Radioactive nuclides contamination

in agricultural soil and sludge in Israel

זיהום קרקעות ובוצה בישראל ברדיונוקלידים כתוצאה מדישון בפוספט

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Abstract

Of the three main ingredients used in agricultural fertilizers, nitrogen, phosphorous and potassium (NPK), the phosphorous and potassium additions contain radio-elements. The P is derived from the use of Senonian aged phosphorite. The extensive Israeli phosphorite deposits (averaging approximately 140 ppm uranium) can be considered a potential low grade uranium ore. Sufficient time has past since the deposits were laid down for secular equilibrium to be achieved in the uranium decay-series. Thus, deposits now include radioactive daughters Th-230, Ra-226, Rn-222, Pb-210, and Po-210. Besides being radioactive, these or their daughters are biologically deleterious elements. The potential dangers of using enriched phosphate derivatives are: (1) adding phosphate radio-metals to the agricultural soils, the uptake by crops, their leakage to the underlying aquifers; and (2), their retention and long term residence in the agricultural top soils. The latter needs to be considered over time, as farmlands are increasingly converted to urban housing. Based upon open source literature from Israel and other countries where phosphate fertilizers have been employed, the implications of the above potential problems are reviewed and evaluated. For Israel, the use of phosphate fertilization does not appear to be an immediate health hazard by increasing the external dose rates or via crop uptake. However, a continuing build up of radio-metals over the phreatic aquifers may warrant a more rigorous monitoring of the water supplies. Various methods of cleaning soils of the radiometal contamination are available, though cost via conventional methods would be prohibitive. The best method of containing the amount of radiometals would be their extraction during the production of the fertilizer. Unfortunately, large quantities of uranium, which is an energy source, are exported from

Israel as a mere contaminant rather than an energy product. In the process of fertilizer production using sulfuric acid, extensive quantities of phosphogypum (PG) are produced. During this process, radium, Pb-210 and Po-210 congregate in the PG, obviating its uses in soil amelioration or for industrial applications. The PG is usually stored in large stacks which can build up significant radiation emission, and can contain concentrations of potentially mobile radium. The PG stacks may release radon in future migrations, and also possibly cause more serious environmental contamination. However, detailed investigation shows that the Israeli PG stacks present neither environmental problems through the release of gamma-radiation nor through radon emanation. The chemistry of the fluids in the stacks prevents potential releases and mobilization of the radio-nuclides before they can affect the groundwater. **An expanded version of this report with more details is available in English directly from the authors.**

Literature Sources

This survey is based upon open literature sources: professional journals, Florida Institute of Phosphates research reports, Springer conference books.

I. Introduction

The major nutrients added via fertilization are nitrogen, potassium and phosphorous (P). Our concern in this report is restricted to uranium and its radioactive daughter products that occur within the phosphates.

Adding P supplements to farm land is often carried out via inorganic fertilization. However, soluble uranium-laden phosphate fertilizers may releases uranium and its daughter products to the farm soils. How this affects the radio-metal burden of the soils, and influences the uptake to its crops, needs to be considered. Israel has farm lands within and juxtaposed to its urban centers. Moreover, farmlands often give way to housing developments. Will residual radio-metals in the soils have a health effect upon populations that live above the previously fertilized lands? Moreover, farms overlie directly the two major aquifers in Israel. Will such radio-metals be added to the phreatic portions of the Coastal Plain and Mountain aquifers? Since these aquifers are open to direct recharge from the surface, the recharge waters may carry radio-metals released by these fertilizers. The potential radio-nuclide dangers to the environment inherent in the use of phosphate based fertilizers, including the gypsum (termed **sludge** or phosphogypsum or PG) by-product of industrial production, will be considered based upon an evaluation of the available pertinent literature.

II. Radioactive Materials

a) Uranium and Thorium in Phosphates

Uranium (predominantly the tetravalent species) is incorporated in the main phosphate bearing mineral apatite (Altshuler, 1980). Phosphorites and fertilizers derived from them are thus midly radioactive (Abbady et al., 2005; Azouazi et al., 2001; Boukhenfouf and Boucenna, 2002; da Conceicao et al, 2009; Khater et al., 2001; Saueia and Mazzilli, 2006). The amount of uranium varies among the different marine phosphorites deposits from less than 20 ppm to greater than 300 ppm, averaging 109 ppm U (Burnett and Veeh, 1992).

