OVERVIEW OF TECHNOLOGICALLY ENHANCED NATURAL RADIOACTIVITY IN FLANDERS

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1 ABSTRACT

In Flanders, that is the northern part of Belgium, a study concerning technologically enhanced natural radiation was carried out. There are quite a few places where enhanced natural radiation can be found, as a result of non nuclear industry. It mostly concerns isotopes from the ^{226}Ra (^{238}U) series but to a lesser extent also isotopes from the ^{232}Th series. The largest volumes of radioactively enhanced materials are produced by the phosphate industry, as a direct consequence of enhanced ^{238}U or ^{232}Th concentrations in the ores, the so called phosphate rock. The former radium production plant in the town of Olen has also caused enhanced radium activity in the environment. Also the burning of fossil fuels such as coal tends to concentrate natural radioactive materials into the fly ash. In coal fuelled power plants, large amounts of fly ash are produced but the activity concentrations are low generally speaking. Recently, on request of the Flemish Environment Agency, an inventory and characterisation of the most important deposits and contaminated sites was made by the SCK. The impact of the enhanced radioactivity on the population was estimated where relevant. Although, generally speaking there is no immediate threat to public health, in some specific cases special attention is needed. Caution should be taken that certain areas now and in the future are not converted into residential areas, as this might cause significantly enhanced radon concentrations in dwellings.

2 INTRODUCTION

Phosphate ores contain different amounts of natural radionuclides, according to their origin. Generally speaking, ores of marine origin contain between 1200 and 1500 Bq/kg of ^{226}Ra, but show hardly any enhanced ^{232}Th concentrations. Phosphate rock originating from Morocco or Florida are well known examples of this. Ores of magmatic origin generally contain less ^{226}Ra, in the order of 100 or 200 Bq/kg, but they contain more ^{232}Th, generally speaking in the order of 100 Bq/kg or otherwise 400 to 500 Bq/kg. This depends on their origin. The values cited are for the two most commonly used magmatic ores in Flanders, Kola ore (Russia) and Palfos ore (South Africa). In different locations in Flanders, five plants have been using phosphate ore, to produce different end product such as phosphoric acid, fertilisers or cattle food. Two of them, UCB in Oostende and Prayon Rupel in Puurs have stopped the acidulation of phosphate ore. The other three, Rhodia Chemie in Zelzate, Tessenderlo Chemie in Ham and BASF in Antwerp still continue the processing of phosphate ore. Different production methods yield different kinds of residual products, such as gypsum (calciumsulphate), calciumfluoride, calciumchloride, and others. Those products are mostly enhanced in ^{226}Ra, which chemically tends to follow the path of

calcium in the production process. Several hundreds of hectares are being used as gypsum deposits or have been to a greater or lesser extent contaminated with ^{226}Ra. In other cases, the radioactive contents of the ores is being transferred straight into the end products, although in diluted form. All those cases will be treated in the following chapter.
A separate case is constituted by the former radium production plant in Olen. As a result of its now ceased activities, environmental contamination with ^{226}Ra has taken place in the past and a separate chapter is dedicated to the present situation in the environment of the plant. Generally speaking, the contaminated area is smaller but activities in some places can be higher as compared to phosphate industry.
Also the burning of fossil fuels such as coal tends to concentrate natural radioactive materials into the fly ash. In coal fuelled power plants for example, large amounts of fly ash are produced but the activity concentrations are low generally speaking. The study of this fell outside the scope of this work.

3 PHOSPHATE INDUSTRY IN FLANDERS

3.1 Acidulation with sulphuric acid : phosphogypsum production.

In this production process, phosphoric acid (P_2O_5) is produced through the (wet) acidulation of phosphate rock with H_2SO_4 (1). The byproduct is insoluble calciumsulphate, or (phospho)gypsum, which has to be filtered of. It contains the bulk of the ^{226}Ra activity, more than 95 % of it. This is because the element calcium can easily be replaced by radium, due to its analogue chemical properties. For each ton of phosphate rock consumed, about 1.5 tons of gypsum is produced. Therefore the radioactivity in the gypsum is diluted with about the same factor, with respect to the ore. To give an example : Moroccan ore of marine origin typically contains between 1200 and 1500 Bq/kg of ^{226}Ra, and phosphogypsum produced of this ore typically contains between 800 and 1000 Bq/kg ^{226}Ra. In Flanders, a lot of this ore has been processed, and numerous related gypsum samples have confirmed these activity concentrations. Most of this gypsum had to be stored in gypsum deposits, although a fraction of it was also used in the building industry in the past. When standing on a semi infinite surface, contaminated with ^{226}Ra, a maximum extra gamma doserate of 0.5 nSv/h per Bq/kg ^{226}Ra is to be expected. So a theoretical maximum doserate of about 400 to 500 nSv/h above natural background is to be expected above a deposit of this type of gypsum. In practice the doserate will be lower because of radon escaping out of the deposits, and by absorption of gamma radiation by moisture or by surface water. The radon concentration above such deposits is more difficult to estimate a priori. Measurements with passive track etch detectors (2), at about 1.5 m above ground level were performed on most deposits. Covering of a deposit with ground, or clay or any other type of cover, will of course reduce the gamma doserates and to a lesser extent also the radon concentrations.

