Heavy metal and radionuclide contamination of fertilizer products and phosphogypsum waste produced by The Lebanese Chemical Company, Lebanon, 2002

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1 EXECUTIVE SUMMARY

The Lebanese Chemical Company (LCC) produces and markets a range of phosphate based fertilizers, including Simple Super Phosphate (SSP) fertilizer and Triple Super Phosphate (TSP) fertilizer. The fertilizers are manufactured at a facility located in the village of Selaata in north Lebanon.

Phosphate fertilizers produced by LCC are derived from phosphate ore. In addition to phosphate minerals, these ores can contain significant amounts of a wide range of impurities, including heavy metals and naturally occurring radionuclides.

The production of fertilizers from phosphate ore using the processes employed by LCC results in the formation of large quantities of solid waste, which is primarily calcium sulfate, commonly known as phosphogypsum.

This study was carried out to determine the content of heavy metals and radionuclides in fertilizer products and waste material produced by LCC.

The two fertilizer samples analysed contained significant concentrations of a number of heavy metals, including cadmium, chromium, vanadium and zinc. The heavy metals present in the fertilizers at elevated concentrations are persistent in the environment, and the ongoing addition of fertilizers containing these metals to soil can result in their accumulation in the soil over time. The presence of cadmium in the fertilizers at elevated concentration is of most concern as a result of the toxicity of this metal and its ability to accumulate in soils, and bioaccumulate in plants and animals. The SSP and TSP fertilizers contained cadmium at 4 and 7 mg/kg respectively, significantly above typical soil background levels of below 1 mg/kg. Cadmium is readily available for uptake in a range of crops including grains, rice and vegetables. Increasing concentrations of cadmium in fertilizers applied to land can result in increased cadmium concentrations in crops.

Both the SSP fertilizer and the phosphogypsum sediment also contained significant levels of many of the gamma emitting radionuclides analysed for. As for heavy metals, many of the radionuclides present are able to accumulate in soils amended with contaminated fertilizers. This accumulation constitutes a source of technologically enhanced natural radiation, increasing the total exposure of humans and other species from natural radionuclides.

The activation concentration of radium (Ra-226) in the SSP fertilizer was found to be 1043 Bq/kg. Although levels in uncontaminated soils can vary, they are typically significantly lower than these levels, with reported values of 12-26 Bq/kg in some unfertilized soils. Ra-226 decays into radon gas (Rn-222), an established human carcinogen. The release of gaseous Rn-222 from these materials may result in elevated levels of exposure to this radionuclide by those involved in the use of these materials, potentially causing elevated health risks.

Although dependent on many factors, elevated soil levels of the radionuclides present in phosphate fertilizers, including Ra-226, can result in elevated levels in certain crops and other plants grown on the soil. This may cause elevated radionuclide exposure to human and animal through ingestion of these crops.
The discharge of radionuclide contaminated phosphogypsum wastes from fertilizer production facilities can result in elevated radionuclide levels in receiving water bodies and aquatic biota such as shellfish. The proposed use of this material as a raw material in cement production will result in the transfer of these contaminants to the cement product, which may result in elevated human exposures to radionuclides, particularly radon gas.

In addition to the impacts from heavy metal and radionuclide contaminants in the fertilizers, their agricultural use can result in serious environmental impacts through phosphate leaching into nearby water bodies, resulting in excessive algal blooms and eutrophication, with severe impacts on the aquatic environment.

The impacts resulting from the production and use of fertilizers derived from contaminated phosphate ores can only be addressed through the conversion to agricultural practices that do not involved the use of these materials, such as organic agricultural practices including the use of natural composts.

The use of end-of-pipe solutions to deal with wastes derived from phosphate fertilizer production, such as the use of phosphogypsum waste as a raw material in cement manufacture, fail to address the issues of concern, and simply shift pollutants from one location to another.
2 INTRODUCTION

The Lebanese Chemical Company (LCC) produces and markets a range of phosphate fertilizer products. The fertilizers are manufactured at a facility located in the village of Selaata in north Lebanon.

