Thessaloniki, have indicated that the concentration of ²²⁶Ra varies between 261 and 688 Bq/Kg, with a mean value of 508 Bq/Kg. (Papastefanou et al., 2006). In the same study, there was conducted a comparison between the values measured in Thessaloniki and values measured around the world. It is shown that Thessaloniki's

phosphogypsum had the lowest value range among other regions, such as Central Florida, where phosphogypsum's concentration was found to be 2000 Bq/kg (May and Sweeney, 1984b).

During the past decades, a fertilizer industry has operated in Drapetsona, Piraeus, Greece (Figures 2,3). The result of this operation was the deposition of 10*10⁶ tons of phosphogypsum, in an old quarry site at the nearby area of Schistos. The raw material used to produce phosphoric acid, was phorphorite from Tunisia, Africa. The deposition of phosphogypsum stopped at the late 80s (1989) and at 2010 the whole deposit was remediated under the supervision of the Environmental Association of Municipalities of Athens-Piraeus (Various Contributors, 2007). In Schistos area in Athens, Greece, no previous studies have been conducted in order to determine the ²²⁶Ra concentrations of phosphogypsum and the amount of heavy metals of the raw material. The GAEC (Greek Atomic Energy Commission) has measured the alpha emission of ²²⁶Ra and ²²²Rn, but the data have not been published (Katsantonis, private communication).



Figure 3: Fertilizer Industry in Drapetsona, Greece.



Figure 4: The deposit of phosphogypsum, in Schistos waste site, before the remediation project.

1.3 Geological backround of Schistos waste site

The geological structure of greater Attica comprises two groups of alpine basement rocks and post–alpine sediments:

- a) The upper group is made mainly of Mesozoic carbonate rocks (limestones and dolomites of Triassic and Jurassic age) overlying a clastic formation of shales and sandstones including olistholite of Permian limestones. Some ophiolitic rocks are locally preserved over the carbonate platform which were tectonically emplaced during the palaeoalpine orogeny of Late Jurassic–Early Cretaceous. Upper Cretaceous shallow water carbonates and early Tertiary flysch cover the previous formations, which belong to the geotectonic unit of Eastern Greece (composed of the Sub-Pelagonian palaeotectionised Unit, the ophiolite nappe of the Axios–Vardar oceanic basin and the Upper Cretaceous transgressive platform). This upper unit extends only to the northwestern part of Attica, forming the major mountain range of Parnitha and the other mountains like Aegaleo in the western side of the Athenian basin.
- b) The lower group is made mainly of metamorphic rocks, including marbles, micaschists e.tc. cropping out in the area of Penteli mountain to the east and Hymittos mountain to the south if the Athenian basin.

The tectonic contact between the two groups of the alpine basement strikes in the NE–SW direction and dips towards the NW. Although this tectonic contact is usually covered by

post-alpine sediments, its position is marked approximately by Kifisos River, which is outfloating in the area of Pireaus. The post-alpine sediments comprise mainly neogene lacustrive lignite bearing deposits and continental quaternary formations. (Papanikolaou et al, 1999)

The Attica Region is mainly formed by the H3 platform (Internal Hellenides). The H3 platform is formed by metamorphosed units (Almopia, Attica, Laurium), but also from unmetamorphosed units (Parnassos, Voiotia, Sub–Pelagonian), and probably from pre–Alpine formations, such as Asterousia, Flabouro and Kastoria. The main characteristic of this terrane is the presence of a shallow-water carbonate platform, since Early–Middle Triassic to Upper Jurassic (Celet, 1962; Celet and Ferriere, 1978; Papanikolaou, 1988c). On this platform the Axios Ophiolithic complex (H4) during Upper Jurassic–Late Cretaceous were obducted during at the so–called paleo–Alpine orogenetic phase (Mercier, 1968; Mercier and Vergely, 1972; Jacobhagen 1979, 1986). According to Mountrakis (1986) the "Pelagonian Zone" was a part of the Kimmerian continent. (Papanikolaou, 1986)

In the study area, the main zone that appears is the following:

<u>1.3.1 Sub – Pelagonian Zone</u>

In our study area, the geotectonical unit that holds a major part of the area is the Sub-Pelagonian Unit. The Sub-Pelagonian zone is mostly unmetamorphosed containing Permo-Triassic to Paleocene sedimentary sequences and Jurassic ophiolites that stayed in a supracrustal position from the time of their emplacement onward. It is strongly tectonized, brittle and semi-brittle structures record post –Paleocene processes, such as material accretion at the European paleo–plate margin succeeded by fragmentation of the upper crust related to extension (Diamantopoulos et al, 2009).

In Attica, the Sub–Pelagonian zone crops out in north and west Attica occupying the Parnitha, Poikilo and Aegaleo mountains. There, the following formations occur supplying debris to the sedimentary basins (Figure 5): 1) Late Carboniferous – Early Triassic clastic sediments (red to greenish sandstones, conglomerates, dark grey to black shells) and carbonates with volcanic intercalations, 2) Triassic–Jurassic platform carbonates (light grey limestones and dolomites), 3) Jurassic ophiolites associated with oceanic sediments including red to greenish cherts, shells, serpentinites, gabbros and altered basalts, and 4) transgressive Cretaceous shallow-marine series with limestones that upwardly pass into Paleocene flysch (Katsikatsos et al, 1986a,b).

After the Palaeocene, within the deeper part of the Sub–Pelagonian Zone, the Carboniferous– Early Triassic clastic series were thrust upon the Triassic–Jurassic platform carbonates and the upper part of the Jurassic ophiolite series, including the Late Cretaceous limestone, were thrust upon Palaeocene flysch (Katsikatsos et al, 1986a, b; Diamantopoulos et al, 2009).



Figure 5: The stratigraphic column of the Sub–Pelagonian Zone. The layers that appear in the column are: i. Clastic formations with black limestones Permian, ii. Volcanic formation Late Triassic, iii. Reddish or green tuberous formations Middle Triassic, iv. Limestones with Megalodones Upper Triassic–Late Jurassic, v. schist–sandstone–hornstone conformation Doggerium, vi. Ophiolites Late Cretaceous.

The structurally uppermost parts of the Sub–Pelagonian nappes are the "Athens schists unit" (eastern slope of Aegaleo and Poikilo Mts, the western slope of Hymittos Mt., hills within the southern Athens basin) and the Afidnai unit. The Athens schist unit comprises Late Creataceous clastic series of sandstones, shales and cherts ("Athens schists" s.s.). These contain few intercalations of (crystalline) limestones and marls and are onerlain by fossiliferous upper Cretaceous limestones (Santon to Campan; Marinos et al, 1974; Dounas and Gaitanakis, 1981).

1.3.2 Neogene sediments

In Attica, the most significant basins are the Athens and Mesogea basins. The altitude of the most prominent topographic ranges, such as Parnitha, Penteli and Hymittos Mts., that confine the basins reaches between 1000 and 1400 m. Sedimentation started in the late Miocene and has continued through the Pleistocene and Quartenary. Continental, i.e. fluvioterrestrial and lacustrine sediments, predominate throughout this time span (Ioakim et al., 2005.) The Mesogea and Athens basins and the confining mountain ranges have been considered as to have evolved in the Miocene (Papanikolaou et al., 2004a). However, only lower Pliocene–Pleistocene sediments are restricted to the topographic basins, where they commonly

distressfully overlay the upper Miocene – lower Pliocene sediments and the basement rocks. Upper Miocene sediments also occur on mountain ranges up to 700 m, e.g. upon the Parnitha Mt. and Profitis Elias hill in the Lavrion area (Marinos and Petraschek, 1956; Katsikatsos et al, 1986a, b).



Figure 6: Geotectonic map of the Attica region. The red star indicates the waste site location. (Krohe et al., 2010)



Figure 7: Geological section of the Athens basin. The blue arrow indicates the waste site position. (Papanikolaou, 2004)

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1.4 Purpose of the present study

Radionuclides distribution in the Schistos area has been an issue for the environment for a few decades now. The lack of existence of any published data (GAEC, Katsantonis, priv. comm.) regarding the radioactivity concentration and distribution in the area was the main motivation behind the present study.

It has been equally important to study the environmental risk by applying a combination of analytical and laboratory techniques to determine the radioactivity levels and assess the significance of its concentration. Moreover, state-of-the-art GIS technologies were available to apply for understanding the distribution of the radionuclides in the environment and its impact to the nearby urban areas.

This is the first time such a study has been undertaken to such extent and detail, partly thanks to the fruitful collaboration with the local government that facilitated the present research project.

2. Materials and Methods

2.1 Sampling

Sampling was carried out during September, in Schistos area, where $10*10^6$ tons of phosphogypsum have been deposited. We collected, in total, 22 samples, both phosphogypsum and soil, using a GPS system to record the exact location of each sample, so that it would be easier to create a GIS map afterwards. The soil samples were collected from the cover of the deposit and the surrounding area, so that any unexpected radiation release could be determined.



Figure 8: The Schistos waste site, as it is today.

Three phosphogypsum samples were collected and measured by γ -ray spectrometry using a HPGe detector of high relative efficiency 50%, manufactured by Eurysis. Twelve soil samples were collected from the cover and six soil samples were collected from the surrounding area. Each and every sample was made to pass through a 2mm sieve, and after that an amount was pulverized in order to be measured by the XRF, XRD, SEM and ICP–MS techniques (Figure 9).



Figure 9: The sampling points around the Schistos waste site. Green sampling points indicate the soil collected from the cap of the site, red sampling points indicate the phosphogypsum samples and yellow sampling points indicate the soil samples from the surrounding area.(Source: Google Earth)

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Figure 10: From left to the right clockwise: 1. Collecting phosphogypsum sample, 2. Soil sample from the surrounding area, also showing the geological background, 3. Collecting soil sample from the cap, 4. Soil sampling.

2.2 Scanning Electron Microscopy (SEM) (Jeol JSM-5600) with the ability of microanalysis (Oxford EDS) and X–ray Diffraction (XRD) Siemens D-5005

2.2.1 X-Ray Diffraction (XRD)

X-Ray Diffraction is applied on samples of powder form or solid form, in order to determine the structure and composition of the sample, which may contain more than one crystal compounds. Any type of solid in terms of chemical composition can be studied, such as simple and complex chemical compounds, metal alloys and minerals, organic molecules and other. The most common way in order for X rays to be produced is when high-energy electrons impinge on the surface of a metal with high atomic number. These electrons hitting the target stimulate the electrons of the inner layers of the metal causing their secondment. The «gap» of the inner layer is filled with electrons that come from layers with higher energy. The energy difference between the two layers, is released in the form of an emitted photon (X ray) (Figure 11).

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Figure 11: Principles of XRD function (http://www.chemist.gr/2011/04/5154/)

Diffraction occurs when radiation strikes a barrier consisting of parallel slots of equal width d and when applicable $\lambda > d$, where λ is the beam wavelength. The X-rays wavelength range between 0,1–10A, and so it's impossible for a mechanical barrier to be constructed, since d may reach 1000A with the existing technology. In 1912, von Laue proposed the use of of natural crystals as diffraction barriers/gratings, since the atoms arrangement may be seen as a series of parallel lattice planes, which distance from one another is of the order of 1A and also equal. Knowing d it is possible to calculate λ , in order for the crystal to be used as an diffraction barrier. The diffraction patterns can be captured either as concentric circles on photographic film, or as three–dimensional grids of bright spots. The necessary condition so that maximum intensity from diffraction can be achieved, was found by W.H. and W.L. Bragg and is expressed by the following equation: $n^*\lambda= 2d^*\sin\theta$, where n is an integer number ranging from 0 to 4 and is reffered to sequential crystalline levels. (Figure 12) (Skoog DA, Holler FJ, Nieman TA, Principles of instrumental Analysis, Publications Kostarakis 2002) (http://www.chemist.gr/2011/04/5154/)



Figure 12: Bragg's law.

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By recording the diffraction angle and the corresponding number of X rays detected at that angle, the result is the diffraction spectrum of the tested material. The XRD pattern is compared with the database of patterns of a large number of materials. The structure of the material can be identified qualitively, while its phase in the material can be determined quantitively. Additional physical and chemical properties of the materials such as residual stresses, the crystals size and microstresses, crystal's orientation and the crystallographic structure of the material can be also determined in that way (*http://www.acutech.gr/gr/articles.asp?catid=33&artid=75*). The characterization of the phosphogypsum material was conducted by X-ray diffraction (XRD), using an XRD Siemens D-5005 (Figure 13). The evaluation was conducted with the use of Match and with a loaded library from the Mineralogical Society of America (www.minsocam.org).



Figure 13: XRD Siemens D - 5005.

2.2.2 Scanning Electron Microscopy (SEM) with the Ability of microanalysis (Oxford EDS)

A Scanning Electron Microscope (Figure 14) is a type of microscope which gives images of a sample by scanning it with a focused beam of electrons. The electrons interact with the atoms in the sample and produce a great variety of signals that can be subsequently detected. Those signals contain information about the sample's surface topography and composition. All samples must be in the appropriate size so that they could fit in the specimen chamber. Besides that, each sample must be prepared in a way that allows them to be electrically conductive and also electrically grounded. Therefore, they are usually coated with gold, gold/palladium alloy, platinum, osmium, iridium, tungsten, chromium and graphite.



Figure 14: SEM – EDS, Jeol JSM – 5600.

2.3 y- ray spectrometry using High – Purity Germanium (HPGe) detector

There are two types of germanium detectors. In the early 1960s germanium detectors, produced by the lithium drifting process (Ge(Li)), became commercially available and for about two decades were used as the common type of large-volume germanium detector. In the early 1980s, the high–purity germanium detectors (HPGe) came to replace the lithium drifting, and so the manufacturers discontinued the production of Ge(Li) in favor of HPGe detectors. This is because of the much greater operational convenience afforded by the HPGe detector, in terms of the temperature that must be obtained while operating each type of detectors. While Ge(Li) detectors must operate exclusively at low temperature, HPGe detectors can be allowed to warm, between uses, at room temperature. While in use, the HPGe detector must be cooled using liquid nitrogen.

In order to be develop high-purity germanium detectors, ultrapure germanium with impurity levels as low as 10¹⁰ atoms/cm³ must be produced. For that purpose, the starting material is bulk germanium, already of high purity, which is further processed using the technique of zone refining. This means that the impurity levels are progressively reduced by locally heating the material and slowly passing a melted zone from one end of the sample to the other. Impurities tend to be more soluble in the molten germanium than in the solid, and that's why they are preferentially transferred to the molten zone and swept from the sample. After repeating this method many times, there are achieved impurity levels as low as 10⁹ atoms/cm³.

Gamma-ray spectrometry was applied in order to determine the natural and artificial radionuclides activity concentrations in the studied samples. All samples were packed in individual plastic beakers of about 260 mL of volume, with a screw cap (Figure 14) and were measured in the HPGe detector, operated at the Aristotle University of Thessaloniki, at the Faculty of Engineering, School of Electrical and Computer Engineering. After closing the beaker, every sample was weighed in order for the net weight to be noted. Every sample was

placed inside the detector carefully so that it wouldn't contaminate the detector (Figure 17). As it is shown in Figure 15 the detector's shield opens from above and the HPGe crystal is protected by an aluminum coating. On top of that there is a disc made of glass where the beaker is placed. After placing the plastic beaker on the disc, the shield closes, before starting the measurement.



Figure 15: Plastic beakers with screw cap.

The detector's shield is made of lead (Pb), which isolates the crystal from radiation not originating from the sample, such as cosmogenic radiation, external sources of radiation etc. However, noise interference can still exists, so it is essential to measure spectra without the presence of radioactive sources. This helps us to determine the background radiation, which includes the radiation from the shield and the environment in which the detector operates.



Figures 16, 17: HPGe detector from the outside and the inside.

The duration of the measurement depends on the sample's activity. This means that a sample with high activity typically needs less time in order to render a full spectrum. Samples with

low activity need more time, so that every specific energy peak is depicted at the spectrum. Each specific energy photo peak (keV) corresponds to a certain radionuclide (Table 1), which interacts with the gamma rays and emits photons. Since the energy of each photo peak is known we can calculate the net counts, which is the amount of photons detected by the detector.

All samples as referred above were placed in plastic beakers and were measured for about 6 hrs, at 20000–80000 counts per peak. In order to calibrate the detector, all three phosphogypsum samples were measured for about 12 hrs each, at 80000 counts. The efficiency was determined and changed, depending on the sample's density. Once the measurement is completed, the result is an emitted spectrum. In the emitted spectrum it is vital to determine specific energy photo peaks which correspond to specific radionuclides. The final report gives us its energy photo peak and the net counts (area), after being corrected, gives us the Bq/Kg of its radionuclide.

Element	Photopeak/Specific Energy (keV)
²³⁴ Th	63
²³⁵ U	143
$^{235}\text{U}/^{226}\text{Ra}$	186
²¹⁴ Pb	352
²⁰⁸ Tl	583
²¹⁴ Bi	609
²²⁸ Ac	911
^{234m} Pa	1001
⁴⁰ K	1460
²¹⁴ Bi	1764

Table 1: Correlation between element and specific energy photo peaks

2.4 Generated Maps using Geographical Information Systems (GIS)

A Geographic Information System (GIS) is a computer system that is designed to capture, store, manipulate, analyze, manage and present all types of geographical data. Modern GIS technologies incorporate digital information, for which various digitized data creation methods are used. The most significant method is digitization, where a hard copy map or survey plan, is transferred into digital medium through the use of a CAD program, and georeferencing capabilities. GIS uses spatio-temporal (space–time) location as the key index variable for all other information. Just as a relational database containing text on numbers can relate many different tables using common key index variables, GIS can relate unrelated information by using location as the key index variable. The key is the location and/or extent in space–time. Locations or extents in Earth space–time may be recorded as dates/times of occurrence, and x,y,z coordinates representing longitude, latitude and elevation, respectively. There are two broad methods used to store data in a GIS: raster images and vector (ESRI).

A GIS includes a set of procedures that are implemented with the use of computers in order to manage and analyze spatial information. The organization of information is very important and is done in such way as to facilitate some functions such as storage and retrieval of

information, and the correlations and spatial analysis. Therefore, the functionally and flexibility of a GIS is directly related to the degree of integrity of the design of the database. A well–designed database is characterized by the following: 1) inclusion of all the necessary information, 2) inclusion of data of variable content, with the ability of their combination, 3) does not contain redundant information, 4) encoding and organization of the data in an effective way, 5) consideration of the requirements of the applications associated with the data and 6) support of the usage requirements. From the above it is clear that the concept of a well–organized database is very important. For the same amount of information, it is possible to design more than one database depending on the application requirements to be implemented. (Zeiler, 1999).

The initial topographic sheets 1:5000, were supplied from the Geographic Military Service. These sheets were scanned and digitized in order to be introduced in the GIS system. As it is known, the representation of entities in continuous vector format, such as representation of elevation contours, is not suitable for quantitative analysis. Therefore, a TIN model (Triangular Surface model) was generated, in which the continuous surface is represented as a set of non–overlapping triangles which have peaks for points with specified values of the variables x, y, z. Next, a Digital Elevation Model (DEM) was created in order to successfully depict depict the continuous spatial data, since each point with coordinates x, y corresponds to a z value. In addition, available aerial photographs from the area were combined and introduced into the system completing thus the reference layers of the GIS. Finally, the sampling site georeferenced layer and corresponding database was created with an attribute table incorporating measured values for each radionuclide at each site. All layers were georeferenced and projected at the GGRS_1987_Transverse_Mercator projecting system.