Four firms in Flanders have used the acidulation with sulphuric acid in the past or are still using it and thus have been or are contributing to the phosphogypsum inventory.

The first is UCB in Oostende, which produced phosphoric acid from 1953 until 1987. They only used Moroccan ore, and the above mentioned production process. A total estimate of about 6 Mt of gypsum was made, and 4 Mt of it was stored on two separate gypsum deposits. It is unclear what happened to the rest, if ever produced. Table 1 gives an overview of the characteristics of the deposits. The measured ^{226}Ra activities are in perfect agreement with the used ore. Radon concentrations are slightly enhanced with respect to a natural 10 Bq/m³ background in Flanders. The deposit in Zandvoorde is still clearly visible because of its height. The one in Oudenburg almost seamlessly blends into its surroundings.

The second is firm is Prayon-Rupel in Puurs. They produced phosphoric acid from 1962 to 1993 from Moroccan ore. Now, the acidulation has been transferred to Morocco and hence also the production of phosphogypsum. About 12 Mt of gypsum was produced, of which somewhat more than 2 Mt could be sold to the building industry mostly for the production of plasterboards. As a result of an increasing debate about radioactivity in plaster, this practice stopped in 1985. A total of 10 Mt of gypsum had to be disposed of. This was done for 70 % in a number of well defined deposits, which are described in table 1. The other 30 % has been disposed of on various sites around the factory, mostly in former claypits. A lot of these terrains are no longer recognisable as deposits, because they are covered, overgrown or because they have got a new use. One example of this is the deposit of Niel-Potaerde, which looks like any ordinary piece of woodland, and which might easily be converted into a residential area in a near future. Another example is the area for daytime outdoor recreation "De Schorre" in Boom. Here about 1.2 Mt gypsum was disposed of in various sites, before these terrains were converted to a recreational area. By the looks of it, it is very difficult to see were gypsum was deposited and where not.

The third firm is Rhodia-Chemicals in Zelzate. They are currently still producing phosphoric acid, and the ore consumption now is about 0.3 Mt per year, resulting in about 0.45 Mt of gypsum each year. The main difference lies in the type of ore used. Until 1985, the same type of Moroccan ore was used as in the previous firms. Since then, only ore of magmatic origin was used, both from Kola in Russia and from Palfos in South Africa. These ores contain besides about 100 à 200 Bq/kg of ^{226}Ra also a certain amount of ^{232}Th. Kola ore contains about 100 Bq/kg of ^{232}Th and Palfos ore about 400 à 500 Bq/kg. Until now about 20 Mt of gypsum had to be disposed of, and it is almost all situated in one single disposal site within the boundaries of the plant. Its characteristics are found in table 1. Interesting is to see that in the gypsum of magmatic origin, the ^{228}Ra and the ^{232}Th are in equilibrium, even in freshly produced gypsum. This was checked through independent measurements : gamma spectroscopy for the ^{228}Ra activity and ICPMS for the ^{232}Th. This means that the activity of the gypsum will not significantly alter anymore in the future. The ^{232}Th activity is about 200 to 400 Bq/kg, the ^{226}Ra activity is about 50 to 150 Bq/kg. The gypsum deposit is still in exploitation and is being raised in separate sectors. In most sectors, now gypsum of magmatic origin is on top, only in a few places marine gypsum can still be found on the surface. It show lows thorium activities and

Table 1 : Main characteristics of the most important phosphogypsum deposits in Flanders