Thorium (Th-232), largely insoluble in sea water, is present in phosphorite rock detrital phases at low-to-mid single digit ppm values (Burnett and Veeh, 1992). Table 1 shows activity concentrations for a representative global suite of phosphate ores. The mass of the bulk rock remains in secular equilibrium as noted by the identical radioactivities of U-238 and Ra-226.

Table 1: Some typical values of activity concentrations in phosphate rock (from Scholten and Timmermans, 1992, p.105).

Origin of phosphate	238U Bq/kg	226Ra Bq/kg	232Th Bq/kg
Florida	1500	1500	16
South Carolina	4800	4800	78
Morocco	1700	1700	30
Kola	90	90	40
China	150	150	25

b) Secular Equilibrium and the Uranium decay-series

Natural uranium is made up of two radioactive decay series, headed by U-238 and U-235 respectively. In nature, the mass ratio between the two is constant and dominated overwhelmingly by the U-238 isotope (approximately 99.3%). When uranium is discussed in this report, it implies the more relevant U-238 isotope. The U-238 decay-series is presented in Table 2, and a comparison of the activities of the uranium isotopes making up natural uranium is presented in Table 3. The amount of thorium is very small compared to the U-238 in the phosphate rock. Thus, our discussion of potential environmental contamination by the use of phosphate fertilizer will focus predominantly around the U-238 decay-series.

Table 2: The U-238 decay chain

(from http://www.wise-uranium.org/rup.html)

Uranium-238 Decay Series

Nuclide	Half-Life	Radiation *
U-238	$4.468 \cdot 10^9$ years	Alpha
Th-234	24.1 days	Beta
Pa-234m	1.17 minutes	Beta
U-234	244,500 years	Alpha
Th-230	77,000 years	Alpha
Ra-226	1,600 years	Alpha
Rn-222	3.8235 days	Alpha
Po-218	3.05 minutes	Alpha
Pb-214	26.8 minutes	Beta
Bi-214	19.9 minutes	Beta
Po-214	63.7 microseconds	Alpha
Pb-210	22.26 years	Beta
Bi-210	5.013 days	Beta
Po-210	138.378 days	Alpha
Pb-206	stable	-

only major decays shown
*** in addition, all decays emit gamma radiation**

Table 3: Specific activity of natural uranium.

0.99 mg U-238 | 0.05 µg U-234 | 7 µg U-235 | 1 mg Unat

(12.3 Bq) (12.3 Bq) (0.6 Bq) (25 Bq)

As uranium undergoes radioactive decay, daughter nuclides arise, eventually leading to a state of radioactive secular equilibrium. In this state, the activity (but not the mass) of each newly created daughter in the series equals the activity of its immediate parent in the series. For the U-238 decay-series, all of the radioactivity daughters seen in Table 2 will be present. Alpha, beta and gamma radiation will be emitted.

In the U-238 decay-series, there are six radio-elements with sufficiently long half-lives to be of environmental or biological concern. Those are, in order of appearance, U-234, Th-230, Ra-226, Rn-222, Pb-210 and Po-210. With the exception of Pb-210, they are all strong emitters of alpha particles. As the effects of alpha and beta particle radiation are quickly attenuated in air over short distances, their external dose rate is less significant compared to their internal dose rate. Thus, the ingestion of these nuclides, through food or water, or inhalation via aerosols or dust, is more harmful. All of these nuclides may cause genetic disruptions and cancers and a wide range of pathologies.

III. Israeli Phosphorites

The phosphate deposits are the most uranium rich rock in Israel. In 1999, Israel produced approximately 4.2 million tons (Mew, 2000). Most Israeli phosphates are used as the raw material in fertilizer production. The uranium content of the Israeli phosphorites average approximately 140 ppm U, ranging between 100-200 ppm (Nathan et al, 1979). The concentration of uranium is directly related to the percentage of phosphate (Nathan and Shiloni,1977; Nathan et al., 1979). The uranium that is incorporated into the apatite structure is strongly retained within the mineral structure (Avital, et al., 1983). The bulk phosphate rock maintains a state of

radioactive secular equilibrium in the U-238 series (Hussein, 1957; Mazor, 1963; Ilani and Strull, 1989). Yet, the phosphorites serve as a large source of radon emanation (Neeman and Steiner, 2001).