Fertilizers produced at this facility are derived from phosphate ore. Products include Simple Super Phosphate (SSP) fertilizer, Triple Super Phosphate (TSP) fertilizer, as well as phosphoric acid (H₃PO₄). While some fertilizer produced by LCC is used in Lebanon, the vast majority is exported to France, Spain, Italy and Turkey and the UK.

2.1 Fertilizer production process

Phosphate ores contain phosphorous in mineral forms that are primarily calcium phosphate (Ca₃(PO₄)₂). Phosphate ores can be defined into two types, sedimentary and igneous (Kroschwitz & Howe-Grant, 1995c). In addition to the phosphate minerals, these ores can contain a wide range of impurities. The composition of the ores can vary considerably with their origin, with sedimentary ores typically containing significantly higher concentrations of impurities, include a range of heavy metals as well as naturally occurring radionuclides (Cowart & Burnett 1994, Manheim et al. 1980). The phosphate ores used by LCC in their production processes are sedimentary in origin.

The production of superphosphate fertilizers involves processes where the phosphate ore is reacted with acid. Simple super phosphate (SSP) fertilizers are produced using sulfuric acid. Triple superphosphate (TSP) fertilizers are produced with the use of phosphoric acid, which is produced from the phosphate ore in a separate process. The production of fertilizers through these processes results in the production of large quantities of solid waste, which is primarily calcium sulfate, commonly known as phosphogypsum (Kroschwitz & Howe-Grant, 1995b).

In the production processes, significant amounts of the impurities present in the ore can be transferred to the fertilizers and phosphoric acid produced. The remainder of the impurities are present in various production wastestreams, mainly in the phosphogypsum solid waste (Erdem et al. 1996).

3 MATERIALS AND METHODS

3.1 Sampling Collection

In 2000 Greenpeace collected a sample of marine sediment from the seabed off the Selaata coast in Lebanon, approximately 50m from the LCC discharge pipe. At this location the seabed is covered with a layer of phosphogypsum sediment resulting from discharges by LCC. In addition, two types of fertilizer produced by LCC, simple super phosphate (SSP) and triple super phosphate (TSP), were purchased in Lebanon by Greenpeace.

All samples were returned to the Greenpeace Research Laboratories in the UK for analysis. Details of the samples are summarised in Table 1.
Table 1. Description of fertilizer products and waste samples associated with LCC, Lebanon.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Sample type</th>
<th>Sample description</th>
</tr>
</thead>
<tbody>
<tr>
<td>MI02023</td>
<td>Sediment</td>
<td>Collected from the seabed, approx. 50m from the LCC discharge pipe</td>
</tr>
<tr>
<td>MI02024</td>
<td>Fertilizer</td>
<td>Simple super phosphate (SSP) fertilizer</td>
</tr>
<tr>
<td>MI02025</td>
<td>Fertilizer</td>
<td>Triple super phosphate (TSP) fertilizer</td>
</tr>
</tbody>
</table>

3.2 Sample Analysis

Both fertilizer products and the sediment samples were analysed for a range of heavy metals at the Greenpeace Research Laboratories. In addition, two samples (MI02024 simple super phosphate fertilizer & MI02023 sediment) were forwarded to The University of Wales for the analysis of gamma emitting radionuclides.

A detailed description of sample preparation and analytical procedures for the heavy metals analysis and a summary of the method employed for the analysis of gamma emitting radionuclides are provided in Appendix 1.

4 RESULTS AND DISCUSSION

The results of the gamma emitting radionuclide and heavy metals analyses of the three samples are presented in Table 2.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>MI02023</th>
<th>MI02024</th>
<th>MI02025</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample type</td>
<td>Sediment</td>
<td>Fertilizer</td>
<td>Fertilizer</td>
</tr>
<tr>
<td>Description</td>
<td>From seabed, approx. 50m from the LCC discharge pipe</td>
<td>Super simple phosphate</td>
<td>Triple simple phosphate</td>
</tr>
</tbody>
</table>