2.5 Radioisotope-induced X - ray Fluorescence Spectroscopy (RI-XRF)

The X-ray Fluorescence spectroscopy is a non-destructive method of analysis for liquids and solids. The sample is radiated with a beam of X-rays which causes a the emission of secondary X-rays which are characterized as fluorescent. The emitted rays can be detected with EDS or WDS. Their energy and wavelength is used to identify the chemical elements present in the tested sample while the elements concentrations are determined by the X-ray's intensity. This method of analysis is characterized as bulk method analysis. Depending on the energy of the emitted beam of rays and the sample's composition, the depth of the analyzed sample varies from 1mm to 1cm. The analyzed elements are from Na to U, but in certain cases lighter elements can be detected from B to F.



Figure 18: RI-XRF with a source of ⁶⁰Co.

X-rays are electromagnetic radiation, which combines the waves properties reflecting their typical characteristics such as diffraction and refraction, with the particle collisions and their interaction with them. When a sample, receives radiation of high energy and short wavelength, then their atoms are stimulated. If this energy is sufficient, then an electron from the inner layer, is released and it is replaced by an electron from a higher energy layer. This transition is resulting in the emission of energy equal to the energy difference between the two layers. The emitted X-ray radiation energy is smaller than the original X-ray irradiation and it is called florescence radiation (Figure 19). This radiation is characteristic of the element from which it is emitted and provides us information for the sample's composition.



Figure 19: Schematic presentation of the creation of X ray fluorescence.

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The phosphogypsum samples were measured in an XRF, using a source of 60 Co, as shown in Figure 18.

2.6 Spectrophotometric Analysis of liquid samples

Spectrophotometric techniques are used to measure the concentration of solutes in a solution by measuring thw amount of light absorbed by the solution in a cuvette placed in the spectrophotometer. Spectrophotometry takes advantage of the dual nature of light. Namely, light has:

- 1) A particle nature which gives rise to the photoelectric effect and
- 2) A wave nature which gives rise to the visible spectrum of light

A spectrophotometer measures the intensity of a light beam after it is directed through and emerges from a solution. An example of this method with copper sulfate ($CuSO_4$) is shown in figure 19.



Figure 20: Example of the method with copper sulfate.

The red part of the spectrum has been completely absorbed by $CuSO_4$ and blue light has been transmitted. $CuSO_4$ absorbs little blue light and therefore it appears to be blue. In spectrophotometry, greater sensitivity can be gained by directing red light through the solution because $CuSO_4$ absorbs strongest at the red end of the visible spectrum. For this, red wavelengths have to be isolated.

In a spectrophotometer, a light source gives off white light which strikes a prism, separating the light into its component wavelengths (See Figure 21). Thus, lightwaves can be separated by frequency.



Figure 21: The set - up of the method.

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The spectrophotometer can measure the amount of light (of certain frequency) transmitted or adsorbed by the solution. This light that has not been absorbed by the solution in the cuvette, will strike the phototube. The photons of light that strike the phototube will be converted into electrical energy. This current that is produced is very small and must be amplified before it can be efficiently detected. The signal is proportional to the amount of light which originally struck the phototube and is thus an accurate measurement of the amount of light which has passed through (been transmitted by) the sample. Different compounds having dissimilar atomic and molecular interactions have characteristic absorption phenomena and absorption spectra. Concentration of every component may be found from the spectrophotometer measurements and calibration curve made using the samples of known concentration.

(http://www2.bren.ucsb.edu/~keller/courses/esm223/Spectrometer_analysis.pdf)

2.7 TCLP and leaching of phosphogypsum with Attica rainwater

The TCLP method is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid and multiphasic wastes. Before applying the TCLP method it is essential to determine the pH of its sample. Weigh out a small subsample of the solid phase of the waste, reduce the solid (if necessary) to a particle size of approximately 1 mm in diameter or less, and transfer 5.0 grams of the solid phase of the waste to a 500 mL beaker or Erlenmeyer flask. Add 96.5 mL of reagent water to the beaker, cover with a watchglass, and stir vigorously for 5 minutes using a magnetic stirrer. Measure and record the pH. If the pH is <5.0, use extraction fluid #1. If the pH from Section 7.1.4.2 is >5.0, add 3.5 mL 1N HCl, slurry briefly, cover with a watchglass, heat to 50 EC, and hold at 50 EC for 10 minutes. Let the solution cool to room temperature and record the pH. If the pH is <5.0, use extraction fluid #1. If the pH is >5.0, use extraction fluid #2.

Extraction fluid #1: Add 5,7 mL glacial CH₃CH₂OOH to 500 mL of reagent water, add 64,3 mLof 1N NaOH, and dilute to a volume of 1L. When correctly prepared, the pH of this fluid must be 4.93 ± 0.05 .

Extraction fluid #2: Dilute 5,7 mL of glacial CH_3CH_2OOH with reagent water to a volume of 1 L. When correctly prepared, the pH will be 2.88 ± 0.05 .

(http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/1311.pdf)

For the purpose of this study, two samples were prepared and treated with the TCLP method. One phosphogypsum sample and one soil sample, which were the most radioactive.

Sample	рН	pH (↑ °C)
PGO2	5,596	1,883
SO2	8,250	4,825

Table 2: The pH measurement before and after the temperature rise.

According to Table 2, it can be easily understood that for the TCLP method, the extraction fluid #2 was used, due to the fact that the samples pH was smaller than 5.0.

After that, the samples were left to stir for 18 hours and then they were placed in the centrifugation for 20 min. Following, they were filtrated in plastic tubes of 50 ml of volume.

The same amount of phosphogypsum sample was used for leaching with rainwater. The same procedure was carried out, but instead of extraction fluid #2, rainwater gathered from the meteorological station of Panepistimiopolis was used. It was stirred for 18 hrs and filtered in plastic tubes of 50 mL of volume. The rain that was used for the leaching procedure had a pH of 6,545.

All filters were collected and analysed by SEM-EDS in order to determine those elements that were not dilluted by the extraction fluid or rain.

2.8 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

ICP–MS is an analytical technique that is used for elemental determinations, which is capable of detecting metals and several non–metals at concentrations as low as one part of 10¹² (part per trillion). The technique was commercially introduced in 1983, with great acceptance in many types of laboratories. Geochemical analysis laboratories were early developers of ICP-MS technology because of its superior detection capabilities, particularly rare earth elements (REEs). ICP–MS has many advantages over other elemental analysis techniques such as atomic absorption and optical emission spectrometry, including ICP Atomic Emmision Spectrometry (ICP–AES), including: 1) Detection limits for most elements equal to or better than those obtained by Grafite Furnace Atomic Absorption Spectroscopy (GFAAS), 2) Higher throughput than GFAAS, 3) The ability to handle both simple and complex matrices with a minimum of matrix interferences due to the high–temperature of ICP source, 4) Superior detection capability to ICP–AES with the same sample throughput, 5) The ability to obtain isotopic information.

An ICP–MS combines a high–temperature ICP (Inductively Coupled Plasma) source with a mass spectrometer. The ICP source converts the atoms of the elements in the sample to ions. These ions are theb separated and detected by the mass spectrometer. More specific, as shown in figure xx, argon gas gas flows inside the concentrin channels of the ICP torch. The RF load coil is connected to a radio–frequency (RF) generator. As power is supplied to the load coil from the generator, oscillating electric and magnetic fields are established at the end of the torch. When a spark is applied to the argon flowing through the ICP torch, electrons are stripped off the argon atoms, forming argon ions. These ions are caught in the oscillating fields and collide with the other atoms, forming an argon discharge or plasma.



Figure 22: The ICP torch showing fate of the sample. (Perkin Elmer, Inc.)

The sample is typically introduced into the ICP plasma as an aerosol, either by aspirating a liquid or dissolved solid sample into the nebulizer or using a laser to directly convert solid samples into an aerosol. Once the sample aerosol is introduced into the ICP torch, it is completely desolvated and the elements in the aerosol are converted first into gaseous atoms and then ionized towards the end of the plasma.

The most important things to remember about the argon ICP plasma are: 1) The argon discharge, with a temperature of around 6000-10000 K, is an excellent ion source, 2) The ions formed by the ICP discharge are typically positive ions, M⁺ or M⁺², therfore, elements that prefer to form negaive ions, such as Cl, I, F, etc, are very difficult to determine via ICP-MS, 3) The detection capadilities of the technique can vary with the sample introduction technique used, as different techniques will allow differing amounts of sample to reach the ICP plasma, 4) Detection capabilities will vary with the sample matrix, which may affect the degree of ionization that will occur in the plasma or allow the formation of species that may interfere with the analyte determination. Once the elements in the sample are converted into ions, they are then brought into the mass spectrometer via the interface cones. The interface region in the ICP-MS transmints the ions travelling in the argon sample stream at atmospheric pressure (1-2 torr) into the low pressure region of the mass spectrometer (< 1 * 10^{-5} torr). This is done through the intermediate vacuum region created by the two interface cones, the sampler and the skimmer (see Figure 21). The sampler and skimmer cones are metal disks with a small hole (\sim 1 mm) in the center. The purpose of these cones is to sample the center position of the ion beam coming from the ICP torch. A shadow stop (see Figure 22) or similar device blocks the photons coming from the ICP torch, which is also an intense light diameters of the orifices in the sampler and skimmer cones, ICP-MS has some limitations as to the amount of total dissolved solids in the samples. Generally, it is recommended that samples have no more than 0,2% total dissolved solids (TDS) for best instrument

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performance and stability. If samples with very high TDS levels are run, the orifices in the cones will eventually become blocked, causing decreased sensitivity and detection capability and requiring the system to be shut down for maintenance. This is why many samples types, including digested soil and rock samples must be diluted before running on the ICP – MS.



Figure 23: The interface region of an ICP – MS (PerkinElmer, Inc.)

The ions from the ICP source are then focused by the electrostatic lenses in the system. Once the ions enter the mass spectrometer used type of mass spectrometer is the quadrupole mass filter. In this type, 4 rods (approximately 1 cm diameter and 15–20 cm long) are arranged as in Figure 23. In a quadrupole mass filter, alternating AC and DC voltages are applied to opposite of the rods. These voltages are then rapidly switched along with an RF–field. The result is that an electrostatic filter is established that only allows ions of a single mass – to – charge radio (m/e) pass through the rods to the detector at a given instant in time. So, the quadrupole mass filter is really a sequential filter, with the settings being change for each specific m/e at a time. However, the voltages on the rods can be switched at a very rapid rate. The result is that the quadrupole ICP–MS is often considered to have simultaneous multielemental analysis properties. The ability to filter ions on their mass – charge ratio allows ICP–MS to supply isotopic information, since different isotopes of the same element have different masses (see Figure 23).



Figure 24: Schematic of quadrupole mass filter.

Bulk chemical analyses for major and trace elements, with regard to solid samples, were performed using a Perkin Elmer ICP-OES and a Perkin Elmer Sciex Elan 9000 ICP-MS following the $LiBO_2/LiB_4O_7$ fusion and HNO_3 digestion. The TCLP liquids and rain-water leachates were also analysed using the above system.

3. Results and Discussion

3.1 Phosphogypsum Characterization

3.1.1 XRD Study

The powder-XRD study for sample PG01 showed gypsum (CaSO₄·2H₂O), meniaylovite (Ca₄[FSO₄SiF₆AlF₆]·12H₂O)-type phase and clays (Figure 25). According to Villalobos et al. (2010), phosphogypsum from an industry at Huelva, SW Spain, contained Ca and S, in the form of calcium sulfate dihydrate. Besides that, it also contained bassanite due to the losses of water in calcium sulfate dihydrate through evaporation at 90 °C (Figure 26).



Figure 25: Powder XRD pattern of phosphogypsum sample (PG01).



Figure 26: Diffraction pattern of PG, which was previously dried at 90°C.(Villalobos et al., 2010)

The X-ray diffraction pattern of PG sample treated with kerosene, which is published by El-Didamony (2013), showed three strong peaks, which characterize gypsum (CaSO₄·2H₂O), and the other were silica, phosphate and metallic impurities such as Na, Al, Fe and Sr. (Figure 27)



Figure 27: X ray diffraction pattern. (El-Didamony et al., 2013)

3.1.2 SEM-EDS Study

SEM investigation indicated the existence of three different solid phases. The first one applies to the gypsum phase and it's characterized by the presence of calcium (Ca) and sulfur (S) in the EDS spectra. The second one is a more complex phase which combines calcium (Ca), sulfur (S), aluminum (Al), silicon (Si) and fluorine (F) and corresponds to meniaylovite (Ca₄[FSO₄SiF₆AlF₆]·12H₂O)-type phase related to chukhrovite (Coates & Woodard 1966). All these elements are combined to form octahedral microcrystals as shown in Figures 28,29 and 31. Thus, the SEM-EDS study approves the XRD investigation. Moreover, there is also a third phase referring to Fe-oxides (Figure 33). Besides that, phosphogypsum also contains nickel (Ni) impurities and quartz (SiO₂). All phases are well-crystallized and in some places it is possible to contain apatite, from the parent phosphorite material, which is not altered. Most gypsum crystals are distinct, while there are also twinned crystals (e.g. Gilbert 1966), as shown in Figure 28. The absence of sphere-shaped aggregates of gypsum crystals indicates the lack of simultaneous effect of both Al^{3+} and F^{-} in the crystal growth (Jun et al. 1997; see Figure 34). On the other hand, Kruger et al. (2001) mentioned that iron (Fe) and potassium (K) show the greatest effect on gypsum crystallization (Figure 35). Al-Hwaiti et al.(2010), found that Jordanian phosphogypsum is enriched in Si in coarse size fraction, which might be attributed to the fact that this element is associated to quartz. (Figure 36)



Figure 28, 29: SEM images of twinned gypsum crystals and meniaylovite (Ca₄[FSO₄SiF₆AlF₆]·12H₂O)-type phase octahedral crystal, respectively, occurring in Shistos phosphogypsum.

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Figure 30: EDS spectrum of meniaylovite (Ca₄[FSO₄SiF₆AlF₆]·12H₂O)-type phase

The meniaylovite octahedral microcrystals, are created during the manufacture of phosphoric acid from phosphorite attacked by sulfuric acid. Lehr et al. (1966) reported on the impurities precipitated from a wet process phopshoric acid preparation which includes a material with the chemical formula $Ca_4AlSiSO_4F_{12}\cdot12H_2O$ and an X–ray powder diffraction pattern of which is in close agreement with that from these octahedral crystals. (Figure 30) (Coates and Woodward, 1966).



Figure 31: Stereoscopic illustration of the unit cell in chucrovite, where a, b and c are the crystallographic axes (Mathew et al., 1981)



Figures 32, 33: Eroded meniaylovite microcrystal (top) and solid phase corresponding to Fe-oxide (bottom), respectively.



Figure 34: Effect of Al³⁺ and F⁻ on gypsum habit (Jun et al. 1997)

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Figure 35: Effect of Fe³⁺ impurity levels on the morphology of gypsum crystals (Kruger et al. 2001)



Figure 36: Crystal overview, crystal shape of the Jordanian phosphogysum (Al-Hwaiti et al., 2010)

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According to Dippel (2004) the Australian phosphogypsum contains, except gypsum, also bassanite, anhydrite and quartz. SEM study indicated a primary phase of calcium suiphur comprised with intermixed silicon, a rare chromium-iron phase, maybe chromite occuring from the miling process or from the ore and the metal ions sourced from the iron hydroxide. Dippel (2004) derived the PG samples, into two different samples, depending on the age of the PG deposited, in the fresh PG and the aged one. They both displayed morphology of clusters of tabular PG crystals commonly 500 microns across with the individual crystals generally being less than 25 microns across. The clusters include fine grains of quartz, the chromium-iron phase and s phosphorous phase. (Figure 37)



Figure 37: Secondary electron image of typical PG morphology(left) and backscatter electron image of PG which shows the little variation in the average chemistry of the grains.(Dippel, 2004)

Villalobos et al. (2010), determined the morphology of PG particles using SEM-EDX in SEI mode. They found that the PG sample exhibited shapes in the form of tables, in acicular form, in tubular form, as small crystal clusters and rhombic forms. (Figure 38)



Figure 38: Morphology of particles found in phosphogypsum: (a) bulk phosphogypsum crystals, (b) shape like tables, (c) small crystals clusters, (d) agglomerates, (e) acicular shape, and (f) cylindrical shape.(Villalobos et al., 2010)

It is obvious that PG particles in microscale, as observed by scanning transmission microscopes, exhibit different morphologies depending on the source phosphate rock and the industrial plant. However, Silva et al. (2010) have attempted to study Brazilian PG ultrafine particles by high-resolution microscopic techniques (FE-SEM and HRTEM/STEM) and they have concluded that there are also nanoscale phase impurities of Fe such as oxides (hematite), sulfides (pyrite) and sulphates (jarosite).

<u>3.1.3 γ-ray Spectra</u>

The γ -ray spectra of two representative phosphogypsum and soil samples collected from the cover (PG02 and SOcap2) are shown in Figures 39 to 46. The spectra are divided in four sequential energy regions to illustrate all important photopeaks in the spectrum.







Figures 41, 42: γ-ray spectra for sample PG02.



Figures 43, 44: γ-ray spectra for sample SOcap2.



Figures 45, 46: γ-ray spectra for sample SOcap2

3.1.4 γ -ray Spectrometry of phosphogypsum samples

All phosphogypsum samples were measured as mentioned above in section (materials and methods) and the following results were obtained, as shown in the following tables.

<u>**Table 3:**</u> Table showing the concentration of each radionuclide for sample PG01.

FGUI											
					Weight (kg)	0,25539		time (s)		81735	
					D 1/0/		<i>ce</i> , ,			- "	
NUCLIDE	ENERGY	AREA	C/S	BKG 17- sent-13	BKG/s (100000s)	NEI C/S	efficiency	FY	corrections	Bq/kg	
					(1000000)		density g/cm3				
Th-234	63	825	0,010094	4111	0,004111	0,005983	0,019653868	0,037		32	
U-235	143	355	0,004343	1727	0,001727	0,002616	0,045331922	0,109	0,72	1,49	
Pb-214	352	111741	1,367113	11658	0,011658	1,355455	0,027120874	0,356		550	
Bi-214	609	85486	1,045892	8435	0,008435	1,037457	0,017938883	0,448		505	
Bi-214	1764	14926	0,182615	2160	0,00216	0,180455	0,008045201	0,1531		574	
Ac-228	911	1064	0,013018	3570	0,00357	0,009448	0,013240976	0,29		10	
TI-208	583	2258	0,027626	5269	0,005269	0,022357	0,018538848	0,307		15	
Pa-234	1001	166	0,002031	879	0,000879	0,001152	0,012333023	0,01021		36	
K-40	1461	2298	0,028115	25603	0,025603	0,002512	0,009273647	0,1067		10	
Ra-226+U-235	186	20876	0,255411	8129	0,008129	0,247282	0,043871662	0,0355		622	
Ra-226 Gilmore correction	186	20876	0,255411	8129	0,008129	0,247282	0,043871662	0,0355	0,571	354,99	
Ra-226 ONLY U-235 fromTh- 234	186	20876	0,255411	8129	0,008129	0,237629	0,043871662	0,0355		597	AVERAGE Ra- 226
Ra-226 ONLY U-235 from Pa- 234	186	20876	0,255411	8129	0,008129	0,236548	0,043871662	0,0355		595	597
Ra-226 ONLY U-235 from 143 keV	186	20876	0,255411	8129	0,008129	0,237665	0,043871662	0,0355		598	
Cs-137	661,6	0	0	0	0	0	0,016852636	0,85		0	

<u>Table 4:</u> Table showing the concentration of each radionuclide for sample PG02.

