Progress Report

Contract: Bi7-006 Sector: A22

Title: Behaviour of Polonium-210 and Lead-210 in European marine environments. Application of bioindicators.

1	Köster	RIVM
2	Guegueniat	CEA - Cherbourg
3	Duursma	NIOZ
4	Galvào	LNETI

I. Summary of Project and Global Objectives

The radiation dose stemming from the marine environment is dominated by the consumption of fishery products. The radionuclide Po-210 (T1/2 138 days), a daughter of Pb-210 (T1/2 21 year), has a dominant part in this. Locally large quantities of these natural radionuclides are released into the coastal environment by non-nuclear industries (e.g. in phosphogypsum effluents of Phosphorous industries).

The study has the general aim to obtain insight into the effects of such industries on the activity levels and distribution of Po-210 and Pb-210 in abiotic components and bioindicators, both in estuaries and in nearby coastal waters. And to apply the obtained insights in the development of a model to predict Po-210 and Pb-210 distribution and levels.

The four participants of the contract cover a wide geographical range. Depending on the situation and expertise each participant directs his research to certain parts of the chain: emission, dissolution/sorption, distribution/ accumulation in the abiotic environment, coupled with modelling and coupled with the study of potential bioindicators. By doing this in a coordinated joint study a better insight will be obtained in the chain from emission to effect and in the geographical differences.

The study encompasses the Westerschelde estuary in the Netherlands, the Seine estuary in France and the Tagus estuary in Portugal. A link will be made to the data of the Rhine estuary executed in 1989 (CEC project Bi6-0328-NL). In each of the above estuaries large quantities of Po-210 and Pb-210 are emitted by local phosphate industries. Natural background levels will be studied in Portugal in the Mira estuary which does not receive any industrial input of Pb-210 and Po-210.

Conclusions of general applicability will be drawn and location specific differences will be identified from the data and from the conclusions of the five estuaries studied. This will give new inputs both to generic and location specific modelling as to the direction of future research.

Head of Project 1: Dr. Köster

II Objectives for the reporting period

1) Sampling and characterisation of effluents of Phosphor producing industries in the Netherlands: two wet process plants near Rotterdam at the Nieuwe Waterweg (approx. Po-210 emission 2 E12 Bq.a^{-1}) and one thermo-process plant near Vlissingen at the Westerschelde (approx. Po-210 emission 1 E11 Bq.a^{-1} via effluents and a fivefold quantity into the atmosphere).
2) Reconnaissance of generic abiotic distribution models for estuaries and an inventory of such models specifically for the Westerschelde.
3) Development/installation and first calculations with an abiotic Westerscheldt model for distribution of Po-210/Pb-210.

III Objectives for the next period

1) Laboratory experiments with effluents samples to study: rate of dissolution into surface water; adsorption on suspended matter in surface water; influence of degree of salinity of surface water; the link to findings in environmental studies.
2) Expansion of simple Westerschelde model with Po-210/Pb-210 disequilibria and atmospheric source term. Calculation of dissolved and particulate Po-210/Pb-210; incorporation of effluent specific parameters; sensitivity analyses and validation; evaluation of the shortcomings/advantages of the simple as compared to a detailed complex DELWAQ-type model.

IV Progress achieved including publications

1. Studies of effluents from phosphor producing industries.

Contacts have been made with Rijkswaterstaat, of the Ministry of Transport and Public Works, to obtain samples of phosphogypsum effluent emitted into the Nieuwe Waterweg by the plants near Rotterdam. Handling of these samples required at all stages special precautions since the gypsum precipitates and hardens when the sample is not in motion. Besides the analyses of the effluent (Table 1), a laboratory study was made of its behaviour upon dilution with artificial seawater without suspended matter (Table 2). Notable results are: similarity of the effluents of the two different fertiliser plants; 25% total solid matter in the effluent; of which an increasing amount dissolves with increasing seawater dilution, 6% remains insoluble at a dilution of 1:2.300. This dilution is about 3 times less than the maximal dilution in the Nieuwe Waterweg. The dissolved Po-210 concentrations found in the Nieuwe Waterweg, 0,4 - 32 Bq.m^{-3} (Berger), show a remarkable similarity with the values found in the laboratory study, 10 - 40 Bq.m^{-3}. The Po-210 activity in the (dry) solid matter increases from 900 in the phosphogypsum to 14.800 Bq.kg^{-1} in the insoluble residue. The latter contains 90% of the Po-210 initially present in the effluent. In some harbour basins near the fertiliser plants Po-210 concentrations of 100 to 3.000 Bq.kg^{-1} have been found in bottom sediments, while in the suspended matter in the Nieuwe Waterweg these concentrations range from 100 to 12.000 Bq.kg^{-1} (Berger). The last value is comparable to the value 14.800 found in the laboratory study. These first results indicate that the laboratory studies provide valuable information for the interpretation of field observations and for the application in distribution modelling.