RADIONUCLIDES

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>MI02023 Activity concentration (Bq/kg dw)</th>
<th>MI02024 Activity concentration (Bq/kg dw)</th>
<th>MI02025 Activity concentration (Bq/kg dw)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thorium (Th-234)</td>
<td>ND</td>
<td>320 ± 16</td>
<td>---</td>
</tr>
<tr>
<td>Protactinium (Pa-234m)</td>
<td>ND</td>
<td>343 ± 35</td>
<td>---</td>
</tr>
<tr>
<td>Radium (Ra-226)</td>
<td>957 ± 47</td>
<td>1043 ± 25</td>
<td>---</td>
</tr>
<tr>
<td>Lead (Pb-214)</td>
<td>598 ± 10</td>
<td>413 ± 8</td>
<td>---</td>
</tr>
<tr>
<td>Bismuth (Bi-214)</td>
<td>579 ± 10</td>
<td>401 ± 8</td>
<td>---</td>
</tr>
<tr>
<td>Potassium (K-40)</td>
<td>3.2 ± 0.4</td>
<td>4.1 ± 0.3</td>
<td>---</td>
</tr>
</tbody>
</table>

METALS

<table>
<thead>
<tr>
<th>Element</th>
<th>MI02023 Concentration (mg/kg dw)</th>
<th>MI02024 Concentration (mg/kg dw)</th>
<th>MI02025 Concentration (mg/kg dw)</th>
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<tbody>
<tr>
<td>Arsenic (As)</td>
<td>1.5</td>
<td>2.0</td>
<td>4.5</td>
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<tr>
<td>Cadmium (Cd)</td>
<td>&lt;1</td>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td>Chromium (Cr)</td>
<td>8</td>
<td>87</td>
<td>198</td>
</tr>
<tr>
<td>Cobalt (Co)</td>
<td>&lt;2</td>
<td>&lt;2</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>5</td>
<td>14</td>
<td>20</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>4</td>
<td>&lt;3</td>
<td>3</td>
</tr>
<tr>
<td>Manganese (Mn)</td>
<td>&lt;1</td>
<td>6</td>
<td>13</td>
</tr>
<tr>
<td>Mercury (Hg)</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>&lt;2</td>
<td>15</td>
<td>27</td>
</tr>
<tr>
<td>Vanadium (V)</td>
<td>2</td>
<td>78</td>
<td>151</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td>3</td>
<td>169</td>
<td>390</td>
</tr>
</tbody>
</table>

Table 2. Gamma emitting radionuclides and heavy metals quantified in samples of fertilizer products and sediment associated with the Lebanese Chemical Company, Lebanon. Metal concentrations are given in mg/kg dry weight. Radionuclide results are quoted as an activity concentrations in Bq/kg dry. ND indicates non-detectable for radionuclide analysis, this is approximately <2 Bq/kg.
4.1 Heavy metals

The two fertilizer samples (MI02024-25) contained significant concentrations of a number of toxic and potentially toxic heavy metals, including cadmium, chromium, vanadium and zinc. The sediment sample (MI02023), which is primarily phosphogypsum waste from LCC, did not contain any of the heavy metals analysed for at significant concentrations.

Both the SSP (MI02024) and TSP (MI02025) fertilizers contained cadmium and zinc at concentrations above those typically found in soils. In addition, the TSP fertilizer also contained chromium and vanadium at concentrations above typical soil concentrations. Average concentrations of these metals in uncontaminated soils are typically 0.01-1.0 mg/kg for cadmium, 1-100 mg/kg for chromium, 100 mg/kg for vanadium and 50 mg/kg for zinc (Alloway 1990).

For all the metals analysed for, their concentrations are higher in the TSP fertilizer (MI02025) than the SSP fertilizer (MI02024). These results are consistent with the production processes used for these two products. The TSP fertilizer is produced from phosphate ore and phosphoric acid, which itself is derived from phosphate ore in a separate process. A significant amount of the impurities present in the ore are retained in the phosphoric acid produced from it, and these impurities are transferred to the TSP fertilizer product (Erdem et al. 1996).

The SSP fertilizer is produced from the phosphate ore using sulfuric acid, which does not contain these significant concentrations of impurities. SSP fertilizer products, therefore, tend to contain lower concentrations of impurities.