PG02											
					Weight (kg)	0.26487		time (s)		88469	
NUCLIDE	ENERGY	AREA	c/s	BKG 17- sept-13	BKG/s (1000000s)	NET c/s	efficiency eeae	FY	corrections	Bq/kg	
							density g/cm3				
Th-234	63	2075	0.023455	4111	0.004111	0.019344	0.019653868	0.037		100	
U-235	143	1583	0.017893	1727	0.001727	0.016166	0.045331922	0.109	0.72	8.89	
Pb-214	352	115379	1.304174	11658	0.011658	1.292516	0.027120874	0.356		505	
Bi-214	609	89173	1.007958	8435	0.008435	0.999523	0.017938883	0.448		470	
Bi-214	1764	15694	0.177395	2160	0.00216	0.175235	0.008045201	0.1531		537	
Ac-228	911	843	0.009529	3570	0.00357	0.005959	0.013240976	0.29		6	
TI-208	583	1049	0.011857	5269	0.005269	0.006588	0.018538848	0.307		4	
Pa-234	1001	356	0.004024	879	0.000879	0.003145	0.012333023	0.01021		94	
K-40	1461	2593	0.02931	25603	0.025603	0.003707	0.009273647	0.1067		14	
Ra-226+U-235	186	27220	0.307678	8129	0.008129	0.299549	0.043871662	0.0355		726	
Ra-226 Gilmore correction	186	27220	0.307678	8129	0.008129	0.299549	0.043871662	0.0355	0.571	414.63	
Ra-226 ONLY U-235from Th- 234	186	27220	0.307678	8129	0.008129	0.268339	0.043871662	0.0355		650	AVERAGE Ra- 226
Ra-226 ONLY U-235 from Pa- 234	186	27220	0.307678	8129	0.008129	0.270245	0.043871662	0.0355		655	629
Ra-226 ONLY U-235 from 143 keV	186	27220	0.307678	8129	0.008129	0.240125	0.043871662	0.0355		582	
Cs-137	661.6	0	0	0	0	0	0.016852636	0.85		0	

PG03 Weight time (s) 81590 0.27799 (kg) NUCLIDE **ENERGY** AREA **BKG 17-**BKG/s NET c/s FY c/s efficiency corrections Bg/kg sept-13 (100000s)eeae density g/cm3 Th-234 63 558 0.006839 4111 0.004111 0.002728 0.019653868 0.037 13 U-235 0.045331922 0.92 143 284 0.003481 1727 0.001727 0.001754 0.109 0.72 Pb-214 352 32879 0.402978 11658 0.011658 146 0.39132 0.027120874 0.356 25828 0.316558 0.008435 **Bi-214** 8435 138 609 0.308123 0.017938883 0.448 0.1531 Bi-214 1764 4575 0.056073 2160 0.00216 0.053913 0.008045201 157 Ac-228 974 0.011938 0.00357 0.008368 0.013240976 0.29 8 911 3570 TI-208 0.018538848 0.307 9 583 1642 0.020125 5269 0.005269 0.014856 Pa-234 0.01021 1001 146 0.001789 879 0.000879 0.00091 0.012333023 26 0.054026 0.025603 K-40 1461 4408 25603 0.028423 0.009273647 0.1067 103 0.084814 8129 0.008129 Ra-226+U-235 186 6920 0.076685 0.043871662 0.0355 177 **Ra-226 Gilmore correction** 186 6920 0.084814 8129 0.008129 0.076685 0.043871662 0.0355 0.571 101.14 Ra-226 ONLY U-235 from Th-8129 0.008129 167 AVERAGE Ra-186 6920 0.084814 0.072284 0.043871662 0.0355 234 226 Ra-226 ONLY U-235 from Pa-6920 0.084814 8129 0.008129 0.068202 0.043871662 0.0355 158 186 234 0.043871662 Ra-226 ONLY U-235 from 186 6920 0.084814 8129 0.008129 0.070239 0.0355 162 143 keV Cs-137 0 0 0 0.016852636 0.85 0 661.6 0 0

Table 5: Table showing the concentration of each radionuclide for sample PG03.

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<u>3.1.5 γ -ray spectrometry of soil samples</u>

In addition, all soil samples were measured as well, by γ-ray spectrometry and the following tables show the results that were obtained.

<u>**Table 6:**</u> Table showing the concentration of each radionuclide for sample SO1.

Weight 0.2337 time (s) 86298 (kg)	
NUCLIDE ENERGY AREA de RKG 17, RKG/s NET de officionau EV corrections Ba/ka	
sept-13 (100000s) eeae	
density g/cm3	
Th-234 63 790 0.009154 4111 0.004111 0.005043 0.019653868 0.037 30	
U-235 143 552 0.006396 1727 0.001727 0.004669 0.045331922 0.109 0.72 2.91	
Pb-214 352 16530 0.191546 11658 0.011658 0.179888 0.027120874 0.356 80	
Bi-214 609 12427 0.144001 8435 0.008435 0.135566 0.017938883 0.448 72	
Bi-214 1764 2083 0.024137 2160 0.00216 0.021977 0.008045201 0.1531 76	
Ac-228 911 2346 0.027185 3570 0.00357 0.023615 0.013240976 0.29 26	
TI-208 583 3216 0.037266 5269 0.005269 0.031997 0.018538848 0.307 24	
Pa-234 1001 142 0.001645 879 0.000879 0.000766 0.012333023 0.01021 26	
K-40 1461 7771 0.090048 25603 0.025603 0.064445 0.009273647 0.1067 279	
Ra-226+U-235 186 6266 0.072609 8129 0.008129 0.06448 0.043871662 0.0355 177	
Ra-226 Gilmore correction 186 6266 0.072609 8129 0.008129 0.06448 0.043871662 0.0355 0.571 101.16	
Ra-226 ONLY U-235 from 186 6266 0.072609 8129 0.008129 0.056343 0.043871662 0.0355 155 AVERAGE Th-234 226	Ra-
Ra-226 ONLY U-235 from 186 6266 0.072609 8129 0.008129 0.057338 0.043871662 0.0355 158 147 Pa-234 Image: Constraint of the second seco	
Ra-226 ONLY U-235 from 186 6266 0.072609 8129 0.008129 0.047316 0.043871662 0.0355 130 143 keV <	
Cs-137 661.6 15081 0.174755 0 0 0.174755 0.016852636 0.85 52	

<u>Table 7:</u> Table showing the concentration of each radionuclide for sample SO2.

SO2											
					Weight	0.22467		time (s)		27769	
					(kg)						
NUCLIDE				DKC 47	DKC/a			FV		Der/leer	
NUCLIDE	ENERGI	AREA	C/S	sept-13	(1000000s)	NET C/S	enciency	FI	corrections	БЧ/КУ	
					(density				
							g/cm3				
Th-234	63	362	0.013036	4111	0.004111	0.008925	0.019653868	0.037		55	
U-235	143	53	0.001909	1727	0.001727	0.000182	0.045331922	0.109	0.72	0.12	
Pb-214	352	6146	0.221326	11658	0.011658	0.209668	0.027120874	0.356		97	
Bi-214	609	4642	0.167165	8435	0.008435	0.15873	0.017938883	0.448		88	
Bi-214	1764	789	0.028413	2160	0.00216	0.026253	0.008045201	0.1531		95	
Ac-228	911	841	0.030286	3570	0.00357	0.026716	0.013240976	0.29		31	
TI-208	583	1301	0.046851	5269	0.005269	0.041582	0.018538848	0.307		33	
Pa-234	1001	94	0.003385	879	0.000879	0.002506	0.012333023	0.01021		89	
K-40	1461	2908	0.104721	25603	0.025603	0.079118	0.009273647	0.1067		356	
Ra-226+U-235	186	2194	0.079009	8129	0.008129	0.07088	0.043871662	0.0355		203	
Ra-226 Gilmore correction	186	2194	0.079009	8129	0.008129	0.07088	0.043871662	0.0355	0.571	115.67	
Ra-226 ONLY U-235 from Th-234	186	2194	0.079009	8129	0.008129	0.056479	0.043871662	0.0355		161	AVERAGE Ra-
Ra-226 ONLY U-235 from	186	2194	0.079009	8129	0.008129	0.047529	0.043871662	0.0355		136	149
Pa-234				0.20		01011020					
Ra-226 ONLY U-235 from 143 keV	186	2194	0.079009	8129	0.008129	0.070212	0.043871662	0.0355		201	
Cs-137	661.6	3146	0.113292	0	0	0.113292	0.016852636	0.85		35	

<u>Table 8:</u> Table showing the concentration of each radionuclide for sample SO3.

SO3

503											
					Weight (kg)	0.25788		time (s)		53162	
NUCLIDE	ENERGY	AREA	c/s	BKG 17- sept-13	BKG/s (1000000s)	NET c/s	efficiency eeae	FY	corrections	Bq/kg	
							density g/cm3				
Th-234	63	458	0.008615	4111	0.004111	0.004504	0.019653868	0.037		24	
U-235	143	175	0.003292	1727	0.001727	0.001565	0.045331922	0.109	0.72	0.88	
Pb- 214	352	4462	0.083932	11658	0.011658	0.072274	0.027120874	0.356		29	
Bi-214	609	3645	0.068564	8435	0 008435	0.060129	0 017938883	0 448		29	
Bi-214	1764	647	0.01217	2160	0.00216	0.01001	0.008045201	0.1531		32	
Ac-	911	2351	0.044223	3570	0.00357	0.040653	0.013240976	0.29		41	
228											
TI-208	583	3462	0.065122	5269	0.005269	0.059853	0.018538848	0.307		41	
Pa-234	1001	77	0.001448	879	0.000879	0.000569	0.012333023	0.01021		18	
K-40	1461	7117	0.133874	25603	0.025603	0.108271	0.009273647	0.1067		424	
Ra-226+U-235	186	1743	0.032787	8129	0.008129	0.024658	0.043871662	0.0355		61	
Ra-226 Gilmore correction	186	1743	0.032787	8129	0.008129	0.024658	0.043871662	0.0355	0.571	35.06	
Ra-226 ONLY U-235from Th-234	186	1743	0.032787	8129	0.008129	0.01739	0.043871662	0.0355		43	AVERAGE Ra-226
Ra-226 ONLY U-235 from	186	1743	0.032787	8129	0.008129	0.019352	0.043871662	0.0355		48	46
Pa-234											
Ra-226 ONLY U-235 from 143 keV	186	1743	0.032787	8129	0.008129	0.018906	0.043871662	0.0355		47	
Cs- 137	661.6	2216	0.041684	0	0	0.041684	0.016852636	0.85		11	

Table 9: Table showing the concentration of each radionuclide for sample SO4.

				weight(kg)	0.22834		time (s)		32579	
ENERGY	AREA	C/S	BKG 17-	BKG/s	NEI C/S	efficiency	FY	corrections	Bq/kg	
			sept-13	(1000000s)		eeae				
						density				
	000	0.007000		0.004444	0.000040	g/cm3	0.007		40	
63	229	0.007029	4111	0.004111	0.002918	0.019653868	0.037	. = .	18	
143	38	0.001166	1727	0.001727	-0.00056	0.045331922	0.109	0.72	-0.36	
352	3840	0.117867	11658	0.011658	0.106209	0.027120874	0.356		48	
609	2832	0.086927	8435	0.008435	0.078492	0.017938883	0.448		43	
1764	540	0.016575	2160	0.00216	0.014415	0.008045201	0.1531		51	
911	1248	0.038307	3570	0.00357	0.034737	0.013240976	0.29		40	
583	1773	0.054422	5269	0.005269	0.049153	0.018538848	0.307		38	
1001	65	0.001995	879	0.000879	0.001116	0.012333023	0.01021		39	
1461	4059	0.124589	25603	0.025603	0.098986	0.009273647	0.1067		438	
186	1560	0.047884	8129	0.008129	0.039755	0.043871662	0.0355		112	
186	1560	0.047884	8129	0.008129	0.039755	0.043871662	0.0355	0.571	63.83	
186	1560	0.047884	8129	0.008129	0.035046	0.043871662	0.0355		99	AVERAGE
										Ra-226
186	1560	0.047884	8129	0.008129	0.029354	0.043871662	0.0355		83	91
186	1560	0.047884	8129	0.008129	0.041815	0.043871662	0.0355		118	
661.6	5334	0.163725	0	0	0.163725	0.016852636	0.85		50	
	ENERGY 63 143 352 609 1764 911 583 1001 1461 186 186 186 186 186 186 186 186	ENERGY AREA 63 229 143 38 352 3840 609 2832 1764 540 911 1248 583 1773 1001 65 1461 4059 186 1560 186 1560 186 1560 186 1560 186 1560 186 1560 186 1560 186 1560 186 1560 186 1560 186 5334	ENERGY AREA c/s 63 229 0.007029 143 38 0.001166 352 3840 0.117867 609 2832 0.086927 1764 540 0.016575 911 1248 0.038307 583 1773 0.054422 1001 65 0.001995 1461 4059 0.124589 186 1560 0.047884 186 1560 0.047884 186 1560 0.047884 186 1560 0.047884 186 1560 0.047884 186 1560 0.047884 186 1560 0.047884 186 1560 0.047884 186 1560 0.047884 186 1560 0.047884 186 1560 0.047884 186 1560 0.047884 186 1560 0.047884 661.6	ENERGYAREAc/sBKG 17-sept-13632290.0070294111143380.001166172735238400.1178671165860928320.086927843517645400.016575216091112480.038307357058317730.05442252691001650.001995879146140590.1245892560318615600.047884812918615600.047884 <td< th=""><th>weight(kg) ENERGY AREA c/s BKG 17- sept-13 BKG/s (1000000s) 63 229 0.007029 4111 0.004111 143 38 0.001166 1727 0.001727 352 3840 0.117867 11658 0.008435 609 2832 0.086927 8435 0.008435 1764 540 0.016575 2160 0.00216 911 1248 0.038307 3570 0.00357 583 1773 0.054422 5269 0.005269 1001 65 0.001995 879 0.008129 1461 4059 0.124589 25603 0.025603 186 1560 0.047884 8129 0.008129 186 1560 0.047884 8129 0.008129 186 1560 0.047884 8129 0.008129 186 1560 0.047884 8129 0.008129 186 1560 0.047884</th><th>weight(kg) 0.22834 ENERGY AREA c/s BKG 17- sept-13 BKG/s (1000000s) NET c/s 63 229 0.007029 4111 0.004111 0.002918 143 38 0.001166 1727 0.001727 -0.00056 352 3840 0.117867 11658 0.011658 0.106209 609 2832 0.086927 8435 0.008435 0.078492 1764 540 0.016575 2160 0.00216 0.014415 911 1248 0.038307 3570 0.00357 0.034737 583 1773 0.054422 5269 0.005269 0.049153 1001 65 0.00195 879 0.000879 0.001116 1461 4059 0.124589 25603 0.025603 0.098986 186 1560 0.047884 8129 0.008129 0.039755 186 1560 0.047884 8129 0.008129 0.035046 <</th><th>weight(kg) 0.22834 ENERGY AREA c/s BKG 17- sept-13 BKG/s (1000000s) NET c/s efficiency eeae density g/cm3 63 229 0.007029 4111 0.004111 0.002918 0.019653868 143 38 0.001166 1727 0.001727 -0.00056 0.045331922 352 3840 0.117867 11658 0.011658 0.106209 0.027120874 609 2832 0.086927 8435 0.008435 0.078492 0.017938883 1764 540 0.016575 2160 0.00216 0.014415 0.00804201 911 1248 0.038307 3570 0.00357 0.034737 0.013240976 583 1773 0.054422 5269 0.005269 0.049153 0.018538848 1001 65 0.001995 879 0.008179 0.001116 0.01233023 1461 4059 0.124589 25603 0.025603 0.098755 0.043871662 186</th><th>weight(kg) 0.22834 time (s) ENERGY AREA c/s BKG 17- sept-13 BKG/s (1000000s) NET c/s (1000000s) efficiency eeae density g/cm3 FY 63 229 0.007029 4111 0.004111 0.002918 0.019653868 0.037 143 38 0.001166 1727 0.001727 -0.00056 0.045331922 0.109 352 3840 0.117867 11658 0.011658 0.106209 0.027120874 0.356 609 2832 0.086927 8435 0.008435 0.078492 0.017938883 0.448 1764 540 0.016575 2160 0.00216 0.014415 0.008045201 0.1531 911 1248 0.038307 3570 0.00357 0.034737 0.018538848 0.307 1001 65 0.001995 879 0.000879 0.001116 0.01233023 0.01021 1461 4059 0.124589 25603 0.025603 0.098986 0.009273647 0.</th><th>weight(kg) 0.22834 time (s) ENERGY AREA c/s BKG 17- sept-13 BKG/s (100000s) NET c/s (100000s) efficiency eeae density g/cm3 FY corrections 63 229 0.007029 4111 0.004111 0.002918 0.019653868 0.037 143 38 0.001166 1727 0.001727 -0.00056 0.045331922 0.109 0.72 352 3840 0.117867 11658 0.011658 0.106209 0.027120874 0.356 609 2832 0.086927 8435 0.008435 0.078492 0.017938883 0.448 1764 540 0.016575 2160 0.00216 0.014415 0.008045201 0.1531 911 1248 0.038307 3570 0.00357 0.034737 0.018238048 0.307 1001 65 0.01995 879 0.008129 0.039755 0.043871662 0.0355 186 1560 0.047884 8129 0.008129 0.039755<th>weight(kg) 0.22834 time (s) 32579 ENERGY AREA c/s BKG 17- sept-13 BKG/s (100000s) NET c/s (100000s) efficiency eeae density g/cm3 FY corrections Bq/kg 63 229 0.007029 4111 0.004111 0.002918 0.01653868 0.037 18 143 38 0.001166 1727 0.001727 -0.00056 0.045331922 0.109 0.72 -0.36 352 3840 0.117867 11658 0.011658 0.106209 0.027120874 0.356 48 609 2832 0.086927 8435 0.008435 0.078492 0.017938883 0.448 43 1764 540 0.016575 2160 0.00216 0.014415 0.008045201 0.1531 51 911 1248 0.038307 3570 0.00357 0.034737 0.013240976 0.29 40 583 1773 0.054422 5269 0.002569 0.049153 0.018538848 0</th></th></td<>	weight(kg) ENERGY AREA c/s BKG 17- sept-13 BKG/s (1000000s) 63 229 0.007029 4111 0.004111 143 38 0.001166 1727 0.001727 352 3840 0.117867 11658 0.008435 609 2832 0.086927 8435 0.008435 1764 540 0.016575 2160 0.00216 911 1248 0.038307 3570 0.00357 583 1773 0.054422 5269 0.005269 1001 65 0.001995 879 0.008129 1461 4059 0.124589 25603 0.025603 186 1560 0.047884 8129 0.008129 186 1560 0.047884 8129 0.008129 186 1560 0.047884 8129 0.008129 186 1560 0.047884 8129 0.008129 186 1560 0.047884	weight(kg) 0.22834 ENERGY AREA c/s BKG 17- sept-13 BKG/s (1000000s) NET c/s 63 229 0.007029 4111 0.004111 0.002918 143 38 0.001166 1727 0.001727 -0.00056 352 3840 0.117867 11658 0.011658 0.106209 609 2832 0.086927 8435 0.008435 0.078492 1764 540 0.016575 2160 0.00216 0.014415 911 1248 0.038307 3570 0.00357 0.034737 583 1773 0.054422 5269 0.005269 0.049153 1001 65 0.00195 879 0.000879 0.001116 1461 4059 0.124589 25603 0.025603 0.098986 186 1560 0.047884 8129 0.008129 0.039755 186 1560 0.047884 8129 0.008129 0.035046 <	weight(kg) 0.22834 ENERGY AREA c/s BKG 17- sept-13 BKG/s (1000000s) NET c/s efficiency eeae density g/cm3 63 229 0.007029 4111 0.004111 0.002918 0.019653868 143 38 0.001166 1727 0.001727 -0.00056 0.045331922 352 3840 0.117867 11658 0.011658 0.106209 0.027120874 609 2832 0.086927 8435 0.008435 0.078492 0.017938883 1764 540 0.016575 2160 0.00216 0.014415 0.00804201 911 1248 0.038307 3570 0.00357 0.034737 0.013240976 583 1773 0.054422 5269 0.005269 0.049153 0.018538848 1001 65 0.001995 879 0.008179 0.001116 0.01233023 1461 4059 0.124589 25603 0.025603 0.098755 0.043871662 186	weight(kg) 0.22834 time (s) ENERGY AREA c/s BKG 17- sept-13 BKG/s (1000000s) NET c/s (1000000s) efficiency eeae density g/cm3 FY 63 229 0.007029 4111 0.004111 0.002918 0.019653868 0.037 143 38 0.001166 1727 0.001727 -0.00056 0.045331922 0.109 352 3840 0.117867 11658 0.011658 0.106209 0.027120874 0.356 609 2832 0.086927 8435 0.008435 0.078492 0.017938883 0.448 1764 540 0.016575 2160 0.00216 0.014415 0.008045201 0.1531 911 1248 0.038307 3570 0.00357 0.034737 0.018538848 0.307 1001 65 0.001995 879 0.000879 0.001116 0.01233023 0.01021 1461 4059 0.124589 25603 0.025603 0.098986 0.009273647 0.	weight(kg) 0.22834 time (s) ENERGY AREA c/s BKG 17- sept-13 BKG/s (100000s) NET c/s (100000s) efficiency eeae density g/cm3 FY corrections 63 229 0.007029 4111 0.004111 0.002918 0.019653868 0.037 143 38 0.001166 1727 0.001727 -0.00056 0.045331922 0.109 0.72 352 3840 0.117867 11658 0.011658 0.106209 0.027120874 0.356 609 2832 0.086927 8435 0.008435 0.078492 0.017938883 0.448 1764 540 0.016575 2160 0.00216 0.014415 0.008045201 0.1531 911 1248 0.038307 3570 0.00357 0.034737 0.018238048 0.307 1001 65 0.01995 879 0.008129 0.039755 0.043871662 0.0355 186 1560 0.047884 8129 0.008129 0.039755 <th>weight(kg) 0.22834 time (s) 32579 ENERGY AREA c/s BKG 17- sept-13 BKG/s (100000s) NET c/s (100000s) efficiency eeae density g/cm3 FY corrections Bq/kg 63 229 0.007029 4111 0.004111 0.002918 0.01653868 0.037 18 143 38 0.001166 1727 0.001727 -0.00056 0.045331922 0.109 0.72 -0.36 352 3840 0.117867 11658 0.011658 0.106209 0.027120874 0.356 48 609 2832 0.086927 8435 0.008435 0.078492 0.017938883 0.448 43 1764 540 0.016575 2160 0.00216 0.014415 0.008045201 0.1531 51 911 1248 0.038307 3570 0.00357 0.034737 0.013240976 0.29 40 583 1773 0.054422 5269 0.002569 0.049153 0.018538848 0</th>	weight(kg) 0.22834 time (s) 32579 ENERGY AREA c/s BKG 17- sept-13 BKG/s (100000s) NET c/s (100000s) efficiency eeae density g/cm3 FY corrections Bq/kg 63 229 0.007029 4111 0.004111 0.002918 0.01653868 0.037 18 143 38 0.001166 1727 0.001727 -0.00056 0.045331922 0.109 0.72 -0.36 352 3840 0.117867 11658 0.011658 0.106209 0.027120874 0.356 48 609 2832 0.086927 8435 0.008435 0.078492 0.017938883 0.448 43 1764 540 0.016575 2160 0.00216 0.014415 0.008045201 0.1531 51 911 1248 0.038307 3570 0.00357 0.034737 0.013240976 0.29 40 583 1773 0.054422 5269 0.002569 0.049153 0.018538848 0