Firm	Deposit	Surface	Contents	Typical ^{226}Ra activity Doserates	Radon	Cover	Remarks
UCB	Oudenburg	8.5 ha	0.9 Mt	840 à 960 $Bq.kg^{-1}$ 50 à 70 nSv/h	30 Bq/m^3	0.5 à 1m ground	Hardly noticeable, 8 m high, overgrown, free access
	Zandvoorde	16 ha	3.1 Mt	930 à 1000 $Bq.kg^{-1}$ 280 à 350 nSv/h	40 Bq/m^3	None	Well noticeable, 16 m high, restricted access
Prayon-Rupel	Puurs	18 ha	1.4 Mt	580 à 710 $Bq.kg^{-1}$ Up to 300 nSv/h	45 Bq/m^3	Partly with ground	Well noticeable, 8 m high, on factory grounds
	Hoeykens	14.3 ha	2.1 Mt	930 $Bq.kg^{-1}$ 50 à 70 nSv/h	30 Bq/m^3	0.5 à 1m ground	Well noticeable, 16 m high, fully overgrown, restricted access
	Hollebeek	32 ha	3.6 Mt	Up to 600 $Bq.kg^{-1}$, samples mixed with ground 50 à 70 nSv/h	35 Bq/m^3	HDPE foil Clay layer Ground cover	Well noticeable, 11m high, partly overgrown, failed tree cover, restricted access
	Niel - Potaerde	6.3 ha	0.12 Mt	700 $Bq.kg^{-1}$ 100 à 150 nSv/h	50 Bq/m^3	15 cm of humus from tree cover	Not noticeable, no elevation, free access
Rhodia-Zelzate	Factory grounds	70 ha	20 Mt	55 à 380 $Bq.kg^{-1}$ (Ra) 50 à 400 $Bq.kg^{-1}$ (Th) 200 à 300 nSv/h	70 à 130 Bq/m^3 (radon + thoron)	Verges covered Top not	Well noticeable, 35 m high, verges overgrown, restricted access

higher radium activity. The radon measurements are being influenced by an undetermined thoron component. The radon detectors are to a certain extent sensible to thoron too, and this has increased the readings. It would be interesting to place both thoron sensitive and thoron insensitive devices on the same spots.
The fourth firm is BASF in Antwerp. Until 1993, they produced phosphoric acid through acidulation with H_2SO_4 until 1993. Since then they only use nitric acid, a process which is discussed later, but which does not produce gypsum or other byproducts. In total about 9.6 Mt of gypsum was produced, mostly from Moroccan ore. This gypsum contained about 1000 Bq/kg ^{226}Ra activity, and hardly any thorium activity. It was dumped into the estuary of the Schelde, the tidal river that flows through Antwerp. It is difficult to say where this gypsum ended up finally. A small part of it must have dissolved, most of it must have settled on the bottom of the estuary. During normal dredging activities, a part of the latter must have ended up on the terrains raised with sand-in-water slurry, but in a very diluted form. Figure 1 shows an overview of the phosphogypsum production in Flanders.

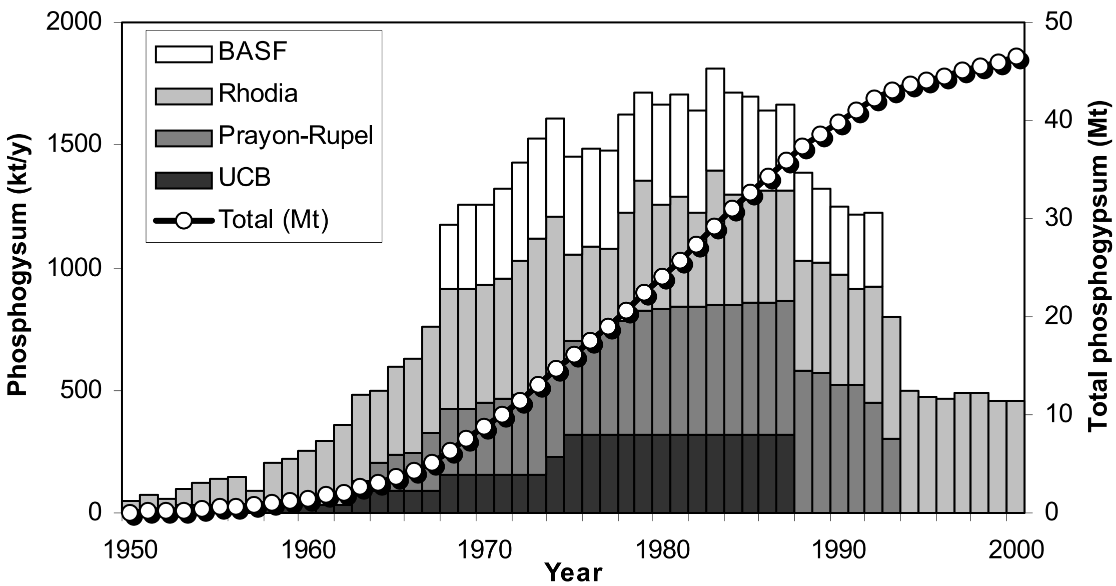


Figure 1 : Phosphogypsum production in Flanders in kt/y for each firm and total production of phosphogypsum in Mt.