These metals are persistent in the environment, and the addition of fertilizer products containing these metals to soil can result in their accumulation in the soil over time, resulting in elevated concentrations above natural background levels (USPHS 2000, Bryan & Langston 1992, Alloway 1990). The presence of cadmium in the fertilizers at elevated concentration is of most concern. Potential environmental and human health impacts resulting from the use of these fertilizers are discussed in Section 4.

4.2 Radionuclides

Phosphate ores, especially sedimentary ores as used by LCC, can be significantly enriched with naturally occurring radionuclides; uranium (U-238) and the ‘daughter’ radionuclides that come from the radioactive decay of U-238. Processing of these ores into fertilizer products and phosphoric acid results in the contamination of the products and waste materials with many of these radionuclides (Erdem et al. 1996).

Uranium (U-238) is an unstable element and undergoes slow decay into thorium (Th-234), which in turn decays into protactinium (Pa-234m). Pa-234 decays, via a number of radionuclides, into radium (Ra-226). Further decay through a number of radionuclides results in the formation of lead (Pb-214), which decays into bismuth (Bi-214). Other than U-238, the radionuclides mentioned above are gamma-emitting radionuclides.

Both the SSP fertilizer (MI02024) and the sediment (MI02023) contained significant levels of many of the gamma emitting radionuclides analysed for, as shown in Table 2. The
activation concentration of Ra-226 in the SSP fertilizer was found to be 1043 Bq/kg. While soils naturally contain low levels of this and other radionuclides, levels in uncontaminated soils are typically significantly lower than these levels. One study found the level of Ra-226 in unfertilized soil to be in the range 12-26 Bq/kg, with levels increasing up to 100 Bq/kg through continued application of phosphate ore derived fertilizer (Ioannides et al. 1997). Background levels of radionuclides in uncontaminated soils can vary with location and soil type.

Discharges of radionuclide contaminated wastes from fertilizer production facilities similar to LCC have resulted elevated levels of a range of radionuclides including U-238 and Ra-226 in water, suspended matter and sediments of the receiving water bodies (Perianez & Martinez-Aquirre 1997, Paridaens & Vanmarcke 2001, Poole et al. 1995).

Elevated levels of certain radionuclides in the decay chain, including polonium (Po-210), have been observed in shellfish near to marine discharge points from phosphate ore processing facilities. In addition to the exposure of marine organisms themselves, elevated human radionuclide exposure through shellfish consumption has also been predicted (Camplin et al. 1996).

The sediment sample (MI02023) does not contain detectable amounts of Th-234 and Pa-234m, but does contains significant quantities of the radionuclides lower down the decay chain; Ra-226, Pb-214 and Bi-214. The marine sediment where sample MI02023 was collected is primarily composed of phosphogypsum waste (calcium sulfate) discharged by LCC. The radionuclide Ra-226 has very similar chemical characteristics to those of calcium. As a consequence, during phosphate ore processing Ra-226 present in the ore will co-precipitate with the calcium sulfate in the form of radium sulfate. This selective precipitation of radium (Ra-226) may explain the presence of this and lower decay chain radionuclides in the sediment sample, while the higher decay chain radionuclides were not detected in the sediment.

The SSP fertilizer (MI02024) contained significant quantities of all gamma-emitting radionuclides analysed for. These results clearly demonstrate the transfer of radionuclide contamination from the ore raw material to the final fertilizer product. A number of studies have shown similar radionuclide contamination of fertilizers derived from sedimentary phosphate ores (Ioannides et al. 1997, Erdem et al. 1996). The potential consequences for the use of radionuclide contaminated fertilizers are discussed in Section 4.

In both samples, the activity concentrations of Ra-226 are higher than those of Pb-214 and Bi-214. The decay of Ra-226 to the lower radionuclides proceeds via radon (Rn-222) which is a gas. While Rn-222 undergoes decay at a relatively rapid rate, a proportion of this radionuclide may escape from the contaminated material prior to decay, resulting in reduced activity concentrations of this and lower decay chain radionuclides.