<u>Table 10:</u> Table showing the concentration of each radionuclide for sample SO5.

SO5											
					weight(kg)	0.24817		time (s)		51457	
NUCLIDE	ENERGY	AREA	c/s	BKG 17-	BKG/s	NET c/s	efficiency	FY	corrections	Bq/kg	
				sept-13	(1000000\$)		eeae				
							g/cm3				
Th-234	63	347	0.006743	4111	0.004111	0.002632	0.019653868	0.037		15	
U-235	143	156	0.003032	1727	0.001727	0.001305	0.045331922	0.109	0.72	0.77	
Pb-	352	4182	0.081272	11658	0.011658	0.069614	0.027120874	0.356		29	
214											
Bi-214	609	3240	0.062965	8435	0.008435	0.05453	0.017938883	0.448		27	
Bi-214	1764	641	0.012457	2160	0.00216	0.010297	0.008045201	0.1531		34	
Ac-	911	1569	0.030491	3570	0.00357	0.026921	0.013240976	0.29		28	
228											
TI-208	583	2438	0.047379	5269	0.005269	0.04211	0.018538848	0.307		30	
Pa-234	1001	56	0.001088	879	0.000879	0.000209	0.012333023	0.01021		7	
K-40	1461	6124	0.119012	25603	0.025603	0.093409	0.009273647	0.1067		380	
Ra-226+U-235	186	1561	0.030336	8129	0.008129	0.022207	0.043871662	0.0355		57	
Ra-226 Gilmore correction	186	1561	0.030336	8129	0.008129	0.022207	0.043871662	0.0355	0.571	32.81	
Ra-226 ONLY U-235 fromTh-234	186	1561	0.030336	8129	0.008129	0.01796	0.043871662	0.0355		46	AVERAGE Ra-226
Ra-226 ONLY U-235 from	186	1561	0.030336	8129	0.008129	0.020257	0.043871662	0.0355		52	49
Pa-234				0.20		0.020201					
Ra-226 ONLY U-235 from 143 keV	186	1561	0.030336	8129	0.008129	0.017411	0.043871662	0.0355		45	
Cs- 137	661.6	4341	0.084362	0	0	0.084362	0.016852636	0.85		24	

Table 11: Table showing the concentration of each radionuclide for sample SO6.

SO6											
					weight(kg)	0.2421		time (s)		94535	
NUCLIDE	ENERGY	AREA	c/s	BKG 17-	BKG/s	NET c/s	efficiency	FY	corrections	Bq/kg	
				sept-13	(1000000s)		eeae				
							density g/cm3				
Th-234	63	650	0.006876	4111	0.004111	0.002765	0.019653868	0.037		16	
U-235	143	392	0.004147	1727	0.001727	0.00242	0.045331922	0.109	0.72	1.46	
Pb-214	352	6679	0.070651	11658	0.011658	0.058993	0.027120874	0.356		25	
Bi-214	609	5002	0.052912	8435	0.008435	0.044477	0.017938883	0.448		23	
Bi-214	1764	911	0.009637	2160	0.00216	0.007477	0.008045201	0.1531		25	
Ac-228	911	3598	0.03806	3570	0.00357	0.03449	0.013240976	0.29		37	
TI-208	583	5077	0.053705	5269	0.005269	0.048436	0.018538848	0.307		35	
Pa-234	1001	136	0.001439	879	0.000879	0.00056	0.012333023	0.01021		18	
K-40	1461	11205	0.118528	25603	0.025603	0.092925	0.009273647	0.1067		388	
Ra-226+U-235	186	2777	0.029375	8129	0.008129	0.021246	0.043871662	0.0355		56	
Ra-226 Gilmore correction	186	2777	0.029375	8129	0.008129	0.021246	0.043871662	0.0355	0.571	32.17	
Ra-226 ONLY U-235 from	186	2777	0.029375	8129	0.008129	0.016785	0.043871662	0.0355		45	AVERAGE Ra-
Ra-226 ONLY 11-235 from	186	2777	0 029375	8129	0.008129	0.016032	0.043871662	0.0355		43	40
Pa-234	100	2111	0.023373	0125	0.000123	0.010032	0.04007 1002	0.0000		-5	-0
Ra-226 ONLY U-235 from 143 keV	186	2777	0.029375	8129	0.008129	0.012352	0.043871662	0.0355		33	
Cs-137	661.6	2934	0.031036	0	0	0.031036	0.016852636	0.85		9	

<u>**Table 12:**</u> Table showing the concentration of each radionuclide of sample SOcap1.

SOcap1											
					weight(kg)	0.28806		time (s)		29103	
NUCLIDE	ENERGY	AREA	C/S	BKG 17-	BKG/s	NET c/s	efficiency	FY	corrections	Bq/kg	
				sept-13	(1000005)		eeae				
							g/cm3				
Th-234	63	224	0.007697	4111	0.004111	0.003586	0.019653868	0.037		17	
U-235	143	120	0.004123	1727	0.001727	0.002396	0.045331922	0.109	0.72	1.21	
Pb-214	352	2420	0.083153	11658	0.011658	0.071495	0.027120874	0.356		26	
Bi-214	609	1805	0.062021	8435	0.008435	0.053586	0.017938883	0.448		23	
Bi-214	1764	362	0.012439	2160	0.00216	0.010279	0.008045201	0.1531		29	
Ac-228	911	1621	0.055699	3570	0.00357	0.052129	0.013240976	0.29		47	
TI-208	583	2237	0.076865	5269	0.005269	0.071596	0.018538848	0.307		44	
Pa-234	1001	38	0.001306	879	0.000879	0.000427	0.012333023	0.01021		12	
K-40	1461	8044	0.276398	25603	0.025603	0.250795	0.009273647	0.1067		880	
Ra-226+U-235	186	904	0.031062	8129	0.008129	0.022933	0.043871662	0.0355		51	
Ra-226 Gilmore correction	186	904	0.031062	8129	0.008129	0.022933	0.043871662	0.0355	0.571	29.19	
Ra-226 ONLY U-235 from Th- 234	186	904	0.031062	8129	0.008129	0.017147	0.043871662	0.0355		38	AVERAGE Ra- 226
Ra-226 ONLY U-235 from Pa- 234	186	904	0.031062	8129	0.008129	0.018957	0.043871662	0.0355		42	40
Ra-226 ONLY U-235 from 143 keV	186	904	0.031062	8129	0.008129	0.014125	0.043871662	0.0355		31	
Cs-137	661.6	0	0	0	0	0	0.016852636	0.85		0	

Table 13: Table showing the concentration of each radionuclide for sample SOcap2.

SOcap2											
					weight(kg)	0.34015		time (s)		52782	
NUCLIDE	ENERGY	AREA	c/s	BKG 17-	BKG/s	NET c/s	efficiency	FY	corrections	Bq/kg	
				sept-13	(1000000s)		eeae				
							g/cm3				
Th-234	63	241	0.004566	4111	0.004111	0.000455	0.01651416	0.037		2	
U-235	143	90	0.001705	1727	0.001727	-2.2E-05	0.036515883	0.109	0.72	-0.01	
Pb-214	352	3158	0.059831	11658	0.011658	0.048173	0.023232449	0.356		17	
Bi-214	609	2489	0.047156	8435	0.008435	0.038721	0.015400649	0.448		16	
Bi-214	1764	465	0.00881	2160	0.00216	0.00665	0.006936303	0.1531		18	
Ac-228	911	1275	0.024156	3570	0.00357	0.020586	0.011385791	0.29		18	
TI-208	583	1758	0.033307	5269	0.005269	0.028038	0.015912945	0.307		17	
Pa-234	1001	50	0.000947	879	0.000879	6.83E-05	0.010609048	0.01021		2	
K-40	1461	5575	0.105623	25603	0.025603	0.08002	0.007989403	0.1067		276	
Ra-226+U-235	186	1238	0.023455	8129	0.008129	0.015326	0.037485843	0.0355		34	
Ra-226 Gilmore correction	186	1238	0.023455	8129	0.008129	0.015326	0.037485843	0.0355	0.571	19.33	
Ra-226 ONLY U-235 from Th- 234	186	1238	0.023455	8129	0.008129	0.01458	0.037485843	0.0355		32	AVERAGE Ra- 226
Ra-226 ONLY U-235 from Pa- 234	186	1238	0.023455	8129	0.008129	0.014694	0.037485843	0.0355		32	33
Ra-226 ONLY U-235 from 143 keV	186	1238	0.023455	8129	0.008129	0.015411	0.037485843	0.0355		34	
Cs-137	661.6	127	0.002406	0	0	0.002406	0.014472894	0.85		0.6	

<u>**Table 14:**</u> Table showing the concentration of each radionuclide for sample SOcap3.

SOcap3											
					weight(kg)	0.33342		time (s)		31584	
NUCLIDE	ENERGY	AREA	c/s	BKG 17- sent-13	BKG/s (1000000s)	NET c/s	efficiency	FY	corrections	Bq/kg	
				copt io	(1000000)		density				
							g/cm3				
Th-234	63	159	0.005034	4111	0.004111	0.000923	0.01651416	0.037		5	
U-235	143	69	0.002185	1727	0.001727	0.000458	0.036515883	0.109	0.72	0.25	
Pb-214	352	1458	0.046163	11658	0.011658	0.034505	0.023232449	0.356		13	
Bi-214	609	1151	0.036443	8435	0.008435	0.028008	0.015400649	0.448		12	
Bi-214	1764	240	0.007599	2160	0.00216	0.005439	0.006936303	0.1531		15	
Ac-228	911	722	0.02286	3570	0.00357	0.01929	0.011385791	0.29		18	
TI-208	583	979	0.030997	5269	0.005269	0.025728	0.015912945	0.307		16	
Pa-234	1001	30	0.00095	879	0.000879	7.08E-05	0.010609048	0.01021		2	
K-40	1461	3045	0.09641	25603	0.025603	0.070807	0.007989403	0.1067		249	
Ra-226+U-235	186	559	0.017699	8129	0.008129	0.00957	0.037485843	0.0355		22	
Ra-226 Gilmore correction	186	559	0.017699	8129	0.008129	0.00957	0.037485843	0.0355	0.571	12.32	
Ra-226 ONLY U-235 from Th- 234	186	559	0.017699	8129	0.008129	0.008055	0.037485843	0.0355		18	AVERAGE Ra- 226
Ra-226 ONLY U-235 from Pa- 234	186	559	0.017699	8129	0.008129	0.008914	0.037485843	0.0355		20	19
Ra-226 ONLY U-235 from 143 keV	186	559	0.017699	8129	0.008129	0.007785	0.037485843	0.0355		18	
Cs-137	661.6	48	0.00152	0	0	0.00152	0.014472894	0.85		0.4	

Table 15: Table showing the concentration of each radionuclide for sample SOcap4.

SOcap4											
					weight(kg)	0.32698		time (s)		54067	
NUCLIDE	ENERGY	AREA	c/s	BKG 17-	BKG/s	NET c/s	efficiency	FY	corrections	Bq/kg	
				sept-13	(1000000\$)		eeae				
							density g/cm3				
Th-234	63	264	0.004883	4111	0.004111	0.000772	0.01651416	0.037		4	
U-235	143	111	0.002053	1727	0.001727	0.000326	0.036515883	0.109	0.72	0.18	
Pb-214	352	2628	0.048606	11658	0.011658	0.036948	0.023232449	0.356		14	
Bi-214	609	2013	0.037232	8435	0.008435	0.028797	0.015400649	0.448		13	
Bi-214	1764	356	0.006584	2160	0.00216	0.004424	0.006936303	0.1531		13	
Ac-228	911	1224	0.022639	3570	0.00357	0.019069	0.011385791	0.29		18	
TI-208	583	1801	0.033311	5269	0.005269	0.028042	0.015912945	0.307		18	
Pa-234	1001	52	0.000962	879	0.000879	8.28E-05	0.010609048	0.01021		2	
K-40	1461	5125	0.09479	25603	0.025603	0.069187	0.007989403	0.1067		248	
Ra-226+U-235	186	1046	0.019346	8129	0.008129	0.011217	0.037485843	0.0355		26	
Ra-226 Gilmore correction	186	1046	0.019346	8129	0.008129	0.011217	0.037485843	0.0355	0.571	14.72	
Ra-226 ONLY U-235 from Th- 234	186	1046	0.019346	8129	0.008129	0.009951	0.037485843	0.0355		23	AVERAGE Ra- 226
Ra-226 ONLY U-235 from Pa- 234	186	1046	0.019346	8129	0.008129	0.010451	0.037485843	0.0355		24	23
Ra-226 ONLY U-235 from 143 keV	186	1046	0.019346	8129	0.008129	0.009946	0.037485843	0.0355		23	
Cs-137	661.6	109	0.002016	0	0	0.002016	0.014472894	0.85		0.5	

Table 16: Table showing the concentration of each radionuclide for sample SOcap5.