IV **Industrial production of phosphate fertilizer**

The production of phosphate fertilizer is generally based on converting phosphorites to a soluble superphosphate (formed by phosphoric acid on powdered phosphate) or the more P-enriched form of triple ammonium superphosphate (produced by the action of concentrated phosphoric acid on anhydrous ammonia). Ammonia phosphate has the advantage of supplying N and P nutrients simultaneously. The required phosphoric acid is produced by first mixing phosphorites with sulfuric acid to produce wet-process phosphoric acid, as shown in Fig. 1. Phosphoric acid production produces phosphogypsum (PG, CaSO4) as a by product.

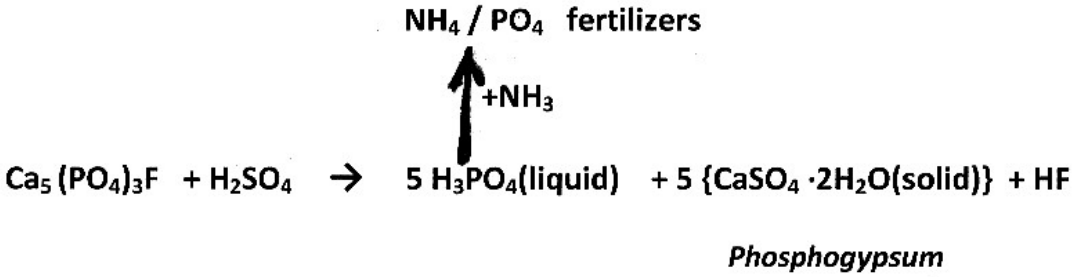

Figure 1: The chemical reactions involved in the industrial production of solid ammonium-phosphate fertilizer from prepared phosphate rock.

The process produces a large amount of phosphogypsum (PG). Three tons (Al-Jundi et al., 2008) of PG are produced for every ton of phosphoric acid produced. A significant factor is that the radium, Pb-210 and polonium partition more strongly into the PG phase. Uranium and thorium tend to partition into the phosphoric acid. Some of the radium may enter the fertilizer. Also, uranium may be found in the PG (Rutherford et al., 1994; Hull and Burnett, 1996). Guttman (1998) found that one sample of Israeli phosphate fertilizer contained 60 ppm equivalent of Ra-226.

V. Application of Phosphate Fertilizer

Uranium is the major radionuclide by mass and activity in phosphate fertilizer. The uptake, retention and potential release by soils is the starting point of any radiological evaluation of the hazards posed to the human environment. One needs first to evaluate the retention in the soils of radioactivity that builds up. It is then necessary to determine to what extent radiometals are transferred from the soils to the air, to edible plants and animal forage, and to groundwater. Figure 2 illustrates radioactivity release mechanisms from the PG stacks.