Contacts have been made also with the industry at Vlissingen to obtain samples of its effluents. In the thermo-process most of the Pb-210 and Po-210 sublimates in the sinterovens. Offgas filter water has been sampled near the sinteroven and close to the point of discharge in the Westerschelde, where large quantities of cooling(sea)water and some waste water from other processes have been added to it. At the point of discharge the offgas filter water contains 4 Bq.kg^{-1}, or 4000 Bq.m^{-3} Po-210 and 0,01

$g.kg^{-1}$ solid matter. Further analyses coupled with laboratory studies of this effluent, as well as the link to field observations and the application of the results in the modelling of the Westerschelde are in progress.

Table 1. Analyses of phosphogypsum effluents (grab samples) from two fertilizer plants near Rotterdam, the Netherlands.

	Vlaardingen		Vondelingenplaat	
	Average	Range	Average	Range
Solid matter (dry) $g.kg^{-1}$	267	259-277	235	233-239
% Insoluble of solid matter (when effl. diluted 2300x)	5,9	5,6-6,3	not analysed	
Pb-210 in effluent $Bq.kg^{-1}$	274	260-291	225	206-238
Po-210 in effluent $Bq.kg^{-1}$	251	240-260	174	166-192

Table 2. Behaviour of Po-210 after dilution of phosphogypsum effluent (Vlaardingen sample) with artificial seawater, laboratory study.

	Ratio seawater/effluent (vol./vol.)			
	0/1	23/1	230/1	2300/1
Po-210 in diluted effluent (total) $Bq.m^{-3}$	297000	12800	1270	128
Po-210 in aqueous phase $Bq.m^{-3}$	450	41	17	10
Po-210 in solid matter $Bq.kg^{-1}$	940	1140[1)]	10700[1)]	16000[1)]

[1)] derived from the activities listed in the same column.

2. Modelinventory.

An inventory of Westerschelde and of generic estuary models has been completed for the most part. The following models were studied in detail:

* *DELWAQ* developed by Delft Hydraulics Laboratory. It can be used to calculate the transport and distribution of heavy metals in the longitudinal, lateral, and vertical direction, in the Westerschelde. It is a rather complex model based on the advection-dispersion-equation, which is solved numerically. It computes the concentrations (total, dissolved, particulate) for each of the compartments distinguished in the model area. The compartments can be linked in all directions. It can perform steady-state as well as dynamic simulations, required to cope with discontinuous waste discharges. DELWAQ is in trust of Delft Hydraulics, and is not freely accessible.

* *"O'Kane - method"* (O'Kane 1980), a simple steady-state model. With this method different compartments, in the longitudinal direction in the model-area can be distinguished. For each compartment a massbalance is written. To obtain the concentration per compartment the system of lineair equations can be solved by matrix manipulation. The exchange between the compartments in the estuary can be calculated from the salinity data. The salinity in the boxes is assumed to depend on advection and dispersion.

* *"Simplified differential equation method"* (Jörgenson, 1988). As in DELWAQ this method solves the advection-diffusion-equation mathematically for the longitudinal direction. Further differences are that it calculates only the concentration for steady-state situations, and that it can cope with only one source-term. The simplified differential equation distinghuishes no compartments, but solves the equation by which a longitudinal gradient for the total estuary is obtained.