3.2 Acidulation with hydrochloric acid : byproducts $CaCl_2$ and CaF_2

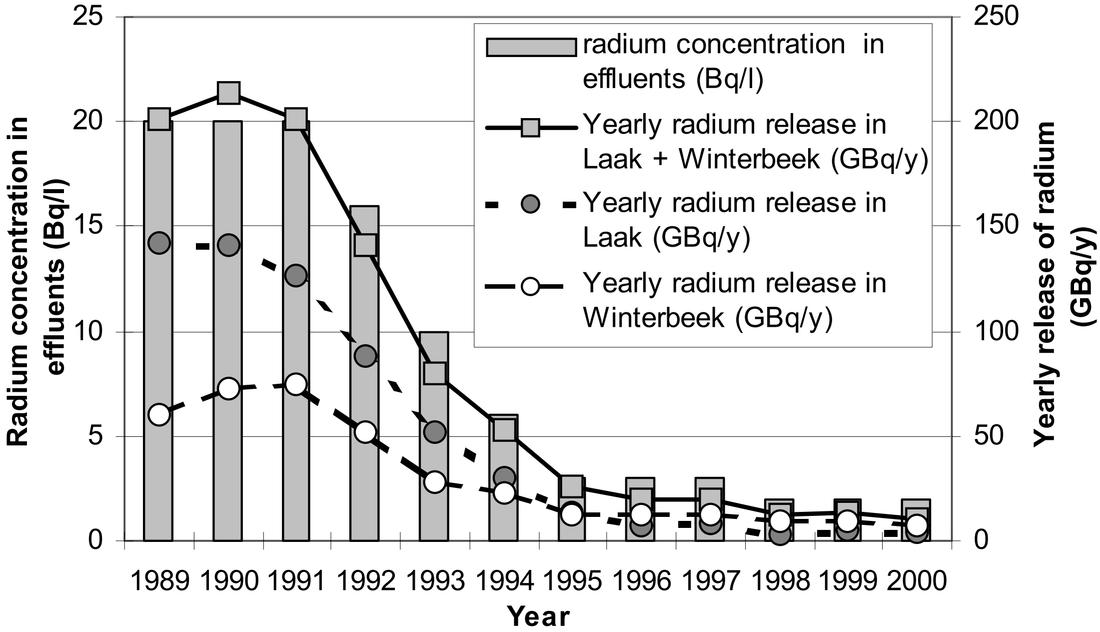
Phosphate rock can also be acidulated with hydrochloric acid, to produce dicalciumphosphate, mostly for the production of cattle food. In Flanders, there is one firm, Tessenderlo Chemie, who uses this process to acidulate Moroccan phosphate rock. They had two plants operating by this process, one of which (Tessenderlo) was closed in 1995. The other one (Ham) is still operative.
The main byproducts here are $CaCl_2$ and CaF_2 and due to the chemical analogy between radium and calcium the bulk of the radium is found in those two fractions. The latter fraction is insoluble, and has to be filtered of as a sludge of

CaF_2. About 0.5 ton of CaF_2 sludge is produced for each ton of processed P_2O_5. This means that ten times less solid waste products are produced when using HCl instead of H_2SO_4. Until the end of 1991, between 30 % and 40 % of the radium load remained in the sludge, giving rise to about 3000 à 4000 Bq/kg ^{226}Ra activity in the sludge. The rest remained in solution as $CaCl_2$ with calcium substituted by radium. It was evacuated with the effluent waters into two small rivers, the "Grote Laak" and the "Winterbeek". The effluents contained between 20 and 25 Bq/l of ^{226}Ra. Since 1992, a process was introduced where the addition of $BaCl_2$ prohibits the dissolving of radium into the waste waters. Now more than 90 % of this radium precipitates as radiumsulphate and is found in the sludge. As a consequence, the radium activity of the sludge now has increased up to 8000 à 10000 Bq/kg, while in the effluents it has decreased below 2 Bq/l. The sludge activity hence is a tenfold of what you normally would find in phosphogypsum produced of the same ore. This is in line with the fact that almost the full radium load is now deposited in the sludge, and that ten times less sludge is produced than gypsum.