Radon (Rn-22) is an established human carcinogen. Exposure is mainly associate with increased risk of lung cancer through Rn-222 inhalation. While this radionuclide is naturally occurring and present in the atmosphere at very low concentrations, many studies have demonstrated that elevated levels of exposure will result in elevated health risks (Samet & Eradze 2000).
The release of gaseous Rn-222 from these materials may result in elevated levels of exposure to this radionuclide by those involved in the use of these materials. This route of exposure is of particular concern where the contaminated material is produced or stored within an unventilated confined area, preventing the dispersal of this gas. In one study, the storage of phosphate fertilizer in a warehouse resulted in levels of Rn-222 in the air that were over ten times higher than background levels in the same area (Ioannides et al. 1997).

The results presented in Table 2 also indicate the low activation concentration of potassium (K-40) in both samples. Potassium, naturally present in soils, contains a small fraction of this radionuclide. The trace amounts of K-40 present in the two samples is not of concern.

In addition to the presence of radionuclides in both the fertilizer product and the phosphogypsum waste from LCC, other routes of radionuclide releases may exist during the ore processing. Studies have shown atmospheric releases of radionuclides in both gaseous and particulate forms from facilities similar to those of LCC, including U-238 and Ra-226. Such releases can result in elevated exposure to workers at the facility and those living in the vicinity (Papastefanou 2001).

5 IMPACTS THROUGH FERTILIZER USE

In addition to the environmental impacts associated with the production of phosphate fertilizers, the use of such materials for their intended purpose can result in additional impacts.

The addition of phosphate fertilizers containing elevated levels of heavy metals and radionuclides to soils will result in the transfer of these contaminants to the soil. As many of these contaminants accumulate in soil, continued application of fertilizer will result in accumulating concentrations of these contaminants over time.

5.1 Metals

Of the heavy metals present in the fertilizers, the presence of elevated concentrations of the cadmium is of greatest concern as a result of its toxicity, and ability to accumulate in soils, and bioaccumulate in plants and animals (Alloway 1990, USPHS 2000).

When present at elevated concentrations in soil, cadmium is readily available for uptake in a range of crops including grains, rice and vegetables. There is a clear association between the cadmium concentration in soil and in the plants grown on that soil (Elinder & Jarup 1996, Cabrera et al. 1994, WHO 1992). Increasing concentrations of cadmium in fertilizers applied to land has been reported to result in increased cadmium concentrations in grain crops (He & Singh 1994).

When present in a bioavailable form, both aquatic and terrestrial organisms are also known to bioaccumulate cadmium (USPHS 2000). The use of animal feed crops grown on soil with elevated cadmium concentrations may result in high levels of cadmium in beef and poultry (especially in the liver and kidneys). This accumulation of cadmium in the food chain has important implications for human exposure (USPHS 2000).
Cadmium has no biochemical or nutritional function, and it is highly toxic to both plants and animals (USPHS 2000, WHO 1992, Alloway 1990). In humans and animals, exposure to cadmium can result in a wide range of health impacts, with the kidney as the main target organ (USPHS 2000, Elinder & Jarup 1996, Goyer 1996, WHO 1992). In addition, cadmium and certain cadmium compounds are listed by the International Agency for Research on Cancer (IARC) as carcinogenic (IARC 1994). The US Department of Health and Human Services in its 9th Report on Carcinogens also lists cadmium and certain cadmium compounds as known human carcinogens (USPHS 2001).

Cadmium toxicity to plants has also been reported, with elevated levels of cadmium in soil resulting in a range of adverse effects on plant growth and yield. Examples of these impacts include stunted growth and toxic signs on the leaves of lettuce, cabbage, carrot and radish plants (Alloway 1990). Other studies have shown reductions in the rates of plant photosynthesis and transpiration (WHO 1992).