3. Model development and calculations

The O'Kane-method has been tested for the Pb-210 distribution in the Westerschelde. The length of this estuary is 70 km from the Belgium/Dutch border till Vlissingen at the North Sea. Five compartments are selected based upon the chloride levels. The inputparameters per compartment are: the geometry (volume, estuary width); the sedimentation rate; the chloride

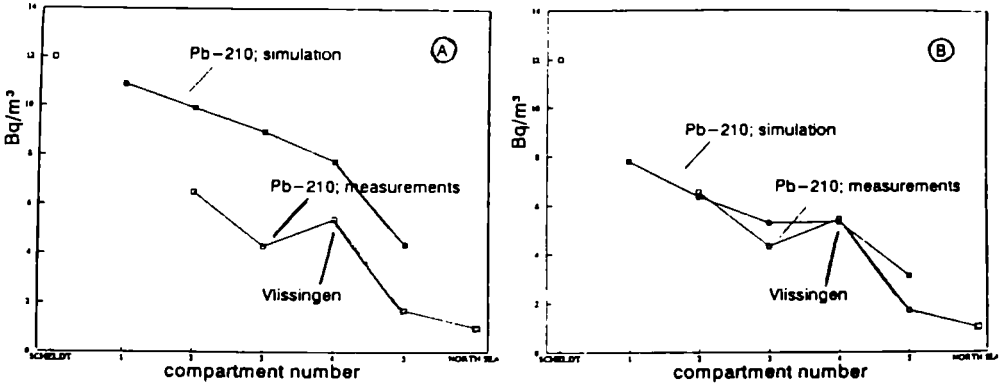
level to express the longitudinal mixing; the suspended matter load; and the parameters listed in Table 3. The flow rate and the Pb-210 activity of the river Scheldt have been used both as source term and as boundary conditions at the Dutch/Belgian border. For the Phosphorous plant at Vlissingen the Pb-210-emission (as specified in its emission permit) has been taken as source term. Two scenario's were defined: scenario A without and scenario B with sedimentationa at a rate of 4,3 mm.a^{-1}.

Table 3. Input-parameters for the calculations of the Pb-210-distribution in the Westerscheldt with the O'Kane model.

Flow rate river Schelde	105	$m^3.s^{-1}$
Pb-210-emission at Vlissingen	1000	$Bq.s^{-1}$
K_d or distribution coefficient of Pb-210	5	$m^3.kg^{-1}$
Pb-210 concentration in the river Schelde	12	$Bq.m^{-3}$
Pb-210 in the North Sea	1	$Bq.m^{-3}$

From the limited comparison it appears, that the measured concentrations do not differ much from the calculations (Figure 1). It can be concluded, that based upon the O'Kane-method a rather satisfactory model has been developped to calculate the steady-state Pb-210 concentrations in the Westerschelde as affected by waste discharges from the phosphate-industry. More detailed conclusions can be drawn after comparison of the calculations with other measurements and after sensitivity analysis of the model.

Fig. 1. The total Pb-210 concentrations (dissolved + particulate) in the 5 compartments in the Westerschelde. Field measurements and results of the model without (A), and with sedimentation (B).



4. Publications, accepted for NRE-V in Salzburg Sept. 1991. Fifth international symposium on the natural radiation environment:
Köster H.W., Marwitz, P.A. (RIVM), Berger G.W. (NIOZ), Weers, A.W. van (ECN), Hagel, P. (RIVO), Nieuwenhuize, J. (DIHO). Po-210, Pb-210 and Ra-226 in aquatic ecosystems, anthropogenic sources, distribution and radiation doses in the Netherlands.
Pennders, R.M.J., Köster H.W., Lembrechts, J.F. Characteristics of Pb-210 and Po-210 in effluents of phosphate producing industries, affecting the distribution of these nuclides upon emission into surface waters.

Head of Project 2: Dr. Guegueniat

II Objectives for the reporting period

In the Seine estuary and the nearby Channel coast a detailed study was made of the Po-210 levels in the mussel Mytilus edulis and in the brown algae Fucus vesiculosus to characterise their potential as bioindicators. Special attention was given to the geographical and seasonal variation in these species.

III Objectives for next period Some striking and unexplicable data were observed. So, the activities of Po-210 will be measured in Mytilus edulis and Fucus vesiculosus as a function of both space and time (Seine estuary and control sites), because of levels of activity are controlled not only by variations of input but also the environmental conditions and certain biological cycles. Po-210 will be measured in sediments where factories have released phosphate gypsum directly into the Seine downstream from Rouen, in order to know the importance of this "source term". Pb-210 will be measured in Mytilus edulis. Studies will be executed to determine the characteristics of Po metabolism by M.edulis.

IV Progress achieved including publications

We have set out to investigate the migration of ^{210}Po in a zone influenced by the discharge of phosphatic gypsum waste which provides a radiolabelled source term, the Seine estuary. In the context of this study, the Marine Radioecology Laboratory developed a technique for the analysis of ^{210}Po, in 1990.