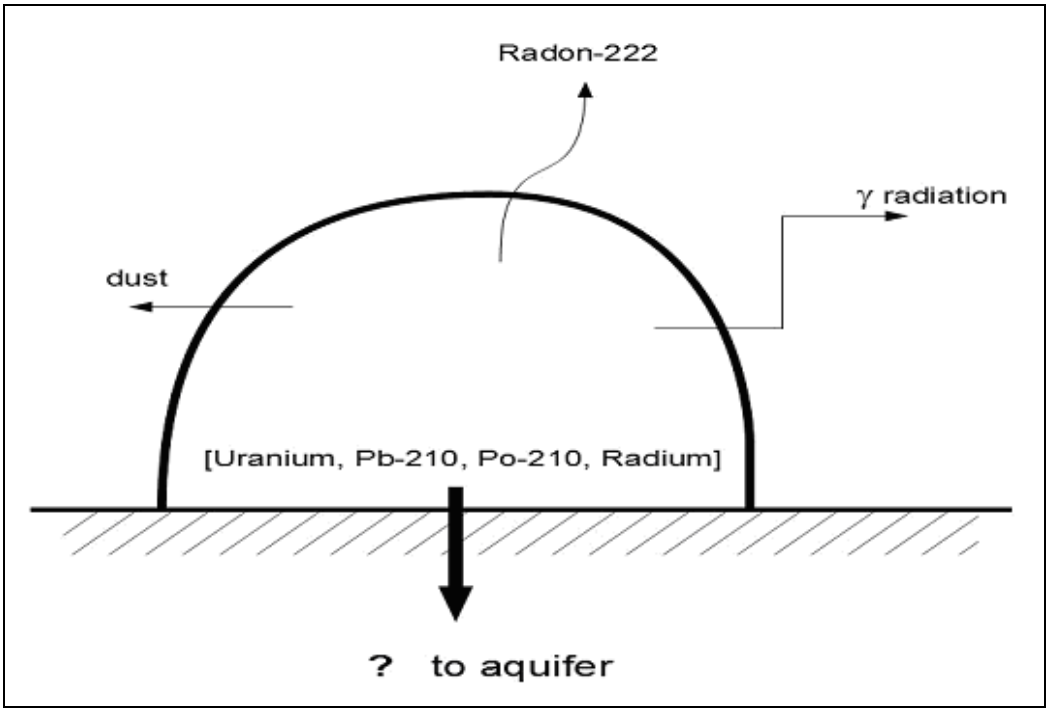

Figure 2: Potential ways that the radioactivity of the PG stacks might adversely affect the environment.

a. Soils

Studies cited below conclude that although phosphate fertilization contributes uranium to the soil in agricultural fields, the absolute quantities are not high. Phosphate fertilization adds uranium to the soils (Schipper et al., 2011; Taylor, 1997). The evidence suggests that most of the uranium and its daughters are concentrated and remain immobile within the top portion of the soil profile (Rothbaum et al., 1979; Yamaguchi et al, 2009; Takeda et al., 2006). Uterman and Fuchs, 2008, reported that farmed soils in Germany are enriched by approximately 0.15mg/kg due to phosphate fertilization compared to soils in forests. Rogasik et al., (2008) and Kim and Taylor estimate the uranium accumulation to be between 1-46 mg/Ha per year. Menzel (1968) concluded that the accumulation of uranium in the top

soil of fertilized farm lands poses no radiological risk. Lauria et al, (2009) calculate that the radionuclides added by fertilization is less than a half of a percent of the amount of radionuclides already residing naturally in the soil.

Therefore, the external exposure dose from the radioactive emissions from the soil is not hazardous(McBride and Speers, 2001; CCME, 2007).

The external exposure dose due to gamma-radiation has been estimated in air at a height of a meter above the ground; and converted into the annual effective dose rate to the population in µSv/year. These calculations show that the gamma-radiation dose rates are low.

Psister et al. (1976) measured the air dose rates over agricultural areas in Germany. They found that the radiation exposure for farmers would be on average only 1µSv/year; the maximum would be at most 23 µSv/year. The mean terrestrial radiation exposure, for the population in Germany is 50 to 55 µSv/year. Thus, the fertilizer contribution is marginal. No danger is associated with the radioactive emissions contributed by fertilization of the soils (Ryan, cited in Jones et al., 1990).

b. Plants

Crops grown on P-fertilized fields do not transfer significant radiation to humans; nor does the forage, plant material eaten by grazing livestock (Bettencourt et al., 1988; Bolca et al., 2007;Carvalho and Oliveira, 2006; Desideri et al., 2010; Guidry, 1998; Martinez-Aguirre and Perianez, 1998; Mortverdt, 1992; Pietrzak-Flis and Skowronska-Smolak, 1995; Pulhani et al., 2005; Taylor and Kim, 2008).

Analyses of radiometal concentrations in plants have been made to insure that foods available to the population are secure from radiation. Many factors influence the uptake of an element. The mineralogy, soil pH, redox conditions, oxidation state, texture, plant species, competing ions, all affect the transfer (Bolca et al., 2007; Huhle et al, 2008;Mortvedt, 1992; Pulhani et al., 2005). A most important factor for transfer is that the element has to become and remain soluble for plant uptake. The amount of uptake also varies among plants species (Zafrir et al., 1992). Within a species, there is a range in values for each element.

