The $^{226}\text{Ra}/\text{Ba}$-ratio as indicator for phosphogypsum contributions to $^{226}\text{Ra}$ levels in sediments

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Phosphogypsum discharges by phosphate-ore processing industries pollute sediments of the Rotterdam harbour area with $^{226}\text{Ra}$. Direct measurement of this radionuclide in sediments does not provide a reliable indication of the elevation of the levels, since $^{226}\text{Ra}$ levels in sediments depend on the particle size. To eliminate the size effect, the $^{226}\text{Ra}/\text{Ba}$ ratio in sediments was tested as a possible indicator for the $^{226}\text{Ra}$ in the discharges. The results indicate almost a doubling of the $^{226}\text{Ra}$ levels in sediment samples due to phosphogypsum discharges. The contribution of phosphogypsum to the sediment mass was calculated in the order of a few percent equivalent.

Introduction*

The Nieuwe Waterweg is the central entrance waterway for the port of Rotterdam, connecting it to both the North Sea and, via the rivers Rhine and Meuse, to the hinterland. Tidal effects, sediments carried by the rivers and increasing heavy draught vessels demand the waterway to be dredged and deepened regularly for its accessibility. Approximately $2.5\times10^9$ kg/year of sediment has to be dredged. Part of this sediment is polluted due to discharges of industries along the river and harbour waters. The least polluted fraction, approximately $10^{-10^9}$ kg/year, is deposited in a man-made depot on the Maasvlakte, an artificial extension of the mainland. It is expected that this depot will serve until 2002. The strongest polluted sediment is stored in another depot at a rate of approximately $1.5\times10^9$ kg/year. When the sediment is classified as “unpolluted”, it is partly returned to the North Sea. However, there is an increasing interest for future use of these sediments for developing recreation and living areas in the below-sea-level polders to a few feet above ground water level.

The long-term policy of the port of Rotterdam is to reduce the discharges by 70 to 90% as far as pollution is concerned. In enforcing discharge regulations, it is important to have means to identify and quantify the contribution of the industries. This study focuses on the $^{226}\text{Ra}$ discharges, since $^{226}\text{Ra}$ via its daughter $^{222}\text{Rn}$ may cause an enhanced radiation dose to the public, when the sediment is used for raising the level of dwelling areas. The prime anthropogenic source of $^{226}\text{Ra}$ are the phosphate ore processing industries located in the Rotterdam harbour area. Phosphate ores contain heavy metals, lanthanides and radionuclides (e.g. $^{226}\text{Ra}$, $^{210}\text{Po}$, $^{210}\text{Pb}$, $^{234}\text{Th}$ and $^{228}\text{Th}$), and some of them are concentrated in the phosphogypsum waste stream.

In an earlier study it was found that a fraction of the radioactivity in sediments is absorbed from the water on the surface of the particles.¹ The specific surface depends on the particle size, which in its turn depends on current patterns in the harbour area. Therefore, direct $^{226}\text{Ra}$ measurement in sediments does not provide a reliable indication of the contribution of the phosphate ore processing industries.

The effect of specific surface may in principle be circumvented by using the ratio between the radionuclide of interest and an element, that behaves chemically similarly. When their sorption behavior is similar indeed, the dependency with the particle size cancels out. The contribution of the discharges may be calculated from the radionuclide/element ratios in unpolluted sediments and phosphogypsum waste, provided that the ratios differ substantially. Moreover, there should not be any unknown third source of substantial discharge of the radionuclide and/or the element.

In an earlier study¹ the $^{210}\text{Pb}/\text{Pb}_{\text{tot}}$ ratio was used to assess the contribution of phosphogypsum discharges to the $^{210}\text{Pb}$ levels of the sediments. Lead (and thus also $^{210}\text{Pb}$) from the phosphate ore is accumulated in the phosphogypsum, and the $^{210}\text{Pb}/\text{Pb}_{\text{tot}}$ ratio differs strongly between unpolluted sediments and phosphogypsum. Thus, from the actual ratio in polluted sediments the degree of pollution may be derived. In this approach the pollution is not only due to solid phosphogypsum particles, but also to sorption of dissolved lead from water, which has been polluted with $^{210}\text{Pb}$ and $\text{Pb}_{\text{tot}}$ by partial dissolution of phosphogypsum. In the calculations, sorbed lead from dissolved phosphogypsum was considered to be taken up as solid phosphogypsum particles. Thus, the phosphogypsum mass derived as taken up, has to be considered as an “equivalent” phosphogypsum mass.

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The results from the $^{210}\text{Pb}/\text{Pb}_{\text{tot}}$ ratio studies, however, have less relevance in assessing the contamination of sediments with $^{226}\text{Ra}$. Radium and lead may have a different behavior in the dissolution of phosphogypsum and/or in the sorption on sediment particles. Thus, a correct result can only be obtained if $^{226}\text{Ra}$ is measured itself. When pursuing assessment of radium via the same approach as for lead, one faces the problem that radium has no stable isotopes. However, radium behaves quite often chemically similarly as barium which stands just above it in Group IIA of the Periodic Table. Therefore barium is often used as a carrier for radium, e.g., in uranium ore processing or water purification.

In natural waters containing sulphate (which applies to the waters under consideration), traces of radium present coprecipitate with barium naturally occurring to Ba(Ra)SO$_4$ which has a quite low solubility product \((\log K_{sp}=-10)\).\textsuperscript{3} Due to the very low ratio of radium to barium, generally $<10^{-8}$, as well as the similar molecular sizes of both elements, coprecipitation of radium via isomorphic incorporation does not influence the structure and growth of the barium sulphate.\textsuperscript{3,4} The distribution coefficient between solid Ba(Ra)SO$_4$ and solution is about 1, implying that radium and barium are incorporated in the precipitate in about the same ratio as they occur in solution.\textsuperscript{3} The radium released by the phosphate ore processing industry is contained in phosphogypsum, CaSO$_4$·xH$_2$O. In this matrix also barium is present and radium is partly associated with barium sulphate particles present in the matrix.\textsuperscript{5} The phosphogypsum dissolves to some extent on its way to sea and as far as radium and barium will come free from the dissolving matrix, they may partly precipitate again with sulphate present in the water.

Barium may be easily determined by instrumental neutron activation analysis via $^{131}\text{Ba}$, while $^{226}\text{Ra}$ can simply be assessed by gamma-ray spectrometry using the 609 keV line of $^{214}\text{Bi}$.

The results obtained with the ratio $^{226}\text{Ra}/\text{Ba}$ have been compared with earlier results obtained with the ratio $^{210}\text{Pb}/\text{Pb}_{\text{tot}}$. 

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Fig. 1. Sampling points and location of the discharging phosphate ore processing industries ('N' and 'S') in Rotterdam harbour region. Sampling in 1993 at points 1, 4, 6, 8, 10, 11, 12, 14, and 15. Sampling in 1995 at points 1, 2, 3, 4, 5, 6, 7, 9, 10, 12, 13, 14, 15, and 16.