SOcap5											
					weight(kg)	0.35461		time (s)		30760	
NUCLIDE	ENERGY	AREA	c/s	BKG 17-	BKG/s	NET c/s	efficiency	FY	corrections	Bq/kg	
				sept-13	(1000000s)		eeae				
							density g/cm3				
Th-234	63	199	0.006469	4111	0.004111	0.002358	0.01651416	0.037		11	
U-235	143	62	0.002016	1727	0.001727	0.000289	0.036515883	0.109	0.72	0.15	
Pb-214	352	1445	0.046977	11658	0.011658	0.035319	0.023232449	0.356		12	
Bi-214	609	1154	0.037516	8435	0.008435	0.029081	0.015400649	0.448		12	
Bi-214	1764	230	0.007477	2160	0.00216	0.005317	0.006936303	0.1531		14	
Ac-228	911	549	0.017848	3570	0.00357	0.014278	0.011385791	0.29		12	
TI-208	583	717	0.023309	5269	0.005269	0.01804	0.015912945	0.307		10	
Pa-234	1001	35	0.001138	879	0.000879	0.000259	0.010609048	0.01021		7	
K-40	1461	2352	0.076463	25603	0.025603	0.05086	0.007989403	0.1067		168	
Ra-226+U-235	186	511	0.016612	8129	0.008129	0.008483	0.037485843	0.0355		18	
Ra-226 Gilmore correction	186	511	0.016612	8129	0.008129	0.008483	0.037485843	0.0355	0.571	10.27	
Ra-226 ONLY U-235 from Th- 234	186	511	0.016612	8129	0.008129	0.004614	0.037485843	0.0355		10	AVERAGE Ra- 226
Ra-226 ONLY U-235 from Pa- 234	186	511	0.016612	8129	0.008129	0.006088	0.037485843	0.0355		13	13
Ra-226 ONLY U-235 from143 keV	186	511	0.016612	8129	0.008129	0.007358	0.037485843	0.0355		16	
Cs-137	661.6	67	0.002178	0	0	0.002178	0.014472894	0.85		0.5	

<u>Table 17:</u> Table showing the concentrations of each radionuclide for sample SOcap6.

SOcap6											
					weight(kg)	0.30065		time (s)		53889	
									-		
NUCLIDE	ENERGY	AREA	c/s	BKG 17-	BKG/s	NET c/s	efficiency	FY	corrections	Bq/kg	
				sept-13	(1000000s)		eeae				
							g/cm3				
Th-234	63	250	0.004639	4111	0.004111	0.000528	0.01651416	0.037		3	
U-235	143	147	0.002728	1727	0.001727	0.001001	0.036515883	0.109	0.72	0.60	
Pb-214	352	2019	0.037466	11658	0.011658	0.025808	0.023232449	0.356		10	
Bi-214	609	1656	0.03073	8435	0.008435	0.022295	0.015400649	0.448		11	
Bi-214	1764	322	0.005975	2160	0.00216	0.003815	0.006936303	0.1531		12	
Ac-228	911	1110	0.020598	3570	0.00357	0.017028	0.011385791	0.29		17	
TI-208	583	1533	0.028447	5269	0.005269	0.023178	0.015912945	0.307		16	
Pa-234	1001	52	0.000965	879	0.000879	8.59E-05	0.010609048	0.01021		3	
K-40	1461	4820	0.089443	25603	0.025603	0.06384	0.007989403	0.1067		249	
Ra-226+U-235	186	893	0.016571	8129	0.008129	0.008442	0.037485843	0.0355		21	
Ra-226 Gilmore correction	186	893	0.016571	8129	0.008129	0.008442	0.037485843	0.0355	0.571	12.05	
Ra-226 ONLY U-235 from Th- 234	186	893	0.016571	8129	0.008129	0.007576	0.037485843	0.0355		19	AVERAGE Ra- 226
Ra-226 ONLY U-235 from Pa-	186	893	0.016571	8129	0.008129	0.007647	0.037485843	0.0355		19	16
204 Do 226 ONILV 11 225 from 142	100	000	0.010571	0100	0.000400	0.00454	0.007405040	0.0255		4.4	
keV	186	893	0.016571	8129	0.008129	0.00454	0.037485843	0.0355		11	
Cs-137	661.6	28	0.00052	0	0	0.00052	0.014472894	0.85		0.1	

<u>Table 18:</u> Table showing the concentration of each radionuclide for sample SOcap7.

SOcap7											
					weight(kg)	0.34258		time (s)		31893	
NUCLIDE	ENERGY	AREA	c/s	BKG 17- sept-13	BKG/s (1000000s)	NET c/s	efficiency eeae	FY	corrections	Bq/kg	
							density g/cm3				
Th-234	63	169	0.005299	4111	0.004111	0.001188	0.01651416	0.037		6	
U-235	143	60	0.001881	1727	0.001727	0.000154	0.036515883	0.109	0.72	0.08	
Pb-214	352	1396	0.043771	11658	0.011658	0.032113	0.023232449	0.356		11	
Bi-214	609	1130	0.035431	8435	0.008435	0.026996	0.015400649	0.448		11	
Bi-214	1764	233	0.007306	2160	0.00216	0.005146	0.006936303	0.1531		14	
Ac-228	911	656	0.020569	3570	0.00357	0.016999	0.011385791	0.29		15	
TI-208	583	959	0.030069	5269	0.005269	0.0248	0.015912945	0.307		15	
Pa-234	1001	39	0.001223	879	0.000879	0.000344	0.010609048	0.01021		9	
K-40	1461	3107	0.097419	25603	0.025603	0.071816	0.007989403	0.1067		246	
Ra-226+U-235	186	559	0.017527	8129	0.008129	0.009398	0.037485843	0.0355		21	
Ra-226 Gilmore correction	186	559	0.017527	8129	0.008129	0.009398	0.037485843	0.0355	0.571	11.77	
Ra-226 ONLY U-235 from Th- 234	186	559	0.017527	8129	0.008129	0.007449	0.037485843	0.0355		16	AVERAGE Ra- 226
Ra-226 ONLY U-235 from Pa- 234	186	559	0.017527	8129	0.008129	0.006216	0.037485843	0.0355		14	16
Ra-226 ONLY U-235 from 143 keV	186	559	0.017527	8129	0.008129	0.008797	0.037485843	0.0355		19	
Cs-137	661.6	0	0	0	0	0	0.014472894	0.85		0.0	

Table 19: Table showing the concentration of each radionuclide for sample SOcap8.

SOcap8											
					weight(kg)	0.3404		time (s)		53637	
NUCLIDE	ENERGY	AREA	c/s	BKG 17- sept-13	BKG/s (1000000s)	NET c/s	efficiency eeae	FY	corrections	Bq/kg	
				·			density g/cm3				
Th-234	63	287	0.005351	4111	0.004111	0.00124	0.01651416	0.037		6	
U-235	143	144	0.002685	1727	0.001727	0.000958	0.036515883	0.109	0.72	0.51	
Pb-214	352	2879	0.053676	11658	0.011658	0.042018	0.023232449	0.356		15	
Bi-214	609	2266	0.042247	8435	0.008435	0.033812	0.015400649	0.448		14	
Bi-214	1764	405	0.007551	2160	0.00216	0.005391	0.006936303	0.1531		15	
Ac-228	911	1466	0.027332	3570	0.00357	0.023762	0.011385791	0.29		21	
TI-208	583	2126	0.039637	5269	0.005269	0.034368	0.015912945	0.307		21	
Pa-234	1001	67	0.001249	879	0.000879	0.00037	0.010609048	0.01021		10	
K-40	1461	7689	0.143353	25603	0.025603	0.11775	0.007989403	0.1067		406	
Ra-226+U-235	186	1259	0.023473	8129	0.008129	0.015344	0.037485843	0.0355		34	
Ra-226 Gilmore correction	186	1259	0.023473	8129	0.008129	0.015344	0.037485843	0.0355	0.571	19.34	
Ra-226 ONLY U-235 from Th- 234	186	1259	0.023473	8129	0.008129	0.013309	0.037485843	0.0355		29	AVERAGE Ra- 226
Ra-226 ONLY U-235 from Pa- 234	186	1259	0.023473	8129	0.008129	0.011918	0.037485843	0.0355		26	27
Ra-226 ONLY U-235 from 143 keV	186	1259	0.023473	8129	0.008129	0.011609	0.037485843	0.0355		26	
Cs-137	661.6	149	0.002778	0	0	0.002778	0.014472894	0.85		0.7	

<u>Table 20:</u> Table showing the concentration of each radionuclide for sample SOcap9.

SOcap9											
					wieght(kg)	0.35538		time (s)		29698	
NUCLIDE	ENERGY	AREA	c/s	BKG 17-	BKG/s	NET c/s	efficiency	FY	corrections	Bq/kg	
				sept-13	(1000000s)		eeae				
							density g/cm3				
Th-234	63	140	0.004714	4111	0.004111	0.000603	0.01651416	0.037		3	
U-235	143	60	0.00202	1727	0.001727	0.000293	0.036515883	0.109	0.72	0.15	
Pb-214	352	1357	0.045693	11658	0.011658	0.034035	0.023232449	0.356		12	
Bi-214	609	1022	0.034413	8435	0.008435	0.025978	0.015400649	0.448		11	
Bi-214	1764	213	0.007172	2160	0.00216	0.005012	0.006936303	0.1531		13	
Ac-228	911	752	0.025322	3570	0.00357	0.021752	0.011385791	0.29		19	
TI-208	583	904	0.03044	5269	0.005269	0.025171	0.015912945	0.307		14	
Pa-234	1001	38	0.00128	879	0.000879	0.000401	0.010609048	0.01021		10	
K-40	1461	2823	0.095057	25603	0.025603	0.069454	0.007989403	0.1067		229	
Ra-226+U-235	186	690	0.023234	8129	0.008129	0.015105	0.037485843	0.0355		32	
Ra-226 Gilmore correction	186	690	0.023234	8129	0.008129	0.015105	0.037485843	0.0355	0.571	18.24	
Ra-226 ONLY U-235 from Th- 234	186	690	0.023234	8129	0.008129	0.014115	0.037485843	0.0355		30	AVERAGE Ra- 226
Ra-226 ONLY U-235 from Pa- 234	186	690	0.023234	8129	0.008129	0.011398	0.037485843	0.0355		24	28
Ra-226 ONLY U-235 from 143 keV	186	690	0.023234	8129	0.008129	0.013961	0.037485843	0.0355		30	
Cs-137	661.6	0	0	0	0	0	0.014472894	0.85		0.0	

<u>Table 21:</u> Table showing the concentrations of each radionuclide for sample SOcap10.

SOcap10											
					weight(kg)	0.33036		time (s)		56092	
NUCLIDE	ENERGY	AREA	c/s	BKG 17- sept-13	BKG/s (1000000s)	NET c/s	efficiency eeae	FY	corrections	Bq/kg	
							density g/cm3				
Th-234	63	314	0.005598	4111	0.004111	0.001487	0.01651416	0.037		7	
U-235	143	128	0.002282	1727	0.001727	0.000555	0.036515883	0.109	0.72	0.30	
Pb-214	352	3081	0.054928	11658	0.011658	0.04327	0.023232449	0.356		16	
Bi-214	609	2434	0.043393	8435	0.008435	0.034958	0.015400649	0.448		15	
Bi-214	1764	463	0.008254	2160	0.00216	0.006094	0.006936303	0.1531		17	
Ac-228	911	1762	0.031413	3570	0.00357	0.027843	0.011385791	0.29		26	
TI-208	583	2539	0.045265	5269	0.005269	0.039996	0.015912945	0.307		25	
Pa-234	1001	70	0.001248	879	0.000879	0.000369	0.010609048	0.01021		10	
K-40	1461	8576	0.152892	25603	0.025603	0.127289	0.007989403	0.1067		452	
Ra-226+U-235	186	1294	0.023069	8129	0.008129	0.01494	0.037485843	0.0355		34	
Ra-226 Gilmore correction	186	1294	0.023069	8129	0.008129	0.01494	0.037485843	0.0355	0.571	19.40	
Ra-226 ONLY U-235 from Th- 234	186	1294	0.023069	8129	0.008129	0.012501	0.037485843	0.0355		28	AVERAGE Ra- 226
Ra-226 ONLY U-235 from Pa- 234	186	1294	0.023069	8129	0.008129	0.011525	0.037485843	0.0355		26	28
Ra-226 ONLY U-235 from 143 keV	186	1294	0.023069	8129	0.008129	0.012776	0.037485843	0.0355		29	
Cs-137	661.6	0	0	0	0	0	0.014472894	0.85		0.0	

Table 22: Table showing the concentration of each radionuclide for sample SOcap11.

SOcap11											
					weight(kg)	0.32577		time (s)		32011	
NUCLIDE	ENEDOX		- 1-	DKO 47	DKO/a		- ff : - : - : : -	FV		Der/leer	
NUCLIDE	ENERGY	AREA	C/S	BKG 17- sent-13	BKG/S (100000s)	NEI C/S	efficiency	FΥ	corrections	вq/кд	
				Sept 10	(10000003)		density				
							g/cm3				
Th-234	63	210	0.00656	4111	0.004111	0.002449	0.01651416	0.037		12	
U-235	143	64	0.001999	1727	0.001727	0.000272	0.036515883	0.109	0.72	0.15	
Pb-214	352	1627	0.050826	11658	0.011658	0.039168	0.023232449	0.356		15	
Bi-214	609	1261	0.039393	8435	0.008435	0.030958	0.015400649	0.448		14	
Bi-214	1764	208	0.006498	2160	0.00216	0.004338	0.006936303	0.1531		13	
Ac-228	911	895	0.027959	3570	0.00357	0.024389	0.011385791	0.29		23	
TI-208	583	1094	0.034176	5269	0.005269	0.028907	0.015912945	0.307		18	
Pa-234	1001	47	0.001468	879	0.000879	0.000589	0.010609048	0.01021		17	
K-40	1461	3373	0.10537	25603	0.025603	0.079767	0.007989403	0.1067		287	
Ra-226+U-235	186	700	0.021867	8129	0.008129	0.013738	0.037485843	0.0355		32	
Ra-226 Gilmore correction	186	700	0.021867	8129	0.008129	0.013738	0.037485843	0.0355	0.571	18.10	
Ra-226 ONLY U-235 from Th-	186	700	0.021867	8129	0.008129	0.00972	0.037485843	0.0355		22	AVERAGE Ra-
234											226
Ra-226 ONLY U-235 from Pa-	186	700	0.021867	8129	0.008129	0.008285	0.037485843	0.0355		19	21
234											
Ra-226 ONLY U-235 from 143	186	700	0.021867	8129	0.008129	0.012677	0.037485843	0.0355		29	
keV											
Cs-137	661.6	0	0	0	0	0	0.014472894	0.85		0.0	

<u>Table 23:</u> Table showing the concentration of each radionuclide for sample SOcap12.

SOcap12											
					weightkg)	0.31404		time (s)		52719	
NUCLIDE	ENERGY	AREA	c/s	BKG 17- sept-13	BKG/s (1000000s)	NET c/s	efficiency eeae	FY	corrections	Bq/kg	
							density g/cm3				
Th-234	63	182	0.003452	4111	0.004111	-0.00066	0.01651416	0.037		0	
U-235	143	118	0.002238	1727	0.001727	0.000511	0.036515883	0.109	0.72	0.29	
Pb-214	352	2521	0.04782	11658	0.011658	0.036162	0.023232449	0.356		14	
Bi-214	609	1863	0.035338	8435	0.008435	0.026903	0.015400649	0.448		12	
Bi-214	1764	350	0.006639	2160	0.00216	0.004479	0.006936303	0.1531		13	
Ac-228	911	1018	0.01931	3570	0.00357	0.01574	0.011385791	0.29		15	
TI-208	583	1524	0.028908	5269	0.005269	0.023639	0.015912945	0.307		15	
Pa-234	1001	50	0.000948	879	0.000879	6.94E-05	0.010609048	0.01021		2	
K-40	1461	5747	0.109012	25603	0.025603	0.083409	0.007989403	0.1067		312	
Ra-226+U-235	186	1000	0.018968	8129	0.008129	0.010839	0.037485843	0.0355		26	
Ra-226 Gilmore correction	186	1000	0.018968	8129	0.008129	0.010839	0.037485843	0.0355	0.571	14.81	
Ra-226 ONLY U-235 from Th- 234	186	1000	0.018968	8129	0.008129	0.010839	0.037485843	0.0355		26	AVERAGE Ra- 226
Ra-226 ONLY U-235 from Pa- 234	186	1000	0.018968	8129	0.008129	0.010197	0.037485843	0.0355		24	24
Ra-226 ONLY U-235 from 143 keV	186	1000	0.018968	8129	0.008129	0.008846	0.037485843	0.0355		21	
Cs-137	661.6	0	0	0	0	0	0.014472894	0.85		0.0	

Sample	²³⁴ Th	²³⁵ U	²¹⁴ Pb	²¹⁴ Bi	²²⁸ Ac	²⁰⁸ Tl	²³⁴ Pa	⁴⁰ K	²²⁶ Ra _{aver}	rage ¹³⁷ Cs
PG01	32	1.49	550	505	10	15	36	10	597	0
PG02	100	8.89	505	470	6	4	94	14	629	0
PG03	13	0.92	146	138	8	9	26	103	162	0
SO1	30	2.91	80	72	26	24	26	279	147	52
SO2	55	0.12	97	88	31	33	89	356	149	35
SO3	24	0.88	29	29	41	41	18	424	46	11
SO4	18	-0.36	48	43	40	38	39	438	91	50
SO5	15	0.77	29	27	28	30	7	380	49	24
SO6	16	1.46	25	23	37	35	18	388	40	9
SOcap1	17	1.21	26	23	47	44	12	880	40	0
SOcap2	2	-0.01	17	16	18	17	2	276	33	0.6
SOcap3	5	0.25	13	12	18	16	2	249	19	0.4
SOcap4	4	0.18	14	13	18	18	2	248	23	0.5
SOcap5	11	0.15	12	12	12	10	7	168	13	0.5
SOcap6	3	0.60	10	11	17	16	3	249	16	0.1
SOcap7	6	0.08	11	11	15	15	9	246	16	0
SOcap8	6	0.51	15	14	21	21	10	406	27	0.7
SOcap9	3	0.15	12	11	19	14	10	229	28	0
SOcap10	7	0.30	16	15	26	25	10	452	28	0
SOcap11	12	0.15	15	14	23	18	17	287	21	0
SOcap12	0	0.29	14	12	15	15	2	312	24	0

<u>**Table 24:**</u> Summarized γ -ray spectrometry results per sample, per nuclide in Bq/Kg.