Analytical methods :

Aliquots (0.5-1.0 g) of the powdered biological and suspensions are placed in Teflon bombs along with a ^{208}Po spike (half-life = 2.9 years) used as an isotopic tracer.

The determination of ^{210}Po is performed by the classic method of acid digestion followed by spontaneous deposition onto a silver disc.

As regards the sea-water samples, both filtered and non-filtered sample aliquots (20 l) are acidified before addition of the ^{208}Po spike.

Then, the pH is brought back to values 8-9, by the addition of concentrated ammonia solution. Subsequently, 1600 mg of $KMnO_4$ (in solution) were added along with H_2O_2 in order to provoke the precipitation of MnO_2. After agitation, the supernatant is decanted off and the precipitate recovered then dissolved in 1.2 M HCl containing H_2O_2.

All the samples are taken up into HCl and made up to 0.3 M HCl. Then, the polonium is deposited spontaneously onto a pellet of silver during agitation at 90°C for four hours. Measurements of ^{210}Po activity are performed on an alpha-ray spectrometer equipped with semiconductor detectors (implanted Si passive junction type; 300 mm^2 area) coupled to an analyser. The extraction yields were 80-100 %.

We participed in intercomparison exercice with the sediment sample coded IAEA-368. The result obtained for ^{210}Po is 26.20 ± 0.98 Bq kg^{-1} dry weight (and for ^{210}Pb : 20.7 ± 1.2 Bq kg^{-1} dry weight, gamma spectrometry).

- Geographical zone covered by Polonium-210 studies
In the estuary, severeal station were chosen on the basis of the presence of the indicator species used in this study. In order to better characterize the labelling of indicator species by industrially-derived waste, collection site were selected as baseline controls in various zone located outside the estuary : to the east of the Seine estuary (Fécamp, Wimereux and Gravelines); in the Baie de Seine, west of the estuary (Luc-sur-Mer, Port en Bessin, Pointe de Moulard); west of the Cotentin peninsula (Agon-Coutainville, Pirou, Herquemoulin).

- Nature of industrial releases
Industries discharging phosphatic gypsum have operated for nearly 60 years in the lower Seine valley; over a period of several years, factories near Rouen have released phosphatic gypsum directly into the Seine downstream from Rouen. This type of waste is also released into the Seine estuary by Norsk Hydro Azote (NHA). From 1974, two factories in the Rouen area began to transport their gypsum waste by barge for disposal in the baie de Seine; these activities continued up to 1984 for one factory and 1987 for the other. At present, all the waste produced from these factories is stockpiled on land. The NHA plant continues to release 70,000 tonnes per month of phosphatic gypsum from an outfall into the Seine estuary; about 25 % of the waste produced by this factory is now stored on land.

- Results
In the Seine estuary, at Le Havre, for sea-water filtered at 0.45 µm, activities fluctuate between 0.5 and 1 mBq l^{-1}. There is a tendency for ^{210}Po levels to fall off between June and October 1990. In non-filtered sea-water samples, activities are higher (from 2.5-14 mBq l^{-1}) and are clearly related to the degree of turbidity. ^{210}Po levels are homogeneous in the suspended matter samples (130-180 Bq kg^{-1} dry weight). For *M. edulis*, activity levels lie in the range 90-700 Bq kg^{-1} on a dry weight basis. Samples from stations in the estuarine zone show a marked fall in ^{210}Po activity from March to May/June. At the estuarine stations, values of the order 250-350 Bq kg^{-1}dry weight were measured in March 1990; after a marked decrease in April and May, activities reached fairly constant levels of 120-180 Bq kg^{-1} dry weight during August and the end of the year. This decrease is even more marked at the NHA outlet pipe, from 700 to 140 Bq kg^{-1} dry weight. At control sites, Wimereux-Gravelines, Pointe de Moulard, Agon-Coutainville-Pirou, ^{210}Po levels in mussels show respective values of 180-250, 90-150, 250-340 Bq kg^{-1} dry weight.
For *F. vesiculosus*, ^{210}Po activities are definitely lower than in mussels; values fall in the range 3-22 Bq kg^{-1} dry weight. Fluctuations are apparent. They are different from mussels. In *F. vesiculosus* collected from the estuarine zone, ^{210}Po levels are always higher than samples taken along the Channel coast