An empirical transfer factor (TF) has been introduced that relates the concentration in plants to the elemental concentration in the associated soil (Shepard ,1985; Sheppard and Sheppard, 1985; Shephard and Evenden, 1988). Uranium has a TF of approximately 0.05, similar to that of Pb. This means that only small amounts of U in the soil are available for plant uptake. Radium transfer to plants from Mediterranean soils is greater than that for U or Th by up to two orders of magnitude (Tome et al., 2003). Fortunately, radium is removed to the PG phase during the industrial process. The TF for Po-210 is very small, reflecting this element's low mobility. The uptake of Po-210 and Pb-210 is dominated by atmospheric deposition from its gaseous radon parent, rather than via the roots. The amount of radon emanation is an important factor in transferring these daughter nuclides to plants, particularly to leafy plants such as tobacco (Othman and Al-Masri, 2007;Kithau, 1996)).

Plants grown on phosphate fertilized fields do not exhibit high absolute concentrations of any of the uranium decay-series nuclides (e.g. Ababneh et al.,2009; Ahmed and El-Arabi, 2005; Bolca et al., 2007; Khater and Al-Sewaidan, 2008; da

Conceicao and Bonotto, 2006; da Conceicao et al., 2009; Al-Karouf et al., 2008; Al-Masri et al., 2008; Mortverdt, 1994). A human daily uptake of uranium was calculated for a basic diet that includes foods grown on fertilized fields, and found to pose no health risks (Schnug et al., 2005; Pais and Benton Jones, Jr., 1997; WHO, 2004).

c. Groundwater

Fertilizer- derived uranium can be leached from soils (Jaques et al., 2005, 2008), but the amounts are generally benign (da Conceicao and Bonotto, 2000; Barisic et al., 1992; Zielinski et al., 1995,1997,2000,2006; Spaulding and Sackett, 1972; Shaf et al., 2007; Knolle et al., 2008; Shultz et al., 2008). The addition of uranium derived from fertilization does not appear to threaten the drinking water supply, at least in the near term. Though uranium enriched phosphate fertilizer is employed in Israel, the groundwaters have not reached unacceptable levels for drinking water.

The current US EPA limits for uranium in drinking water is set at 30µg/l. In Israel, this level is not seen in groundwater under fertilized fields (Guttman, 1998). Yet, leaching of uranium from phosphate fertilizers is often noted. In Germany, the concentration of uranium in water flowing through farmlands (0.8 µg/l) is about an order of magnitude higher than in streams flowing through forests (0.08 µg/l), (Birke et al.,2008). The percentage increase is great, but the absolute amount is not. Low U concentrations in groundwater may be due in part to re-adsorption on the surface of clays (Guidry et al; 1991; Zielinski, 1997) .

In Israel, leaching of the raw phosphate rock by ground water has raised the concentration of uranium in the Mountain (Judea Group) aquifer, as it flows beneath the phosphorite

bearing strata in the Beersheva region. Here, the uranium concentration in the drinking water was seen to rise from approximately 1µg/l to almost 8µg/l (Kronfeld et al.,1979). Guttman (1998) noted the increase in the uranium content in fish ponds that use recycled irrigation water and drainage from fertilized fields. The amount though is well beneath the safety limit set for drinking water.

d. Additional Considerations

Uranium retention in soils may become more problematic (considering radon emanation) as farmlands are increasingly converted to housing. Cleaning the soil (environmental remediation) is prohibitively expensive by removal, transport, treatment, refilling. However, *in situ* methods are being developed for low level radiation site reclamation (Gavrilescu, 2006, and Gavrilescu et al., 2009). Huang et al. (1998) found that certain organic acids can be added to soils to increase U desorption from soil to soil solution and to trigger a rapid U accumulation in plants. The advantages of such techniques are that they are inexpensive and they may be carried out in situ.