As shown in the above Table 24, it is easily understood that the greater values in ²²⁶Ra concentrations are found at the phosphogypsum samples. This is more than expected, since as referred in literature, phosphogypsum is likely to contain high concentrations in ²²⁶Ra, and other radionuclides. (Fukuma et al., 2000; Azouazi et al., 2001; Santos et al., 2006; Papastefanou et al., 2006; Bituh et al., 2009; Villalobos et al., 2010; Al Attar et al., 2011; Okeji and Agwu, 2012; El-Didamony et al., 2013, Figure 47)

Fukuma et al. (2000) analysed phosphogypsum taken from Itataia (Brazil), by y-ray spectrometry and found a mean 226 Ra radioactivity concentration of 13 ± 1 Bq/kg. 226 Ra, 228 Ra and ²¹⁰Pb were predominant in phosphogypsum, whereas ²²⁸Th, ²³⁰Th and ²³²Th in the uraniumfree phosphoric acid. Papastefanou et al. (2006) found that the ²²⁶Ra content in phosphogypsum samples taken from a fertilizer industry in Thessaloniki, varied from 261 to 688 Bq/kg (mean value of 508 Bq/kg). They suggested continuous ²²⁶Ra control (monitoring) of phosphogypsum available for use in agricultural land is needed before any use. Santos et al. (2006) found by measuring phosphogypsum samples with γ -ray spectrometry for Industry A and Industry B, both operating in Brazil, a mean value of 811 Bg/kg and 350 Bg/kg of ²²⁶Ra, respectively. Bituh et al. (2009) found that the mean value of 226 Ra content in phosphogypsum, determined by γ -ray spectrometry, was 483±1,90 Bq/kg. The ²²⁶Ra concenctrations in phosphogypsum were 10 times higher than the content in soil samples from the surrounding area. Villalobos et al. (2010) indicated ²²⁶Ra content of phosphogypsum taken from a fertilizer industry in Huelva (Spain), was 785±42 Bq/kg. Zielinski et al. (2011) found that the mean activity concentration of ²²⁶Ra in the composite samples of phosphogypsum was 601±98 Bq/kg (ranged from 468 to 746 Bq/kg). All phosphogypsum samples of this study exceed a ²²⁶Ra concentration of 370 Bq/kg which is considered to be the upper limit for phosphogypsum use as a soil amendment by the US Environmental Protection Agency. Al-Attar et al. (2011) in Syrian phosphogypsum found that the ²²⁶Ra content, determined by γ -ray spectrometry with high relative efficiency 80% and HPGe detector (P-type, Eurisys, France) fitted with Interwinner software (version4), had a mean value of 318 Bq/kg (ranged from 259 to 381 Bq/kg), lower than the EPA recommended limit for phosphogyspum use in agriculture. Over 80% of ²³²Th, ²¹⁰Po and ²¹⁰Pb was found to partition in phosphogypsum with mean concentrations of 2.1, 1014 and 507 Bq/kg respectively; while ²³⁸U remained in the phosphoric acid produced. Apart ²¹⁰Po and ²¹⁰Pb the mean activity concentrations of the studied radionuclides in Syrian phosphogypsum were among the lowest reported values. This conclude that Syrian phosphogypsum could be used as a resource material for soil amendment. According to the above referenced case studies the phospshogypsum, in Schistos waste site, values of ²²⁶Ra radioactivity concentrations can be characterized as typical. (Figure 47)

Besides the high phosphogypsum radioactivity concentrations observed above, it can also be noted that two (red colour) out of six soil samples from the surrounding area, show high radioactivity concentrations (²²⁶Ra), which is not expected. This may have happened because of airborne transfer of phosphogypsum, due to the fact that it is currently exposed. Concerning the geological background of the Schistos waste site, represented by the Sub-Pelagonian (Triassic) Ano Liosia limestones, it is known that there are negligible amounts of U and Th (Godelitsas, personal communication), which means that there is little or no interference in the measured radioactivity of the deposited phosphogypsum.

Papageorgiou Fani M.Sc. Thesis, Geology - Geoenvironment Department, University of Athens, 2014



Figure 47: Chart showing the ²²⁶Ra (Bq/kg) concentration in different countries. Red indicates our studied area.

3.1.6 RI-XRF Analyses

Below are given the X-ray fluorescence spectra for the three phosphogypsum samples, PG01, PG02 and PG03. As it is shown in each spectrum phosphogypsum contains varius concentrations of calcium (Ca), potassium (K), phosphorus (P), iron (Fe), titanium (Ti) and chromium (Cr).



Figure 48: PG01 spectrum measured by RI-XRF.

Figure 49: PG02 spectrum measured by RI-XRF



Figure 50: PG03 spectrum measured by RI-XRF.

Villalobos et al. (2010) analysed phosphogypsum by XRF and confirmed that it mainly consisted of $CaSO_4.2H_2O$. The mass of S and Ca is close to 90% of total weight. The major content impurities in phosphogypsum were SiO₂, P₂O₅, Fe₂O₃, Al₂O₃ and Na₂O, and to a lesser extent, K₂O and TiO₂. In phosphogypsum SiO₂ may by found as quartz, and together with Al₂O₃, NaO and/or K₂O, might indicate the presence of clay minerals.

3.1.7 Chemical composition of phosphogypsum

The results of the ICP – MS analyses for phosphogypsum are presented in Table 25. The solid material was analyzed for major and trace elements., where red colour are indicated those elements which are considered to be dangerous in some concentrations. After that, phosphogypsum was normalized based on chondrite, upper continental crust, average shale and average phosphorite, as shown below in tables 26, 27, 28, 29.

Major elements	MDL	wt.%	Trace elements	MDL	ppm	Trace elements	MDL	ppm	Trace elements	MDL	ppm
CaO	0.01	33.65	Sr	0.5	705	Gd	0.05	7.7	Lu	0.01	0.81
LOI		21.8	K	83	581	Pr	0.02	7.1	Со	0.2	0.80
Total S	0.02	15.2	Ti	60	180	As	0.5	6.5	Sb	0.1	0.70
SiO2	0.01	3.64	Y	0.1	107	Er	0.03	6.2	Cs	0.1	0.30
P2O5	0.01	1.99	Ba	1	84	Sm	0.05	5.6	Hf	0.1	0.30
Total C	0.02	0.52	La	0.1	49	Cd	0.1	5.5	Tl	0.1	0.20
Al2O3	0.01	0.48	Cr	14	41	Yb	0.05	5.3	Та	0.1	0.10
Na2O	0.01	0.39	V	8	32	Rb	0.1	2.6	Hg	0.01	0.08
Fe2O3	0.04	0.29	Nd	0.3	32	Но	0.02	2.0	Au	0.0005	0.0049
MgO	0.01	0.18	Zn	1	28	Th	0.2	1.60	Sc	1	<1
MnO	0.01	< 0.01	Ce	0.1	21	Se	0.5	1.50	Be	1	<1
			U	0.1	13	Eu	0.02	1.49	Sn	1	<1
			Zr	0.1	12	Ag	0.1	1.40	Ga	0.5	< 0.5
			Pb	0.1	9.4	Tb	0.01	1.25	W	0.5	< 0.5
			Ni	0.1	9.4	Nb	0.1	1.00	Bi	0.1	< 0.1
			Cu	0.1	8.8	Tm	0.01	0.90			
			Dy	0.05	8.8	Мо	0.1	0.90			

Table 25: Phosphogypsum rock sample analyzed for major and trace elements, after being hand pulverized.

Phosphogypsum	Cs	Rb	Ba	Th	Pb	U	K	Та	Nb	W	La	Ce	Р	Sr
	0.3	2.6	84	1.6	9.4	13.4	581	0.1	1	0.4	49.2	20.8	8684.	704.9
													00	
	Cs	Rb	Ba	Th	Pb	U	K	Та	Nb	W	La	Ce	Р	Sr
Chondrite	0.188	2.31	2.41	0.031	2.63	0.0081	544	0.014 5	0.279	0.096	0.242	0.622	967	7.81
Phosphogypsum/Ch ondrite	1.59574	1.1255 4	34.8548	51.6129	3.57414	1654.32 1	1.0680 1	6.896 55	3.584 23	4.166 67	203.3 06	33.44 05	8.980 35	90.256 1
Upper Continental Crust	4.9	82	628	10.5	17	2.7	23224	0.9	12	1.19	31	63	655	320
Phosphogypsum/U CC	0.06122 4	0.0317 07	0.13375 8	0.15238 1	0.55294 1	4.9629	0.0249	0.111	0.083 33	0.336 13	1.597	0.330 1	13.26 68	2.228
Average Shale	5	140	580	12	20	3.7	26600	0.8	11	0.8	92	59	700	300
Phosphogypsum/Av . Shale	0.06	0.0185 71	0.1448	0.13333	0.47	3.6216	0.0218	0.125	0.090 9	0.5	0.534 7	0.352 5	12.40 5	2.3496
Average Phosphorite	-	-	350	6.5	50	120	3487	-	10	-	133	104	13800 0	750
Phosphogypsum/Av . Phosphorite	-	-	0.24	0.2461	0.188	0.1116	0.166	-	0.1	-	0.3 6 9 9	0.2	0.062 9	0.9398

Tables 26, 27, 28, 29: Tables showing the normalization of phosphogypsum based on chondrite, upper continental crust, average shale and average phosphorite.

Table 27

Phosphogypsum	Nd	Hf	Zr	Sm	Eu	Ti	Pr	Gd	Tb	Dy	Ho	Er	Tm	Yb
	31.7	0.3	12.4	5.57	1.49	180	7.05	7.69	1.29	8.76	2.01	6.24	0.9	5.34
	Nd	Hf	Zr	Sm	Eu	Ti	Pr	Gd	Tb	Dy	Но	Er	Tm	Yb
Chondrite	0.471	0.106	3.62	0.152	0.0578	451	0.0946	0.205	0.038 4	0.255	0.057 2	0.163	0.026 1	0.169

Phosphogypsum/Ch ondrite	67.303	2.8301	3.4254	36.6447	25.778	0.39911	74.524 3	37.51 2	32.55 2	34.35 2	35.13 9	38.28 2	34.48 2	31.597
Upper Continental Crust	27	5.3	193	4.7	1	3837	7.1	4	0.7	3.9	0.83	2.3	0.3	2
Phosphogypsum/U CC	1.174	0.0566	0.0642	1.1851	1.49	0.0469	0.992	1.922 5	1.785 7	2.246 1	2.421 6	2.713	3	2.67
Average Shale	24	2.8	160	6.4	1	4600	5.6	6.4	1	4.6	1.2	2.5	0.2	2.6
Phosphogypsum/Av . Shale	1.3208	0.1071	0.0775	0.8703	1.49	0.0391	1.2589	1.201 5	1.25	1.904 3	1.675	2.496	4.5	2.0538
Average Phosphorite	98	-	70	20	6.5	640	21	12.8	3.2	19.2	4.2	23.3	1.2	13
Phosphogypsum/Av . Phosphorite	0.3234	-	0.1771	0.2785	0.2292	0.28125	0.3357	0.600 7	0.390 6	0.456 25	0.478 5	0.267 8	0.75	0.4107

<u>Table 28</u>

Phosphogypsum	Lu	Y	Ga	Au	Мо	As	Sb	Se	Bi	Sn	Со	Zn	Cu	Ni
	0.81	107.3	0.4	0.0049	0.9	6.5	0.7	1.5	0.09	0.9	0.8	28	8.8	9.4
	Lu	Y	Ga	Au	Mo	As	Sb	Se	Bi	Sn	Со	Zn	Cu	Ni
Chondrite	0.0253	1.53	9.71	0.146	0.973	1.74	0.145	20.3	0.11	1.63	506	323	131	10800
Phosphogypsum/Ch	32.0158	70.130	0.0411	0.0335	0.9249	3.7356	4.8275	0.073	0.818	0.552	0.001	0.086	0.067	0.0008
ondrite		7						89	1		58	6	1	7
Upper Continental	0.31	21	17.5	1.5	1.1	4.8	0.4	0.09	0.16	2.1	17.3	67	28	47
Crust														
Phosphogypsum/U	2.6129	5.1095	0.02285	0.00326	0.8181	1.3541	1.75	16.66	0.562	0.428	0.046	0.417	0.314	0.2
CC								6	5	57	2	9	2	
Average Shale	0.7	26	19	-	2.6	13	1.5	0.6	-	6	19	95	45	68

Phosphogypsum/Av	1.1571	4.1269	0.021	-	0.3461	0.5	0.4666	2.5	-	0.15	0.042	0.294	0.195	0.1382
. Shale											1	1	5	
Average	2.7	260	4	0.0014	9	23	7	4.6	0.06	3	7	200	75	53
Phosphorite														
Phosphogypsum/Av	0.3	0.4126	0.1	3.5	0.1	0.2826	0.1	0.326	1.5	0.3	0.114	0.14	0.117	0.1773
. Phosphorite								0			2		3	

Table 29

Phosphogypsum	V	Cr	Sc	Cd	Be	Hg	TI
	32	41	0.9	5.5	0.9	0.06	0.2
	V	Cr	Sc	Cd	Be	Hg	Tl
Chondrite	54.3	2650	5.9	0.674	0.021	0.35	0.142
Phosphogypsum/Chondrite	0.5893	0.01547	0.1525	8.160	42.8571	0.2285	1.408
Upper Continental Crust	97	92	14	0.09	2.1	0.05	0.9
Phosphogypsum/UCC	0.3298	0.4456	0.0642	61.11	0.4285	1.6	0.2222
Average Shale	130	90	13	0.3	3	-	1.4
Phosphogypsum/Av. Shale	0.24154	0.4555	0.0692	18.33	0.3	-	0.1428
Average Phosphorite	100	125	11	18	2.6	0.06	-
Phosphogypsum/Av. Phosphorite	0.32	0.328	0.0818	0.3055	0.3461	1.333	-

Taking into consideration Figure 51, it is clear that compared to the upper continental crust phosphogypsum is enriched to U, Se, Cd and REE. While compared to the Average phosphorite is found to be depleted for the same elements.


Figure 51: Plot showing the normalization of the studied phosphogypsum based on the chondrite, ucc, av. shale and av. Phosphorite.

3.1.8 Enrichment Factor

The Element Enrichment Factors (EFs) were initially developed in order to speculate the origin of elements in the atmosphere, precipitation or seawater (Goldberg, 1972; Chester and Stoner, 1973; Zoter et al., 1974; Peirson et al., 1974; Duce et al., 1975; Rahn, 1976; Buat – Menard and Chesselet, 1979), which was progressively extended to the study of soils, lakes sediments, peat, tailings and other environmental materials (Ragaini et al., 1977; Loska et al., 1997). The formula to calculate EFs can be generalized from Chester and Stoner (1973) or Zoller et al (1974) to be:

$$EF_{E} = \frac{[E]_{sample} / [E_{R}]_{sample}}{[E]_{crust} / [E_{R}]_{crust}}$$
(2)

where "E" is the element under consideration , the square brackets indicate concentration and " E_R " is the chosen reference element. As " E_R ", is often chosen to be Al, Si, Sc, Zr or Ti, although Fe (Chester and Stoner, 1973) or Mn (Loska et al., 1997), has been used. In our case, we used Fe to be our reference element and we compare it to the Average Shale elemental concentrations. Since our studied material is phosphogypsum, we didn't use the upper continental crust due to the fact that it is not sensitive enough in order to be precise enough to detect enrichments due to human activity. Therefore, we preferred Average Shale elemental concentrations.

Table 30:	Class	of enrich	factor
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EF	Polluted Conditions	Health Risk Level	EF	Polluted Conditions	Health Risk Level
<1	Absence	0	5 - 20	Intermediate – level	3
1 – 2	Minimal	1	20 - 40	High – level	4
2-5	Low – level	2	>40	Intensity	5

	Fe	Cr	V	U	Pb	Ni	As	Cd	Th	Tl	Hg
Phosphogypsum	2028.00	41.00	32.00	13.00	9.40	9.40	6.50	5.50	1.60	0.20	0.08
AV. SHALE	47200	90	130	3.7	20	68	13	0.3	12	1.4	0.05
EF		10.602	5.729	81.774	10.938	3.2173	11.637	426.6	3.103	3.324	37.23

Table 31: Calculation of enrichment factor using the Fe concentration and the Average Shale.

Taking into consideration Table 31, we are able to classify the phosphogypsum sample, both for health risk levels and polluted conditions, for each element of interest. This means that for U and Cd there is a class of health risk , which means intensity in polluted conditions, and a health risk level 4 (High – level in polluted conditions) for Hg.





3.2 Leaching Experiments

3.2.1 SEM - EDS

Besides the rock sample, there were also scanned the filters used at the TCLP procedure, in order to determine how the HNO₃ reacted with the raw material and also how the rain affected it as well. The results, including both spectra and images, of these filters are given below.



Figure 53: Gypsum crystal in filter used for the rainwater leaching procedure (left) and spectrum of the same filter (right).



Figure 54: Filter used in the TCLP procedure (left) and spectrum of the same filter (right).

As it is shown, when it comes to the phosphogypsum sample which was leached by rainwater, the sample still contains gypsum (indicated by Ca, 0, S), in the form of dissolved gypsum crystals (Figure 53). The sample that reacted with HNO₃, TCLP procedure, showed that the phosphogypsum alternates fully and there is formed a different phase, which is the matrix. It consists mainly of Ca, Si, Al, P, S, and F, as shown in figure 54.

3.2.2 ICP-MS analyses of liquid samples

Besides the ICP - MS measurements for the rock sample, there were also examined the solutions used for leaching experiments.

Element	ppb	Element	ppb	Element	ppb	Element	ppb
Ag	<100	Fe	<10000	Pb	<4000	Ti	<100
Al	1382	Ga	*	Pd	*	TI	*
As	<3000	Gd	*	Pr	*	Tm	*
Au	<500	Ge	*	Pt	*	U	<3000
В	<400	Hf	*	Rb	*	V	<200
Ва	<80	Hg	*	Re	*	W	<2000
Ве	*	Но	*	Rh	*	Υ	*
Bi	<3000	In	*	Ru	*	Yb	*
Br	*	К	2	S	391	Zn	<300
Са	1059.2	La	<200	Sb	<2000	Zr	*
Cd	<700	Li	<1000	Sc	*		
Ce	*	Lu	*	Se	*		
Cl	*	Mg	21	Si	*		
Cr	<300	Mn	284	Sm	*		
Со	<300	Мо	<300	Sn	*		
Cs	*	Na	78	Sr	2817		
Cu	<80	Nb	*	Та	*		
Dy	*	Nd	*	Tb	*		
Er	*	Ni	<300	Те	*		
Eu	*	Р	52356	Th	<500		

Table 32: Chemical composition of leachates obtained by TCLP procedure.

Table 33: Dissolved elements in the Attica rainwater used in leaching experiments.

Element	ppb	Element	ppb	Element	ppb	Element	ppb
Ag	<0.05	Fe	<10	Pb	3.1	Ti	<10
Al	1	Ga	<0.05	Pd	<0.2	TI	<0.01
As	<0.5	Gd	< 0.01	Pr	<0.1	Tm	<0.01
Au	<0.05	Ge	<0.05	Pt	< 0.01	U	<0.02
В	0.61	Hf	< 0.02	Rb	0.06	V	<0.01
Ва	<0.05	Hg	3	Re	< 0.01	W	<0.02
Ве	<0.05	Но	< 0.01	Rh	< 0.01	Υ	<0.01
Bi	<0.05	In	< 0.01	Ru	<0.05	Yb	< 0.01
Br	<5	К	0.09	S	<1	Zn	7.2
Са	0.67	La	< 0.01	Sb	<0.05	Zr	<0.02
Cd	<0.05	Li	<0.1	Sc	<1		
Ce	<0.01	Lu	< 0.01	Se	<0.5		
Cl	<1	Mg	<0.05	Si	<40		
Cr	<0.05	Mn	0.41	Sm	< 0.02		

Со	<0.02	Мо	<0.1	Sn	<0.05
Cs	<0.01	Na	0.35	Sr	0.93
Cu	0.9	Nb	<0.01	Та	<0.02
Dy	<0.01	Nd	<0.01	Тb	<0.01
Er	< 0.01	Ni	<0.2	Те	<0.05
Eu	<0.01	Р	<10	Th	<0.05

Table 34: Total elements in the Attica rainwater used in leaching experiments.