except Pirou (Nov. 1990); values obtained range from 12 to 20 Bq kg^{-1} dry weight. Outside the estuary to the west, levels are of the order 4-6 Bq kg^{-1} dry weight, whereas Wimereux in the east shows levels around 10 Bq kg^{-1} dry weight.
The Seine estuary appears as a distinct source-term for ^{210}Po in *F. vesiculosus* at all times, whereas *M. edulis* shows an influence from fluvial input only during the sampling campaign of March 1990. In fact, activities are enhanced in the estuarine zone with respect to control stations along the Channel coast. However, this effect is less clear in the case of mussels collected after March 1990. Although it is true that mussels from the estuarine zone have slightly higher activities than mussels in the Baie de Seine (Pointe de Moulard, Port en Bessin, Luc sur Mer), mussels from other control stations (Agon-Coutainville and Wimereux) have activities which are higher than those recorded in the estuary itself.
The evolution of ^{210}Po levels are difficult to explain since the discharge of phosphatic gypsum from the NHA plant varies only very slightly with time. Thus, to account for the variations in ^{210}Po activity, it may be necessary to invoke other source-terms apart from the NHA outlet, including fluvial inputs from the Seine. Furthermore, we need to improve our understanding of the impact of other ecological factors (e.g flow rates, turbidity, storm effects...) on the ^{210}Po activities observed in mussels.

Publication
An abstract is submitted to "Fifth International symposium on the natural radiation environment". Salzburg, sept. 1991
GERMAIN, P., LECLERC, G., SIMON, S., Distribution of ^{210}Po in Mytilus edulis and Fucus vesiculosus along the Channel french shore : influence of the industrial releases in the Seine river and estuary.

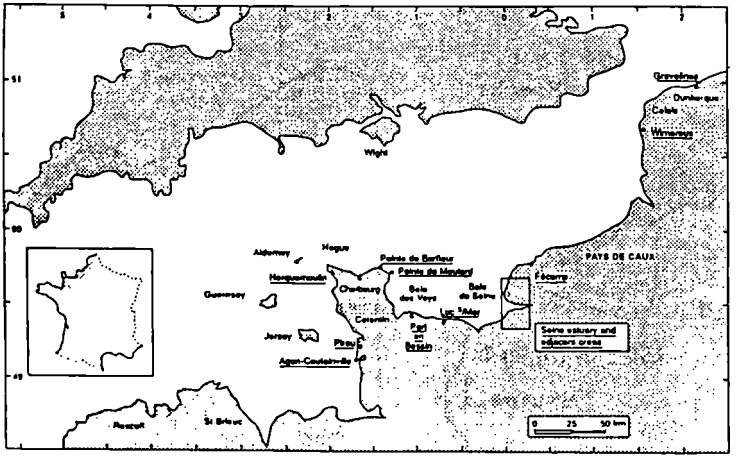


Figure 1 - Sketch map showing location of sampling stations

Head of Project 3: Prof.Dr. Duursma

II. Objectives for the reporting period

The objectives for the reporting period (june 1990 - june 1991) were:
-- to carry out a sampling programme in the Westerscheldt estuary and the coastal zone
-- to analyse the obtained samples in order to get insight in the sources, pathways, sinks and distribution of Po-210 and Pb-210 in this area as a logical continuation of work that has been done by the NIOZ under EC contract B16-0328-NL in the Nieuwe Waterweg in previous years

III. Objectives for next period

Attention will be payed to the analyses of Pb-210 in order to study Po-210/Pb-210 equilibria, to the analyses of Po-210 and Pb-210, dissolved in water in order to estimate K_d values. Will be analyzed in sediment and suspended matter samples so that excess Pb-210 and Po-210 can be estimated. The need for additional sampling in view of the modelling of the data will be evaluated in cooperation with the RIVM, Bilthoven, The Netherlands.

VI. Progress achieved including publications

During the first week of October 1990 a sampling cruise was undertaken in the Westerscheldt. Due to weather conditions sampling in the coastal zone was not possible.
Altogether 58 samples were taken: 37 water and suspended matter samples, 21 sediment samples. Besides, suspended matter concentration, watertemperature and salinity were measured. In the sediment and particulate matter samples Po-210 has been analysed.