Hu et al. (2008) and Schnug and Haneklaus (2011) advocate extracting the uranium from the fertilizers to minimize the potential adverse effects of the U loads to agricultural soil, and to extract the fuel (Ragheb, 2010; IAEA,1989,2001). Chemical extraction techniques are reviewed by Gupta and Singh (2003). Uranium extraction is limited by economics and by the absence of requiring regulations. At today's commodity prices, approximately $50/lb, Israel exports free more than $15M of uranium for each million tons of phosphate fertilizer (assuming a mean U content of 140 ppm). The sale of such uranium could offset the extraction expense. As the spot price of U increases, this might become a profitable endeavor.

VI. Phosphogypsum (PG, Sludge)

During the wet process of phosphoric acid production from phosphorite, several hundred million tons of gypsum are produced each year worldwide. This gypsum is termed phosphogypsum (PG), or Sludge, to differentiate it from naturally occurring gypsum which exhibits lower radiation levels. The radioactivity in natural gypsum is approximately 10 Bq/Kg, while it averages about 867 Bq/Kg for PG in Israel (Neeman and Steiner, 2001). This latter value is above the 370 Bq/kg permissible limit for Ra-226 for agricultural application (USEPA, 2009). Today, dumping of the PG waste into the sea has been restricted; thus, the most economical way of disposal is storing it on land in large piles or stacks. Yet, these large volumes of acidic material (pH=2-5), containing elevated activities of radio-elements, present potential environmental problems. The high radium concentration (Jacomino et al., 2009), and the build up of radon and her progeny, limits the use of PG as an animal feed supplement (Golushko, 1982), or as a substitute for natural gypsum in home building materials (Conklin 1992;Rutherford et al., 1994). The problems are serious for the use or disposal of the material.

The PG that is produced in the factories in the Negev is stored on land in large stacks near the Kishon river, in the Haifa Bay region. Monitoring of these stacks and their surroundings has been carried out (Neeman and Steiner, 1999-2001). The Th-232 activity is low in the stacks, averaging 2.6 Bq/kg. The Ra-226 in the stacks was much higher; ranging from 20-2369 Bq/kg, averaging 867 Bq/kg. All of the stacks except one contain PG that is above the 370 Bq/kg permissible for agricultural application (USEPA). Some stacks have activities above the 1000 Bq/kg limit that would require regulatory attention, and possible further treatment (Lovat, 2006).

Gamma-radiation is another environmental hazard posed by PG stacks. Over time, daughter products build up, particularly Bi-214. Exposure to this gamma-radiation can increase the annual radiological dose rate to PG workers by an additional 0.45 to 0.85 mSv over background (Laiche and Scott, 1991; Hussein, 1994; Mas et al, 2001; Palhalidis, 2009). In Israel, the stack having the highest gamma-ray activity yields a dose of 239 μrem/h. For effective doses under 3mSv (300 rem), the risk is considered minimal (USCEAR, 2000). Thus, the gamma-ray emissions from PG stacks in Israel are not a cause for concern.

The build up of radon, and its subsequent emanation from the stacks (Lysandrou et al., 2007), will raise the radiation dose to those exposed to the gaseous cloud that is continuously being released. The USEPA adopted that Rn-222 release should be limited to an average of 0.74 Bq per square meter (Rutherford, et al., 1994; Duenas et al., 2007). The radon release can be mitigated almost completely by plant (Komnitsas et al., 1999) and soil cover (Duenas et al., 2007) over the stacks. This cover would reduce the redox conditions and induce insoluble metal sulfide formation that would reduce the mobility of most radio-metals. Yet, as has been suggested (Carbonell-Barrachina et al., 2002), reductive decomposition of the highly insoluble radium sulfate may occur. This would actually facilitate the release of Ra-226.

A further hazard can be attributed to fine dust bearing radio-nuclides, being blown off from the stacks, and distributed by the winds (Guidry, 1990). Breathing in of this dust can result in the fine material accumulating in the lungs. This can result in the irradiation of sensitive tissue for long periods of time. Likewise, the fine dust may be ingested. This would further add to the internal dose rate. In Israel, the stacks are far

removed from the population concentrations. So the release of dust or radon emissions poses no health hazards to most of the population.