In total about 2.4 Mt of sludge are produced until now. It is stored on four different deposits, only one of which is still in exploitation. The oldest one has an area of 5.6 ha, is uncovered and situated within the plant boundaries. Doserates on average are 1000 nSv/h and there is an average increase in radon concentration of 50 Bq/m³. It contains about 0.15 Mt of old sludge, with radium activities between 3000 and 4000 Bq/kg. A second and larger deposit has similar characteristics : 19.7 ha, uncovered, 1000 nSv/h, 50 Bq/m³ radon increase, 0.55 Mt sludge, 3000 à 4000 Bq/kg radium. It has restricted access. A third one is only 2.5 ha large, and contains 0.12 Mt of sludge. It access is restricted. It is covered with HDPE foil, a clay layer and 1.5 m of ground. Only very locally on the verges some enhanced doserates can still be seen. Finally, the deposit which is still in exploitation has a surface of 55 ha, it contains about 1.5 Mt of sludge. Due to the increasing activity of the sludge in the last years, from 4000 Bq/kg to 10000 Bq/kg, the doserates nowadays are about 2600 nSv/h. The increases in radon concentration amount to 200 Bq/m³. In total 83 ha of sludge deposits exist, all in the immediate environment of the plants of Tessenderlo Chemie.

The effect of the liquid effluents is clearly visible. A study of the "Grote Laak" (3) has shown that about 12 ha of land are contaminated with doserates above 150 nSv/h. They are situated within a narrow strip of land on both sides of the river, mostly no larger than 10 m. Doserates were measured on 375 lines perpendicular to the river on both banks. The average maximum of the lines was 135 nSv/h on the left bank and 270 nSv/h on the right bank. Of 75 soil samples mostly taken on local maxima, the average radium activity was 5000 Bq/kg with a maximum of 10000 Bq/kg. In the flooding zones of the river no significant increase in doserates was found. From a preliminary study of the "Winterbeek", the situation here seems more serious. Doserates on average seem to be 3 to 4 times higher, and based on 6 soil samples, the soil radium activities seem to be at least double. Also, several places were found where the contamination extends hundreds of metres perpendicular to the river. An estimate of 200 ha of contaminated land seems not unreasonable. In total 8.7 TBq of radium were released in the Grote Laak, and about 4.3 TBq in the

Winterbeek. The difference in contamination has to be searched in the hydrological differences between both rivers. Figure 2 shows an overview of the



radium releases in both rivers during the last years.

Figure 2 : Radium releases by Tessenderlo Chemie in the Grote Laak and the Winterbeek during the last decade. Releases have decreased a lot lately. The environmental radium contamination around both rivers is therefore mostly historical.

3.3 Acidulation with nitric acid : the ODDA process

At BASF in Antwerp, acidulation with HNO_3 is the only method that is still being used for processing phosphate rock. Here, no substantial waste flows are being produced. This automatically implies that the radioactivity is transferred from the ore towards the end products, in this case fertilisers. BASF produces a multitude of different types of fertilisers each year, from different kinds of ore. The exact distribution of ore is considered to be commercially sensitive information and is therefore not released by them. Hence we cannot give an exact mass balance of the process. Suffice it to say that BASF processes about 0.4 Mt à 0.45 Mt of phosphate rock yearly, to produce about 2 Mt of fertilisers. This leads to a dilution with a factor 3 to 5 of the radioactivity in some of the end products. Typical activity concentrations in some samples of fertilisers taken by us were about 130 Bq/kg of ^{226}Ra and negligible amounts of thorium, but this depends of course on the ore used and the fertiliser considered. In total, until now, about 6 TBq of radium and 0.4 TBq of thorium were processed with the ODDA process.

4 THE FORMER RADIUM PLANT IN OLEN

At Union Minière in Olen, until 1969 radium was produced. As a consequence of this, environmental contamination with radium has taken place. The situation is adequately described elsewhere (4), so that we can limit ourselves to a small overview. The most important contaminated sites are the following four. There is a waste deposit with a surface of 10 ha, with a mixture of radioactive and chemical waste. Average doserates are around 3 µSv/h but maxima up to 1 mSv/h occur. Radium concentrations vary between 50 Bq/kg and 1 MBq/kg. Radon concentrations 1.5 m above the deposit vary between 100 and 500 Bq/m³. Plans for remediation are currently being explored. The deposit is not accessible to the public.