The lower concentration of impurities in the SSP fertilizer does not necessarily mean that use of this product will result in a lesser environmental impact than use of the TSP fertilizer. In addition to lower concentrations of impurities, SSP fertilizers also contain lower concentrations of phosphorus than the TSP fertilizer. To achieve the same level of phosphorus addition to land being fertilized, a larger amount of SSP fertilizer needs to be added compared to when using the TSP fertilizer, which may result in even higher quantities of the impurities being added to the land. This can be seen from the concentrations of cadmium and phosphorus in the LCC fertilizers as detailed below, though the same can apply for radionuclide contaminants.

The concentration of cadmium in fertilizers is often expressed as a fraction of the amount of phosphorus (in the form of its oxide, P₂O₅), rather than as a fraction of the whole product, as is the data presented in Table 2.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>MI02024</th>
<th>MI02025</th>
</tr>
</thead>
<tbody>
<tr>
<td>Description</td>
<td>Super simple phosphate</td>
<td>Triple simple phosphate</td>
</tr>
<tr>
<td>Cadmium (mg/kg dry weight)</td>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td>Phosphorus, as P₂O₅ (%)</td>
<td>19</td>
<td>46</td>
</tr>
<tr>
<td>Cadmium per Phosphorus (mg Cd /kg of P, as P₂O₅)</td>
<td>21</td>
<td>15</td>
</tr>
</tbody>
</table>

Table 3. The concentration of cadmium in the two fertilizer samples (MI02024-25) expressed as a fraction of the quantity of phosphorus as P₂O₅.

As a result of the impacts on soil from the accumulation of cadmium present as a trace impurity in fertilizer product, the European Union is currently considering regulation regarding the allowable levels of cadmium in fertilizers (CSTEE 2002).
5.2 Radionuclides

The application of fertilizers containing elevated levels of radionuclides has similarly been shown to cause many-fold accumulative increases in the levels of such radionuclides in treated soils, including Ra-226, a precursor to radon gas, Rn-222 (Ioannides et al. 1997). This accumulation constitutes a source of technologically enhanced natural radiation, increasing the total exposure of humans and other species from natural radionuclides. Elevated levels of radionuclides present in fertilizers have also been found in urine, hair and skin smear samples of humans using the fertilizers, which may constitute elevated risk of cancer (Santos et al. 1995).

The uptake of radionuclides from soil into plants is highly complex and dependant on many factors including the plant species, soil conditions and the radionuclide soil concentrations. In addition, concentrations of radionuclides taken up by plants can vary significantly between different parts of the plant (Mortvedt, J.J. 1994).

Dependant on the local conditions, studies have shown that elevated soil levels of radionuclides present in phosphate ores and fertilizers, including Ra-226, can result in elevated levels in certain crops and other plants grown on the soil. In other cases, however, elevated levels of radionuclides have not been found in crops grown on such amended soils (Martinez-Aguirre et al. 1997, Mortvedt, J.J. 1994).

Radionuclides present in food crops are available for uptake by animals and humans, though uptake, exposure and effects from these sources are highly complex (Linsalata 1994).

These studies indicate potential impacts on animal and human food chains and subsequent exposures to radionuclides resulting from the use of fertilizers containing significant levels of radionuclides. Although it is not possible to draw direct links between radionuclide contamination of LCC fertilizers and health effects resulting from the consumption of food grown on soil amended with the fertilizer, there is clearly cause for concern over the use of such fertilizers on agricultural land.

5.3 Phosphate

The addition of large quantities of phosphorus to agricultural land through the use of phosphate fertilizers can result in serious environmental impacts even where the fertilizer is not contaminated with toxic metals or radionuclides.

Following the addition of fertilizer to land, phosphate can leach from the land into the surrounding environment, resulting in high phosphate levels in receiving water bodies such as rivers and seas. These elevated nutrient levels can cause excessive algal blooms and eutrophication of the water body, with severe impacts on the aquatic environment (Nixon 1990).

In addition to the agricultural source of phosphate to water bodies, the use of phosphate containing detergents constitutes an additional significant source. Detergents contributes approximately 25% of the amount found in untreated municipal wastewater in the European Union countries where it is still used, the remainder coming from agriculture. In light of the problems associated with eutrophication caused by elevated phosphorous levels in water
bodies, a recent study compiled for the European Commission has recommended a ban of the use of phosphates in detergents (EC 2002). This suggested ban indicates the need to greatly reduce phosphate inputs to water bodies from all sources, and has clear implication for the major contributor, the large scale use of phosphate fertilizers on agricultural land.