Element	ppb	Element	ppb	Element	ppb	Element	ppb
Ag	1.89	Fe	148	Pb	25.9	Ti	11
Al	188	Ga	0.08	Pd	<0.02	TI	0.05
As	0.6	Gd	0.01	Pr	0.03	Tm	<0.01
Au	0.14	Ge	<0.05	Pt	< 0.01	U	0.05
В	28	Hf	0.02	Rb	0.39	V	1.3
Ва	5.18	Hg	5.6	Re	< 0.01	W	0.13
Ве	<0.05	Но	<0.01	Rh	<0.01	Y	0.16
Bi	0.29	In	< 0.01	Ru	<0.05	Yb	< 0.01
Br	6	К	0.35	S	<1	Zn	70.1
Са	2.26	La	3.55	Sb	0.27	Zr	0.87
Cd	0.08	Li	0.7	Sc	<1		
Се	0.4	Lu	<0.01	Se	<0.5		
Cl	3	Mg	0.12	Si	275		
Cr	4.6	Mn	4.42	Sm	0.04		
Со	0.23	Мо	0.9	Sn	1.08		
Cs	<0.01	Na	1.18	Sr	3.5		
Cu	13.9	Nb	0.06	Та	0.03		
Dy	0.01	Nd	0.19	Tb	<0.01		
Er	0.01	Ni	4.6	Те	0.72		
Eu	< 0.01	Ρ	116	Th	0.22		

Table 35: Attica rainwater composition determined by spectrophotometry.

Measured for	mg/L
Sulfate	0.4
Nitrate	5
Phosphorus	0.519
Chromium	0.054
Chloride	1.62
Nitrite	0.0154

Element	ppb	Element	ppb	Element	ppb	Element	ppb
Ag	<100	Fe	<10000	Pb	<4000	Ti	<100
Al	<600	Ga	*	Pd	*	TI	*
As	<3000	Gd	*	Pr	*	Tm	*
Au	<500	Ge	*	Pt	*	U	<3000
В	<400	Hf	*	Rb	*	V	<200
Ва	<80	Hg	*	Re	*	W	<2000
Ве	*	Но	*	Rh	*	Y	*
Bi	<3000	In	*	Ru	*	Yb	*
Br	*	К	2	S	541	Zn	<300
Са	627.7	La	<200	Sb	<2000	Zr	*
Cd	<700	Li	<1000	Sc	*		
Се	*	Lu	*	Se	*		
Cl	*	Mg	5	Si	*		
Cr	<300	Mn	<50	Sm	*		
Со	<300	Мо	<300	Sn	*		
Cs	*	Na	61	Sr	1838		
Cu	<80	Nb	*	Та	*		
Dy	*	Nd	*	Tb	*		
Er	*	Ni	<300	Те	*		
Eu	*	Р	<4000	Th	<500		

Table 36: Chemical composition of leachates obtained by Attica rain water leaching experiments. A summary, for the Attica rainwater leaching experiments, is also presented.

Element	Са	к	Mg	Na	S	Sr	Th	U
Unit	ppm	ppm	ppm	ppm	ppm	ppb	ppb	ppb
Rainwater (diss. elements)	0.67	0.09	<0.05	0.35	<1	0.93	<0.05	<0.02
Rainwater (total elements)	2.26	0.35	0.12	1.18	<1	3.50	0.22	0.05
PG leachate	627.70	2.00	5.00	61.00	541	1838.00	<500	<3000

According to the above leaching results, it is obvious that there is a significant dissolution of phosphogypsum in Attica rainwater, corresponding to the majority of Ca and S release. At the same time, there is a severe release of Sr, Na and K, which, however, are not critical in environmental issues. The presence of Sr in PG is reasonable, due to the valence and

ionic radious similarity of Sr^{2+} and Ca^{2+} in eight-fold coordination into gypsum crystal structure (^[8] $Sr^{2+} = 1.26$ Å and ^[8] $Ca^{2+} = 1.12$ Å). Regarding actinides, related to the observed radioactivity, it has been concluded that Th release is negligible (also accordingly to its very low concentration in the studied PG: 1.6 ppm) but the release of U, though rather low (i.e., 3 ppm in solution, compared to 13 ppm in the solid), needs further research with special ICP-MS and/or α -spectrometry. Nevertheless, U, and particularly ²³⁸U and its decay products, may be released in the aquatic environment and follow bioaccumulation processes (Figure 55).



Figure 55: The circulation of the phosphogypsum waste heap radionuclides (Borylo et al. 2012)

Moreover, Perez-Lopez et al. (2007) found that the metal contents in the mobile fraction are in the following relative abundance order: Ba (71%)> Sr (56%)> Cd (48%)> Zn (26%)> U (23%)> Ni (5%). The most potentially toxic fraction, that is, the bioavailable fraction is composed of U (23%), Ba (21%), Cu (6%), Sr (6%), Cd (5%), Ni (5%) and Zn (2%) (Figure 56). Thus, the mobile content of U and Ni is leached in the bioavailable fraction.



Figure 56: Metal release from Spanish phosphogypsum by means of sequential extraction (Perez-Lopez et al. 2007)

Al-Masri et al. (2004) found when phosphogypsum is leached with water, Cu and Cd are easily transferred to water and then to the surrounding environment, and 21% of U is present as water soluble surface species. This means that water dilutes gypsum and the content in U is released and so is the content in 226 Ra. (Figure 57)



Figure 57: Metal release from Syrian phosphogypsum using distilled water (Al Masri et al. 2004)

Santos et al. (2006) sequential extraction results showed that most of the radium and lead are located in water-insoluble (non-CaSO₄) fractions. The results obtained in the sequential experiments show that Th, Ba and REE were found predominantly in the residual phase.

Haridasan et al. (2002) conducted leaching studies which indicated that phosphogypsum might enhance ²²⁶Ra levels in the phosphogypsum disposal environment. Leaching of radium may be slow in field conditions as the experiment simulating natural conditions resulted in the release of only 1% of the ²²⁶Ra activity in one month. However, considering the quantity of phosphogyspum disposed at individual sites dispersion of activity in surface water and contamination of groundwater is likely at the local environment.

Al-Hwaiti et al. (2010) found that the Jordan phosphogypsum contains low concentration of As, Cd, Cr, Cu, U, and Zn to those reported worldwide. The assessments of the bioavailability of toxic elements using aqua regia leaching experiments indicate that there is no appreciable amount of element transferred to the surrounding environment. Elements showin high mobility in phosphogypsum include Cu and U. Moderate mobility include As and Zn. Low mobility includes Cd and Cr. Overall, their results indicate that the toxic metals in phosphogypsum are not likely to be leached from the phosphogypsum stacks to the surrounding aquatic environment when phosphogypsum is to be used as an amendment to agricultural soil.

3.2.3 GIS implementation and radioactivity assessment of the Schistos waste site

The maps generated with ArcGIS showing the distribution of each radionuclide concentration, in each sampling location, in the study area are presented here. At first, the generated maps, quantify the results using graduated symbols.



Map 1: The quantified distribution of ²²⁸Ac at the studied area.

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Map 2: The quantified distribution of $^{214}\text{Bi}_a$ at the studied area.



Map 3: The quantified distribution of $^{214}\text{Bi}_b$ at the studied area.



Map 4: The quantified distribution of ¹³⁷Cs at the studied area.



Map 5: The quantified distribution of 40 K at the studied area.



Map 6: The quantified distribution of ²³⁴Pa at the studied area.



Map 7: The quantified distribution of ²¹⁴Pb at the studied area.



Map 8: The quantified distribution of ²²⁰Ra at the studied area.



Map 9: The quantified distribution of ²³⁴Th at the studied area.



Map 10: The quantified distribution of 208Th at the studied area.



Map 11: The quantified distribution of 235 U at the studied area.

Except of the maps showed above, we generated maps, indicating the spatial distribution of each radionuclide.



Map 12: The spatial distribution of 228 Ac at the studied area.



Map 13: The spatial distribution of ${}^{214}\text{Bi}_a$ at the studied area.



Map 14: The spatial distribution of $^{\rm 214}{\rm Bi}_{\rm b}$ at the studied area.



Map 15: The distribution of 137 Cs at the studied area.



Map 16: The spatial distribution of 40 K at the studied area.



Map 17: The spatial distribution of ²³⁴Pa at the studied area.



Map 18: The spatial distribution of ²¹⁴Pb at the studied area.



Map 19: The spatial distribution of ²²⁶Ra at the studied area.



Map 20: The spatial distribution of ²³⁴Th at the studied area.



Map 21: The spatial distribution of ²⁰⁸Tl at the studied area.



Map 22: The spatial distribution of 235 U at the studied area.

3.3 Radium in phosphogypsum components

As it is evident ²²⁶Ra seems to be the main potential environmental issue in specific areas of the studied phosphogypsum waste site, as also has been indicated by the Greek Atomic Energy Commission (personal communication).

Ra isotopes (²²⁴ Ra, ²²⁶ Ra and ²²⁸ Ra) occur in nature as decay products of ²³⁸ U and ²³² Th. ²²⁶Ra is of particular concern in environmental studies due to its long half – life (1,622 years) and high radiotoxicity. Several industrial processes lead to Ra accumulation, which can threaten human health. Radium can be easily incorporated into the bones of mammals due to their chemical and biological behaviour similarity to that of other alkaline earth metals (Ca, Sr, Ba), therefore consumption of food and water with increased concentration of Ra isotopes leads to accumulation of those isotopes in bones (70 – 80%) and uniformly in the muscle tissue of human beings, which enhances the total annual effective radiation dose contribution (Jia and Jia, 2012;Hetman et al., 1998; Jia and Torri, 2007).

Roselli et al. (2009) during their study came to the conclusion that since radium belongs to the alkaline earth metal group, its chemical behavior is similar to calcium, therefore it is incorporated into phosphogypsum during acidulation of phosphatic rock. The difference that was observed at the concentration activites of the radionuclides that were studied, it could be due to the different concentrations of uranium and thorium series radionuclides in tha raw material (phosphatic rock) and to the different composition of fertilizers.

Besides the fact that, ²²⁶Ra is one of the main contaminants in concern within the uranium ore processing waters, its abundance in mining environments is so low that no proper mineral phase has ever been found. Its mobility can be lowered by interactions with surrounding mineral phases present in tis environment, such as surface interactions and/or formation of a solid solution. ²²⁶Ra uptake by sulfate, clays and ferrous oxides, is already known, but gypsum (CaSO₄.2H₂O) and barite (BaSO₄) are the two main sulfates found in ²²⁶Ra environment (Lestini et al, 2013; Klinkeberg et al. 2014,Figure 58). In oil industry it is extensive the barite use as a weighting agent for drilling fluids. The mixing of these fluids with Ra – containing formation waters causes the precipitation of radiobarite. Storage ponds of pumped – out waters can accumulate dangerously high radiation levels (Fisher, 1998).



Figure 58: Uptake of Ra during the recrystallization of barite (Klinkeberg et al. 2014) and evolution of A(t)/A0(t) solution ratio with time in case of Ra uptake by recrystallized gypsum (Lestini et al. 2013)

Even though the difference in ionic radii between Ca^{2+} and Ra^{2+} is too high (~ 30%) to allow any substitution, two different values of D have been previously determined, both via coprecipitation experiments of ²²⁶Ra in gypsum. One is estimated to be about 0,03, determined by Gnanaprasagam and Lewis (1995). In another study by Yoshiba et al. (2009), estimates a considerable higher value of about 0.3. Sorption/desorption and coprecipitation experimental results have shown no evolution of ²²⁶Ra's activity neither in the solution nor in the solid with time, suggesting that these two other mechanisms are not more efficient than incorporation in reducing Ra's mobility by interactions with gypsum. The lack of interactions between ²²⁶Ra and gypsum can be explained by the two main criteria governing element substitution which are the ion charge and the ionic radius. Whereas calcium and radium have the same ion charge (+2), the difference between their ionic radii in eight - coordination (Ca's coordination number in gypsum) is significantly high: 1.12 Å for Ca and 1.48 Å for Ra. Ra²⁺ appears to be large to enter Ca^{2+} sites in gypsum. Furthermore, gypsum has a high solubility product (logKsp = -4.58) compared to barite ($\log K_{SP} = -9.97$), which is propably another factor inhibiting the incorporation of Ra^{2+} in gypsum by substitution of Ca^{2+} (Lestini et al., 2013). Since Ra is poorly incorporated into gypsum, a solid solution between gypsum and radium sulfate (Ca,Ra)SO₄.2H₂O cannot be considered perse. Other sulfate phases, with intermediate solubility product between gypsum's and barite's, such as celestite $(SrSO_4)$ and anglesite $(PbSO_4)$, could be more favorable to incorporation of Ra^{2+} .



Figure 59: Gypsum (CaSO₄.2H₂O) crystal structure (green: Ca, blue: O, yellow: S).

Jones et al. (2011) pointed out that radium forms a large, divalent ion which is easily removed from aqueous solution, especially in systems of low ionic strengthwhere little competition occurs for reactive sites on mineral surfaces. It is relatively mobile in the environment, and it has been known for a long time that it is readily assimilated into food chains. Radium in natural aquatic systems is believed to exist as the aquated cation or as a RaSO₄ ion pair (Benes, 1990; Puigdomenech and Bergstrom, 1995; Tachi et al., 2001). Absorption is believed to be the principal control of Ra at trace concentrations in natural systems, through cation exchange on the surfaces of minerals such as Fe (hydr)oxides, clays and also organic substrates(Benes, 1990; Krishnaswami et al., 1982; Ames et al., 1983a,b). Jones et al. (2011) observed two different groups of substrates shown in figure 60. It is evident that the first group of substrates comprises rhodocrosite, strontianite, dolomite, with erite and calcite, and uptake in these systems increases with Ra concentration. The second group, ankerite, siderite and magnesite, uptake either shows no dependency on Ra concentration, or decreases as it increases. This differing sorption behavior observed for the different minerals suggests that, in the group where uptake increases with Ra concentration, Ra solubility may be limited by phase formation, and the trend is consistent with the solubilities of the minerals. In any case, the experiments showed that measurable uptake of Ra from the solution occurs with any one of the eight major carbonate minerals. Whereas for the minerals calcite, dolomite, witherite, strontianite and rhodocrosite, uptake increases with increasing Ra concentration, for siderite, magnesite and ankerite there is either a decrease in uptake with increasing concentration or no dependency.



Figure 60: Isotherm plot for Ra uptake by carbonate minerals. (Jones et al., 2011)



Figure 61: Barite (BaSO₄) crystal structure (yellow :S, blue: O, red: Ba).
Curti et al. (2010) determined the radium uptake by barite by monitoring the decrease of ²²⁶Ra activity in the aqueous solution with alpha spectrometry, after filtration of the suspensions and sintering. The evaluation of the Ra uptake experiments, indicated the formation of non-ideal solid solutions, with moderately high Margules parameters (W_{AB} =3720-6200 J/mol, a_0 =0.5). These parameters are significantly large than an estimated value from the literature (W_{AB} =1240 J/mol, a_0 =0.5). It was also confirmed that radium forms solid solutions with barite at fast kinetic rates and in complete thermodynamic equilibrium with the aqueous solutions.

Since barite crystals have not been detected, by XRD and SEM-EDS, in Schistos phosphogypsum, in the frame of the present study, there is no clear indication for Ra due to the presence of the above material. Barite has been confirmed for Jordanian phosphogypsum (Zielinski et al. 2011; Figure 62) as well as for phosphogypsum sample from the former fertilizer industry of Thessaloniki, Greece, as seen in Figure 63 (Godelitsas, personal communication).



Figure 62: Barite into Jordanian phosphogypsum (Zielinski et al. 2011)



Figure 63: Barite into phosphogypsum sample from the former fertilizer industry of Thessaloniki, Greece (Godelitsas, personal communication)

According to Santos et al. (2006) Fe-oxides, involved in the residual water-insoluble (non- $CaSO_4$) fraction in sequential leaching experiments, may host Ra in phosphogypsum (Figure 64).



Figure 64: Results obtained from the sequential extraction experiment. The chart shows that Fe - oxide hosts the most ²²⁶Ra. (Santos et al. (2006)

Thus, gypsum itself, as well Fe-oxides, may be the hosting materials of Ra in Shistos phosphogypsum. However, more detailed study using high-resolution microscopic and spectroscopic techniques (such as TEM/STEM and ToF-SIMS, Klinkeberg et al. 2014; Figure 65) is required, in the frame of future research, to clarify the above assumption.



Figure 65: SEM image and ToF-SIMS analyses of recrystallized barite grains (Klinkenberg et al.2014).

4. References

Al - Attar, L., Al - Oudat, M., Kauakri, S., Budeir, Y., Khalify, H., 2011. [1] Radiological Impacts of phosphogypsum. Journal of Environmental Management 92, pp. 2151 - 2158.

Al-Hwaiti, M.S., Ranville, J.F., Ross, P.E., 2010. Bioavailability and mobility [2] of trace metals in phosphogypsum from Aqaba and Eshidiya, Jordan. Chemie der Erde 70, pp. 283 - 291.

Al-Masri, M.S., Amin, Y., Ibrahim, S., Al-Bich, F., 2004. Distribution of [3] some trace metals in Syrian phosphogypsum. Applied Geochemistry 19, pp. 747 - 753.

Abdel-Aal, E.A., 2004. Crystallization of phosphogypsum in continuous [4] phosphoric acid industrial plant. Crystal Research and Technology 39, No.2, pp. 123 -130.

Aronnof, S., 1989: Geographic Information Systems: A management [5] perspective. Wdl Publications, Ottawa, Canada.

[6] Azouazi, M., Ouahidi, Y., Fakhi, S., Andres, Y., Abbe, J.Ch., Benmansour, M., 2001. Natural radioactivity in phosphates, phosphogypsum and natural waters in Morocco. Journal of Environmental Radioactivity 54, pp. 231 - 242.

Battistoni, P., Carniani, E., Fratesi, V., Balboni, P., Tornabuoni, P., 2006. [7] Chemical and physical pretreatment of phosphogypsum leachate. Ind. Eng. Chem. Res. 45, pp. 3237 - 3242.

Becker, P., 1989. Phosphates and Phosphoric Acid: raw materials, [8] technology, and economics of the wet process. Fert Sci Technol Ser, Second Edition; 6, pp. 752.

Benes, P., 1990. Radium in (continental) surface water. In: The [9] Environmental Behavior of Radium. Technical Reports Series No. 310, IAEA, Vienna, pp. 373 – 418.