The uptake of plants grown on soils having PG radioactivity higher than USEPA limit has been studied. Soils treated with PG held higher radium activities, which were indeed reflected in a higher radium concentration in each of the crops studied. Papastefanou et al. (2006) estimated the annual effective dose to be 0.86 μSv/yr compared with the average worldwide exposure from natural radiation sources of 2.4 mSv/yr. He concludes that the activity values of Ra-226 in crops produced from treated and untreated soils (with PG) can be considered comparable, in that both yield negligible dietary health concerns. The policy in Israel is to follow the USEPA (1999) 370 Bq/kg permissible limit for Ra-226 for agricultural application of PG.

The PG stacks have the potential to adversely affect the groundwater supply, since the acidic sludge contains heavy metals in addition to the radio-metals. In the stacks, most of the Ra-226 is immobilized in the PG. Leaching experiments (using distilled water) by Haridasan et al., (2002) confirm that the removal was very slow. The Th-232 is found to be contained in insoluble minerals such as monazites (Santos et al., 2006). The Po-210 is generally firmly bound to fine particulates (Graves, 1989). Leaching by distilled water releases less than 8.5%, unless the solutions are more acidified (Santos et al, 2006). Then, 20% of the Po-210 is released. Yet, the Po-210 mobility can increase in the presence of sulfide ions, that can be formed by bacterial action within the PG stack. The Uranium is particularly mobile in the stack fluids under the generally prevailing low pH conditions (2-5.5) (Lysandrou et al., 2008; Burnett, 1988;

Burnett and Elzerman, 2001; Hull and Burnett, 1996; Zielinski et al., 2011). With time and continued exposure to rain, the pH increases, approaching pH=7.

Miller and Sutcliff (1984) believe that the most important pathway from PG stacks to humans is by their contamination of groundwater. The potential for radiometal release from the stacks, particularly U, Pb, and radium, and the threat to the underlying ground water is considered. Lysandrou and Pashilidis (2008), studying the mobility in PG stacks along the coast of Cyprus, have found that increased salinity in the leaching solution can increase the release of the metals by up to a factor of 100, depending on the concentration. Loewengart (1964) demonstrated that sea spray in the Haifa Bay can deposit significant amounts of salts inland. However, the amounts decrease with distance from the shoreline. The stacks in Israel are situated far from the coast, which makes moot any accelerated leaching. As radium resides in the stacks, more mobile Pb-210 will be produced. This, along with the uranium, will be prone to release. Yet, by analogy with the studies on the PG stacks in Florida (Burnett and Elzermann, 2001), there would seem to be little environmental hazard even if leakage of fluids were to take place; for they noted a geochemical barrier to metal transport was in place. Empirically, it was found that there was little radionuclide transfer below the stacks.

It was suggested that barite, a mineral consisting of barium sulfate, might form from the elements in the stack fluids; which would coprecipitate radium. Recent studies by Zielinski et al., (2011) on PG stacks in Jordan validate this conjecture. Radium follows barium closely chemically. Barium and sulfate are enriched in the gypsum phase. Small mineral grains of very acid insoluble barite are formed, which

effectively remove the radium from solution. An inexpensive but effective method of insuring that radium does not migrate out of the stacks towards the water table, would be to added soluble barium salts and to ensure thereby the co-precipitation of radium with the barite.

VII. Conclusions

The uranium and its daughters that are added by way of phosphate fertilization to farmland do not present radiological hazards in the short term. The amounts of radionuclides transferred to plants and animal forage does not induce radiological nor chemical harm (Eisenbud and Gesell, 1997). There does not appear to be any near term danger to the groundwater supply. Before farmlands are converted to sites of habitation, the soils should be treated to lower the future radon emanations. The problem is not the radon emanation to the atmosphere where it is readily diluted; but, rather, its leakage into buildings (i.e. through cracks in the foundation), driven by a pressure gradient (Gates and Gundersen, 1992). The gypsum waste that is stored in stacks in Haifa bay region are well situated to prevent harm to centers of population. The phosphogypsum waste is large. Its storage and monitoring costs money and is an inconvenience. Yet, there does not appear to be a better alternative for handling this material (McDonald et al., 1992), other than extracting the U from the fertilizers. The PG radioactivity prevents its being used in agriculture or as additives in building materials; but, it does not present a danger to the environmental nor to the groundwater.

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