6 PHOSPHOGYPSUM WASTE IN CEMENT PRODUCTION

The cement manufacturer, Holcim, is currently considering making use of phosphogypsum waste from LCC as a raw material in cement production.

The analyses of the sediment sample (M102023), which is primarily phosphogypsum waste from LCC, demonstrates the significant amounts of radionuclides in this material. The use of this material in cement production will result in the transfer of these contaminants to the cement product (Kroschwitz & Howe-Grant 1995a).

Of particular concern is the presence of radium (Ra-226) in the phosphogypsum waste. As discussed above, this radionuclide decays to the gaseous radionuclide radon (Rn-222). Use of cement containing Ra-226 is likely to result in releases of Rn-222 from the cement.

The use of such cement in the construction of buildings may result in the release and build up of Rn-222 in enclosed areas, leading to elevated radiation exposure through inhalation of this gas by those occupying the building. The potential impacts of this elevated exposure on human health are discussed in Section 3.2.

In addition, weathering and erosion of cement produced from this waste will, over time, cause the release back to the environment of contaminants present in the waste. The demolition of structures constructed from cement, or mechanical operations (such as drilling) on such materials will result in the release of fragments and dusts, including respirable particles, containing the radionuclides present in the phosphogypsum raw material. In addition to the production of potentially harmful dusts, such physical fragmentation will hasten the releases of radionuclides into the environment as well as pose a human and animal health threat through the inhalation of contaminated dust particles.

7 CONCLUSIONS

The analyses of phosphate fertilizer products and phosphogypsum waste from the LCC facility in Selaata has shown that these materials are contaminated with a range of toxic and potentially toxic heavy metals, as well as gamma-emitting radionuclides.

Both the production of these fertilizers and their use on agricultural land can result in impacts to the environment and human health. Ongoing additions of these fertilizers to agricultural land will result in accumulative impacts to the land. These impacts can potentially result in elevated levels of many of these contaminants in crops grown on that land.

The use of end-of-pipe solutions to deal with wastes derived from phosphate fertilizer production, such as the use of phosphogypsum waste as a raw material in cement manufacture, fail to address the issues of concern, and simply shift pollutants from one
location to another. The use of cement from such raw materials may result in human health impacts.

The impacts resulting from the production and use of fertilizers derived from contaminated phosphate ores can only be addressed through the conversion to agricultural practices that do not involved the use of these materials, such as organic agricultural practices including the use of natural composts.

8 References


APPENDIX 1: ANALYTICAL METHODOLOGY

A1.1 Radionuclide Analysis

Analysis for the gamma emitting radionuclides was carried out at the University of Wales, using a standard gamma-spectrometric method.

Samples for analysis were prepared as variable geometry solids in standard counting vials. Where necessary, samples were dried to produce a standard geometry matrix. Samples were then presented in a standard orientation to an n-type ORTEC Gamma-X Ge detector. The detector measures a known proportion of the total number of gamma rays emitted by the sample, and their energy. By comparison with standards in identical geometries prepared using National Physical Laboratory (UK) mixed gamma standards, the activities of the particular radionuclides in the sample were calculated and converted to an activity concentration (Bq/kg) using the sample mass.

A1.2 Heavy Metal Analysis

A1.2.1 Preparation of samples for heavy metal analysis

All chemicals were of High Purity Aristar Grade. All glassware was cleaned in detergent, rinsed with tap water and deionised water, soaked in 10% nitric acid overnight, rinsed with deionised water and dried in an oven.