The banks of a small river have been contaminated with radium over a distance of about 1400 m, but only up to about 10 m perpendicularly to the river. Doserates of 1 µSv/h occur frequently, maxima up to 50 µSv/h also occur. Here in total about 0.7 ha is contaminated, and freely accessible.

The former flooding zones of the same river are also affected. About 21.5 ha of farming land here is contaminated, showing doserates above 100 nSv/h, with maxima above 1 µSv/h.

Underneath a few streets in Olen and Geel, some radioactivity is still present. It used to be an area of 0.37 ha, but this situation has partly been remediated at present.

Generally speaking, it would seem that the degree of contamination is somewhat higher as compared with the contamination resulting from phosphate industry, without therefore being immediately alarming. The situation needs to be followed further, and it must be said that scenarios for a global mitigation are currently being investigated.

5 RADIOLOGICAL IMPACT AND DURABILITY

When trying to assess the radiological impact of the described situations, one must take into account the gravity of each contamination, and the possible ways of exposure, considering the use of the contaminated terrains. Moreover, one must try to assess the durability of the existing situations, since radium and thorium contamination are of course characterised by the very long half-lives that occur. Terrains that are inaccessible or recognised as dumps at present will not necessarily continue to be so in the future, as the collective memory hardly ever extends over more than one or two generations. Performing this exercise for each deposit or contaminated area here would lead us much too far, a detailed treatment can be found in (5). In general we can say that the risk of direct gamma irradiation is mostly small for the general public at present. Doserates are usually low and the residence times are small or non existing. Radon risks in open air are small too. However there is a risk of building on top several of these deposits. In fact, some of the deposits already at present, blend in seamlessly into their environment, making it impossible to recognise them as such. This is for example the case for one of the deposits in Oostende, and much more so for the former clay pits filled with phosphogypsum in and around Puurs and Boom. Also some areas around the Grote Laak and the Winterbeek are sensible to this problem. The major problem is that some of these terrains have already been converted to residential areas, or that they will be in the near future. Construction of dwellings or working places on top of radium contaminated ground without special precautions will give rise to enhanced indoor radon concentrations. Those would then clearly constitute the major radiation risk towards workers or the general population. Therefore, precautions should be taken to avoid this in the future, and investigations should be undertaken to discover locations where this has already taken place.

6 CONCLUSIONS

The main source of technologically enhanced concentrations of natural radionuclides in Flanders is the phosphate industry. In total, by five different companies, since the twenties, until now, about 65 TBq of radium and 2.7 TBq of thorium has been processed. About 36 TBq radium and 2.3 TBq of thorium ended up in 48 Mt of phosphogypsum. Of this, 36 Mt can still be found on deposits in Flanders, 10 Mt was dumped into the Schelde estuary, 2 Mt was sold to the building industry, mostly for plaster boards. Some 10 TBq of radium ended up in 2.4 Mt of calciumfluoride sludge in several deposits. About 13 TBq of radium was released into the Grote Laak and Winterbeek, an undefinable fraction of which can now be found in the river valleys. Some 6 TBq of radium and 0.4 TBq of thorium ended up in fertilisers, and hence in the environment. In Flanders somewhat less than 250 ha of organised deposits with enhanced concentrations of natural radionuclides exist, this does not include the missing phosphogypsum deposits around Puurs of which we have no estimate. The environmental radioactive contamination due to the phosphate industry, can primarily be found around the Grote Laak with about 12 ha and much more so around the Winterbeek, where an estimate of over 200 ha seems realistic.
The historical radium plant in Olen has also given rise to environmental radium contamination. The total contaminated area, including the waste deposit can be estimated at 33 ha, a lot smaller than from the phosphate industry but somewhat more contaminated in some places.

From a radiological point of view, the situation does not pose any acute threats. Some places however need further investigation, with special emphasis on the control of indoor radon concentrations. In some places, restriction of land use, or even remediation would be advisable. There is definite need for reassuring the durability of the various sites, so that they will continue to be recognised as deposits with enhanced natural radioactivity.

7 ACKNOWLEDGEMENTS

This study was performed on request of the Flemish Environment Agency, A. Van de Maelestraat 96, B-9320 Erembodegem, e-mail: info@vmm.be. It fits within the framework of the yearly report on environment and nature in Flanders. Financial support is acknowledged.

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