- Beretka, J. (1990) The current state of utilization of phosphogypsum in [10] Australia. In: Proceedings of the Third InternationalSymposium on Phosphogypsum, Orlando, FL, FIPR Pub. No. 01-060-083, December 1990, vol. II 394-401
- Berish, C.W., 1990. Potential Environmental hazards of phosphogypsum [11] storage in central Florida. Proceedings of the third international symposium on phosphogypsum. Orlando, FL, FIPR Pub. No.01060083;2,pp. 1 – 29.
- Bituh, T., Marovic, G., Franic, Z., Sencar, J., Bronzovic, M., 2009. [12] Radioactive contamination in Croatia by phosphate fertilizer production. Journal of Hazardous Materials 162, pp. 1199 - 1203.
- Borrough, P.A., 1986: Principles of Geographical Information Systems for [13] land resources Assessment, Oxford University Press, New York, USA.
- Borylo, A., Skwarzec, B., Olszewski, G., 2012. The radiochemical [14] contamination (²¹⁰Po and ²³⁸U) of zone around phosphogypsum waste heap in Wislinka(northern Poland). Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering Volume 47, Issue 5, pp. 685 - 687.
- Carbonell Barrachina, A., DeLaune, R.D., Jugsujinda, A., 2002. [15] Phosphogypsum chemistry under highly anoxic conditions. Waste Management 22 (6), pp. 657 – 665.
- Carvalho, F.P., 2001 2005. Disposal of phosphogypsum waste containing [16] enhanced levels of radioactivity. Nuclear Technological Institute Department of Radiological and Nuclear Safety E.N. 10, P-2686-953 Sacavem, Portugal.
- Chauhan, P., Chauhan, R.P., Gupta, M., 2013. Estimation of naturally [17] occuring radionuclides in fertilizers using gamma spectrometry and elemental analysis by XRF and XRD techniques. Microchemical Journal 106, pp. 73 - 78.

Papageorgiou Fani M.Sc. Thesis, Geology - Geoenvironment Department, University of Athens, 2014

- [18] Chester R., Stoner JH., 1973.Pb in particulates from the lower atmosphere of the Eastern Atlantic. Nature, 245, pp. 27 – 28.
- Coates, Woodward. 1966. Similarity between "chukrovite" and the octahedral [19] crystals found in the gypsum in the manufacture of phosphoric acid. Nature, 212, 392
- Curti, E., Fujiwara, K., Iijima, K., Tits, J., Cuesta, C., Kitamura, A., Glaus, [20] M.A, Muller, W., 2010. Radium uptake during barite recrystallization at $23\pm2^{\circ}$ C as a function of solution composition: An experimental ¹³³Ba and ²²⁶Ra tracer study. Geochimica et Cosmochimica Acta 74, pp. 3553 - 3570.
- Diamantopoulos A., Krohe, A., Mposkos, E., 2009. Kinematics of conjurate [21] shear zones, strain partitioning and fragmentation of the Upper Rigid Crust during denudation of High - P rocks (Pelagonian and Sub - Pelagonian Zones, Greece). In : Robertson, A.H.F, Parlak, O., Kaller, F., (Eds), Tethyan Tectonics of the Mediterranean Region: Some recent Advances. Tectonophysics, vol.473, pp. 84 – 98.
- [22] Dippel, K.Susan, M.Sc. Thesis, 2004. Mineralogical and geochemical characterisation pf phosphogypsum waste material and its potential for use as backfill at WMC fertilizers' mine site Phosphate Hill, N-W Queensland. School of Earth Sciences, James Cook University.
- Doumas, A., Gaitanakis, P., 1981 Statigraphic and Structural observations in [23] Aegaleo mountain and in the western part of Athens basin. Mineral Wealth 13, pp. 1 - 11
- [24] Duce RA., Hoffmann GL., Zoller WH., 1975. Atmospheric trace metals at remote northern and southern hemisphere sites: pollution or natural?. Science, 187, pp. 59 - 61.
- [25] El-Didamony, H., Gado, H.S., Awwad, N.S., Fawzy, M.M., Attallah, M.F., 2013. Treatment of phosphogypsum waste produced from phosphate ore processing. Journal of Hazardous Materials 244-245, pp. 596 - 602.
- EPA, 1998. Code of Federal Regulations, 1998. Title 40, Vol. 7, Parts 61.202 [26] and 61.204
- (40CFR61.202 and 40CFR61.204). [27]
- [28] ESRI, 2011"Geographical Information Systems as an intergrating technology : Context, Consepts and Definitions.
- [29] Fisher, R.S., 1998. Geologic and geochemical controls on naturally occurring radioactive materials (NORM) in produced water from oil, gas and geothermal operations. Environ. Geosci. 5, pp. 139 – 150.
- Fourati, A., Faludi, G. (1988) Changes in radioactivity of phosphate rocks [30] during the process of production. Journal of Radioanalytical and Nuclear Chemistry 125: 287-293.
- Fukuma, H.T., Fernandes, E.A.N, Quinelato, A.L., 2000. Distribution of [31] natural radionuclides during the processing of phosphate rock from Itataia - Brazil for production of phosphoric acid and uranium concentrate. Radiochim. Acta 88, pp. 809 - 812.
- Gnanaprasagam, E.K., Lewis, Bag., 1995. Electric strain energy and the [32] distribution coefficient of radium in solid solutions with calcium salts. Geochim Cosmochim Acta, 59 – 24, pp. 5103 – 5111
- Goldberg ED, editor, 1972. Baseline studies of pollutants in the marine [33] environment and research recommendations. The International Decade of Ocean Exploration (IDOE) Baseline Conference.

Papageorgiou Fani M.Sc. Thesis, Geology - Geoenvironment Department, University of Athens, 2014

- Guogang, Jia., Jing, Jia, 2012. Determination pf Radium isotopes in [34] environmental samples by gamma spectrometry, liquid scintillation counting and alpha spectrometry: a review of analytical methodology. Journal of Environmental radioactivity 106, pp. 98 - 119.
- Haridasan, P.P., Maniyan, C.G., Pillai, P.M.B., Khan, A.H., 2002. Dissolutiom characteristics of ²²⁶Ra from phosphogypsum. Journal of Environmental [35] Radioactivity 62, pp. 287 - 294.
- Hetman, A., Dorda, J., Zipper, W., 1998. Determination of radium isotopes [36] concentrations in mineral waters by liquid scintillation method. Nukleonika 43 (4), pp. 481 - 488.
- [37] Ioakim, Ch., Rondoyanni, Th., Mettos, A., 2005. The Miocene basins of Greece (Eastern Mediterranean) from a paleoclimatic perspective. Revue de Paleobiologie 24, pp. 735 – 748.
- Jia, Guogang, Torri, Giancarlo, 2007. Estimation of radiation doses to [38] members of the public in Italy from intakes of some important naturally occurring radionuclides in drinking water (²³⁸U, ²³⁴U, ²³⁵U, ²²⁶Ra, ²²⁸Ra, ²²⁴Ra and ²¹⁰Po). Appl. Rad. Isot. 65, pp. 849 - 857.
- [39] Jones, J.M., Butchins, L., Charnock, J.M., Pattrick, R.A.D., Small, J.S., Vaughan, D.J., Wincott, P.L., Livens, F.R. 2011. Reactions of radium and barium with the surfaces of carbonate minerals. Applied Geochemistry 26, pp. 1231 – 1238.
- Jun, L., JianHua, W., YunXiang, Z., 1997. Effect of the impurities on the [40] habit of gypsum in wet-process phosphoric acid. Ind. Eng. Chem. 36, pp. 2657 -2661.
- Kacimi, L., Simon Masseron, A., Ghomari, A., Derriche, Z., 2006. [41] Reduction of clinkerization temperature by using phosphogypsum. Journal of Hazardous Materials 137 (1), pp. 129 - 137.
- Katsikatsos, G., Migiro, G., Triantafillis, M., Mettos, A., 1986a. Geological [42] structure of Internal Hellenides (E. Thessaly - SW Macedonia, Euboa - Attica -Northern Cyclades islands and Lesvos). Geological and Geophysical Research, Special Issue pp. 191 – 212
- [43] Khalifa, N.A., El - Arabi, A.M., 2005. Natural radioactivity in farm soil and phosphate fertilizer and its environmental implications in Qena governate, Upper Egypt. Journal of Environmental Radioactivity 84 (1), pp. 51 - 64.
- [44] Khater E.M. Ashraf, 2013. Uranium and Heavy Metals in phosphate fertilizers. Uranium Mining and Hydrogeology, 2008, pp. 193 - 198.
- Klinkenberg, M., Brandt, F., Breuer, U., Bosbach, D., 2014. Uptake of Ra [45] during the Recrystallization of Barite: A Microscopic and Time of Flight-Secondary Ion Mass Spectrometry Study. Environmental Science and Technology 48 (12), pp. 6620 - 6627.
- Kobal, I., Brajnik, D., Kaluza, F., Vengust, M. (1990) Radionuclides in [46] effluents from coal mines, a coal-fired powerplant, and a phosphate processing plant in Zasanje, Slovenia (Yugoslavia). Health Physics 58: 8-85.
- Krishnaswami, S., Graustein, W.C., Turekian, K.K., Dowd, J.F., 1982. [47] Radium, thorium and radioactive lead isotopes in ground waters: application to the insitu determination of adsorption rate constants and retardation factors. Water Resour. Res. 18, pp. 1663 – 1675.
- [48] Krohe, A., Mposkos, E., Diamantopoulos, A., Kaouras., G., 2010. Formation of basins and mountain ranges in Attica (Greece): The role of Miocene to Recent low - angle normal detachment faults. Earth - Science Reviews 98, pp. 81 - 104.
- [49] Kruger, A., Focke, W. W., Kwela, Z., Fowles, R., 2001. Effect of Ionic Impurities on the crystallization of gypsum in wet-process phosphoric acid. Ind. Eng. Chem. 40, pp. 1364-1369.

Papageorgiou Fani M.Sc. Thesis, Geology - Geoenvironment Department, University of Athens, 2014

- [50] Laiche, T.P., Scott, M.L. (1991) A radiological evaluation of phosphogypsum. Health Physics 60: 691-693.
- [51] Lehr, J.R., Frazier, A.W., Smith, J.P. Precipitated Impurities in Wet-Process Phosphoric Acid. Journal of Agricultural and Food Chemistry, Vol.14, No. 1, pp. 27 -33.
- [52] Lestini et al, 2013. Radium uptake by recrystallized gypsum : an incorporation study. Procedia Earth and Planetary Science 7, pp. 479 - 482.
- Li Y.H and Schoonmaker J. (2003) in: F.T. Mackenzie (Ed.)H.D. Holland, [53] K.K. Turekian (Eds.), Sediments, Daigenesis, and Sedimentary Rocks, Treatise on Geochemistry, vol. 7, Elsevier-Pergamon, Oxford (2003) 1-35.
- [54] Loska K., Cebula J., Pelizar J., Wiechula D., Kwapilinski J., 1997. Use of enrichment and contamination factors together with geoaccummulation indexes to evaluate the content of Cd, Cu and Ni in the Rybnik water reservoir in Polland. Water, Air and Soil Pollution, 93, pp. 347 – 365.
- Luther, S.M., Dudas, M.J., Rutherford, P.M. (1993) Radioactivity and [55] chemical characteristics of Alberta phosphogypsum. Water, Air, and Soil Pollution 69: 277-290
- Marinos, G., Katsikatsos, G., Mirkou Peripopoulou, P., 1974. The system [56] of Athens schists :stratigraphy and tectonic. Annales Geologique des Pays Hellenique XXV, pp. 439-444.
- Marinos, G., Petraschek, W.E., 1956. Laurium Geological and Geophysical [57] Research, Special Issue, pp. 1 - 247.
- Mathew, M., Takagi, S., Waerstad, K. R., Frazier, A.W., 1981. The crystal [58] structure of synthetic chukrovite Ca₄A1Si(SO₄)F₁₃.12H₂O. American Mineralogist, Volume 66, pp. 392 - 397.
- [59] May, A., Sweeney, J.W., 1984. Assessment of environmental impacts associated with phosphogypsm in Florida. In: R.A. Kuntze (Ed.). The Chemistry and Technology of Gypsum. ASTM Special Technical Publication No. 861, pp. 116 – 139
- Mullins, G.L., Mitchell Jr., C.C. (1990) Use of phosphogypsum to increase [60] yield and quality of annual forages. FIPR Pub. No. 01-048-084, Auburn University, 56.
- Okeji, M.C., Agwu, K.K., Idigo, F.U. (2012) Assessment of natural [61] radioactivity in phosphate ore, phosphogypsum, and soil samples around a phosphate fertilizer plant in Nigeria. Bull Environ Contam Toxico 89:1078-1081
- Oliveira, S.M.B., Imbernon, R.A., 1998. Weathering alteration and related [62] REE concentration in the Catalao I carbonatite complex, central Brazil. Journal of South American Earth Sciences 11 (4), pp. 379 – 388.
- [63] Peirson DH., Cawse PA., Cambray RS., 1974. Chemical uniformity of airborne particulate material and a maritime effect. Nature 252, pp. 675 - 679.
- Perez Lopez, R., Alvarez Valero, A., Nieto, J.M., 2007. Changes in [64] mobility of toxic elements during the production of phosphoric acid in the fertilizer industry of Huelva (SW Spain) and environmental impact of phosphogypsum wastes. Journal of Hazardous Materials 148, pp. 745 – 750.
- Papanikolaou, D., 1989. Are the medial crystalline masifs of the eastern [65] Mediterranean drifted Godwanian fragments? In : Papanikolaou, D., Sassi, F.P., (Eds), Special publications of the Geological Society of Greece. Newsletter, Athens, pp. 821 - 840.
- [66] Papanikolaou, D., 1997. The tectonostratigraphic terranes of the Hellenides. Annales Geologiques des Pays Helleniques 37, pp. 495 – 514.

Papageorgiou Fani M.Sc. Thesis, Geology - Geoenvironment Department, University of Athens, 2014

- [67] Papanikolaou, D., 2012. Tectonostratigraphic models of the Alpine terranes and subduction history of the Hellenides. Tectonophysics vol. 595 - 596 (2013), pp. 1 - 24.
- [68] Papanikolaou, D., Bassi, E. - K., Kranis, Ch., Danamos, G., 2004a. Paleogeographic evolution of the Athens basin from the Late Miocene up to present. Bulletin of the Geological Society of Greece XXXYI, pp. 816-825.
- Papastefanou, C., Stoulas, S., Ioannidou, A., Manolopoulou, M., 2006. The [69] application of phosphogypsum in agriculture and the radiological impact. Journal of Environmental Radioactivity 89, pp. 188 - 198.
- Parreira, A.B., Kobayashi Jr, A.R.K., Silvestra, O.B., 2003. Influence of [70] Portland cement type on unconfined compressive strength and linear expansion of cement – stabilized phosphogypsum. Journal of Environmental Engineering 129, pp. 956 - 960.
- Puigdomenech, I., Bergstrom, U., 1995. Calculation of distribution [71] coefficients for radionuclides in soils and sediments. Nuclear Safety 36 (1), pp. 142 – 154.
- Ragaini RC., Ralston HR., Roberts N., 1977. Environmental trace metal [72] contamination in Kellogg, Idaho, near a lead smelting complex. Environmental Science and Technology 11, pp. 773 – 781.
- [73] Rahn K.A., 1976. The chemical composition of the atmospheric aerosol. Technical report of the Graduate School of Oceanography, University of Rhode Island, Kingston, R.I. USA.
- [74] Roessler, C.E., Smith, Z.A., Bolch, W.E., Prince, R.J. (1979) Uranium and radium-226 in Florida phosphate materials. Health Physics: 37 269-277
- [75] Roselli, C., Desideri, D., Assunta Meli, M., 2009. Radiological characterization of phosphate fertilizers:Comparison between alpha and gamma spectrometry. Microchemical Journal 91, pp. 181 – 186.
- Rudnick, L.R., Gao, S., (2003) The composition of the continental crust ,in: [76] R.L. Rudnick (Ed.)H.D. Holland, K.K. Turekian (Eds.), The Crust, Treatise on Geochemistry, vol. 3, Elsevier-Pergamon, Oxford 1-64
- [77] Rutheford, P.M., Dudas, M.J., Arocena, J.M., 1996. Heterogeneous distribution of radionuclides, barium and strontium in phosphogypsum by-product. Science of the Total Environment 180 (3), pp. 201 – 209.
- Santos, A.J.G., Mazzilli, B.P., Favaro, D.I.T., Silva, P.S.C., 2006. [78] Partitioning of radionuclides and trace elements in phosphogypsum and its source materials based on sequential extraction methods. Journal of Environmental Radioactivity 87, pp. 52 - 61.
- Silva, L.F.O., Hower, J. C., Izquierdo, M., Querol, X., 2010. Complex [79] nanominerals and ultrafine particles assemblages in phosphogypsum of the fertilizer industry and implications on human exposure. Science of the Total Environment 408, pp. 5117 - 5122.
- [80] Shannon, D.R., 1976. Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides. Acta Cryst. A32, pp. 751 -767.
- [81] Συλλογικό Έργο, 2007. Ανώνυμη Ελληνική Εταιρεία Χημικών Προϊόντων και Λιπασμάτων (1909 - 1993): Λιπάσματα Δραπετσώνας. Εκδόσεις : Πολιτιστικό Ίδρυμα Πειραιώς.

Papageorgiou Fani M.Sc. Thesis, Geology - Geoenvironment Department, University of Athens, 2014

- [82] Tachi, Y., Shibutani, T., Sato, H., Yui, M., 2001. Experimental and odeling studies of sorption and diffusion of radium in bentonite. J. Contam. Hydrol. 47, pp. 171 – 186.
- [83] Tayibi Hanan, Chouva Mohamed, Lopez A. Felix, Alguacil J. Francisco, Lopez - Gelgado Aurora, 2009. Environmental impact and management of Phosphogypsum. Journal of Environmental Management 90, pp. 2377 - 2386.
- [84] UNSCEAR (1993) sources and effects of ionizing radiation United Nations Scientific Committee on the effects of Atomic Radiation, UNSCEAR 1993 Report to the General Assembly with Scientific Annexes, New York.
- [85] Villalobos, M. R., Vioque, I., Mantero, J., Manjon, G., 2010. Radiological, chemical and morphological characterizations of phosphate rock and phosphogypsum from phosphoric acid factories in SW Spain. Journal of Hazardous Materials 181, pp. 193 - 203.
- [86] Vinograd, V.L., et al, 2013. Solid acqueous equilibrium in the BaSO4 -RaSO4 - H2O system : First principles calculations and a thermodynamic assessment. Geochemica et cosmoclinica Acta 122, pp. 398 - 417.
- [87] Wolf E. Ruth, Ph.D., Research Chemist USGS/CR/UST, 2005. What is ICP MS and what can we do?. <u>http://crustal.usgs.gov/laboratories/icpms</u>
- [88] Yang, J., Liu, W., Zhang, L., Xiao, B., 2009. Preparation of load bearing building materials from autoclaved phosphogypsum. Construction and Building Materials, 23, pp. 687 – 693.
- [89] Yoshiba, Y., Nakazawa, T., Yoshikawa, H., Nakanishi, T., 2009. Partition coefficient of Ra in gypsum. J Radioanal Nucl Chem, 280 3, pp. 541 545.
- [90] Zeiler, M., 1999: Modelling our world, The ESRI Guide to Geodatabase Design, ESRI Press.
- [91] Zielinski, R.A., Al-Hwaiti, M.S., 2011. Radionuclides, trace elements, and radium residencein phosphogypsum of Jordan. Environmental Geochemistry and Health 33, pp. 149 165.
- [92] Zoller WH., Gladney ES., Duce RA., 1974. Atmospheric concentrations and sources of trace metals at the South Pole. Science 183, pp. 199 201.