For the analysis of all metals other than mercury and arsenic, all samples were air dried until weighing readings became constant. The samples were then crushed using a pestle and mortar until homogenous and sieved through a 2-mm mesh. 0.5 g of each sample was separately weighed into a glass 100 ml boiling tube and to this 10 ml of deionised water was added, followed by 7.5 ml of concentrated hydrochloric acid and 2.5 ml of concentrated nitric acid. The samples were digested at room temperature overnight prior to being placed onto a Gerhardt Kjeldatherm digestion block (40 space) connected to a Gerhardt Turbosog scrubber unit (filled with 10% w/v sodium hydroxide). The samples were then refluxed at 130°C for four hours. After cooling to ambient temperature, the digests were filtered into volumetric flasks, diluted with deionised water, made up to a volume of 50 ml and mixed.

For the determination of arsenic and mercury in the samples, the above procedure was repeated in an identical method other than the heated digest was carried out at 80°C for four hours.

Standard Reference Materials, BCR-143 (trace elements in a sewage sludge amended soil), certified by the Commission of the European Communities, Brussels) and CRM-7004 (Loam with elevated analyte levels, certified by the Czech Metrological Institute), as well as a blank sample, were prepared with each batch of samples. All were prepared in an identical matrix, i.e in 15% v/v hydrochloric acid and 5% v/v nitric acid.
A1.2.2 Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

Following preparation, samples were analysed by ICP-AES, using a Varian Liberty-100 Sequential Spectrometer. The following metals were quantified directly: cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), manganese (Mn), nickel (Ni), vanadium (V) and zinc (Zn). A multi-element instrument calibration standard was prepared at a concentration of 10 mg/l, matrix matched to the samples (i.e. in 15% v/v hydrochloric acid and 5% v/v nitric acid). The calibration was validated using a quality control standard (8 mg/l), prepared internally from different reagent stocks. Any sample exceeding the calibration range was diluted accordingly, in duplicate, and re-analysed.

Mercury (Hg) was determined using Cold Vapour Generation ICP-AES. Hg (II) was reduced to Hg (0) i.e. a vapour, following reduction of the sample with sodium borohydride (0.6% w/v), sodium hydroxide (0.5% w/v) and hydrochloric acid (10 molar). The vapour was carried in a stream of argon into the spectrometer. Two calibration standards were prepared, at 10 µg/l and 100 µg/l, matrix matched to the samples (i.e. in 15% v/v hydrochloric acid and 5% v/v nitric acid). The calibration was validated using a quality control standard (80 µg/l), prepared internally from different reagent stock. Any sample exceeding the calibration range was diluted accordingly, in duplicate, and re-analysed.

Arsenic (As) was determined using Cold Vapour Generation ICP-AES. Prior to analysis, a 10ml portion of the digest solution from each sample was transferred to a boiling tube. The tubes were placed in a Gerhardt Kjeldatherm digestion block (40 space) connected to a Gerhardt Turbosog scrubber unit (filled with 10% w/v sodium hydroxide). The samples were then heated at 110°C until evaporated to dry. After cooling to ambient temperature, the solid material was taken up into v/v 5% hydrochloric acid solution (5ml) and transferred to a 10ml volumetric flask. Each boiling tube was washed twice with 1ml portions of v/v 5% hydrochloric acid solution, and these were added to the first portion. 0.5ml of Potassium iodide (KI) solution (0.4M) in 5% hydrochloric acid was added, and the volume made up to 10 ml with v/v 5% hydrochloric acid to give a final potassium iodide concentration of 0.02M. With each batch of samples, a blank solution (15% v/v hydrochloric acid and 5% v/v nitric acid) and a quality control solution (400 µg/l arsenic in 15% v/v hydrochloric acid and 5% v/v nitric acid) were similarly prepared.

For analysis, Arsenic (III) was converted to arsenic gas (AsH3) following reaction of the samples with sodium borohydride (0.6% w/v), sodium hydroxide (0.5% w/v) and hydrochloric acid (10 molar). The vapour was carried in a stream of argon into the spectrometer. Three calibration standards were prepared, at 50 µg/l, 100 µg/l and 500 µg/l, matrix matched to the samples (i.e. in 0.02M potassium iodide in 5% v/v hydrochloric acid). The calibration was validated using a quality control standard (400 µg/l), prepared internally from different reagent stock. Any sample exceeding the calibration range was diluted accordingly, in duplicate, and re-analysed.