Preliminary results

Figure 1 shows, the map of the Scheldt estuary, the sampling locations and the general distribution pattern of Po-210 adsorbed on suspended material.
Po-210 concentrations adsorbed on suspended material are in the range from 70 Bq.kg-1 (coastal water) to 250 Bq.kg-1 (Zelzate, Channel of Sas van Gent naar Terneuzen). Relatively high concentrations are found between Doel and BASF and in the western part of the estuary near Vlissingen.

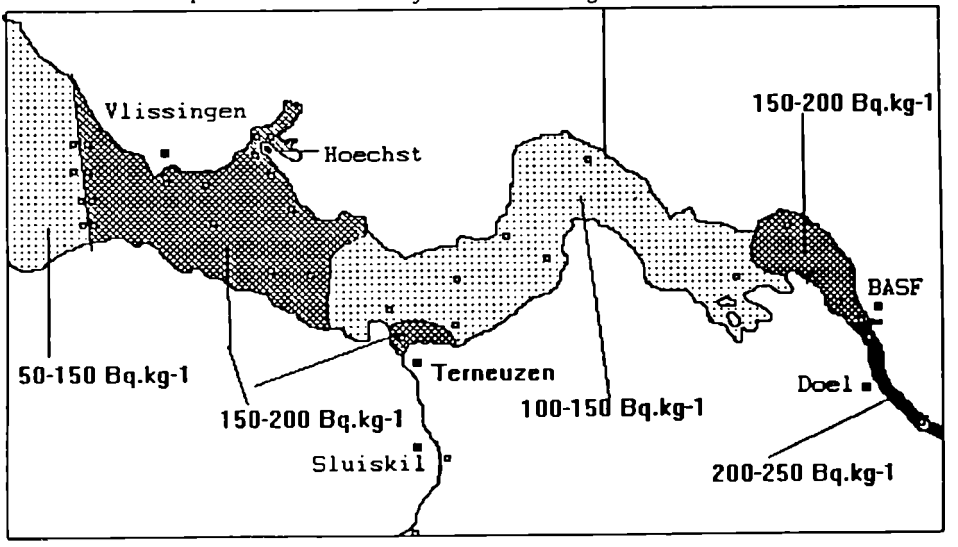


Fig.1 Concentration of Po-210 in suspended material.

Po-210 concentrations in sediments collected in Westerscheldt estuary range from 6 to around 400 Bq.kg-1. The highest concentration is found in the Channel of Sas van Gent naar Terneuzen near the former phosphate processing plant "Zoutchemie". Sediment collected near BASF (concentration 170 Bq. kg-1) seems to be above the natural background, as is the case with a sample taken in the Sloehaven, Vlissingen (148 Bq.kg-1).

Discussion and preliminary conclusion

In the reporting period samples were taken in order to study sources, sinks and the dynamics of the distribution of Po-210 and Pb-210 in the Westerscheldt.
Although not all of the samples taken in the reporting period have been analyzed or interpreted, some preliminary conclusions can be drawn.
Compared with for instance the Nieuwe Waterweg, it seems that the Westerscheldt estuary does not act as a sink for Po-210. The concentrations in the sediment is more or less around the natural background (< 100 Bq.kg-1), with the exception of the Sloehaven and near BASF. This is confirmed by previous Pb-210 measurements in sediments in areas in the Westerscheldt where relatively fine material settles (Berger, G.W. & D. Eisma, 1988b).
This does not hold for Po-210 concentrations as found in suspended matter. The average concentration is around 150 Bq.kg-1, which is higher than concentration as found in the North Sea in previous studies (Berger, G.W. & D. Eisma, 1988; Köster et al., 1990)
The results of this project will be presented at the Radstomp 91 Symposium (Radionuclides in the study of marine processes, 9-14 september 1991, Norwich, UK), title: "Sources, distribution and radiological effects of Po-210, Pb-210, Ra-226 and Th isotopes in Dutch rivers and coastal waters related to the discharges of ore processing plants".

G.W. Berger, Netherlands Institute for Sea Research, Texel.

Literature

Berger, G.W. & D. Eisma, 1988a, Report of Po-210 en Pb-210 measurements in the Dutch coastal waters, rivers and Westerscheldt estuary (in Dutch, VROM project) NIOZ report 1988-2

Berger, G.W. & D. Eisma, 1988b, Dating of sediments in the Westerschelde with the isotopes Cs-134/137 and Pb-210. NIOZ report 1988-12 (RWS project, in Dutch)

Köster, H.W., P.A. Marwitz, G.W. Berger, A.W. van Weers, P.Hagel, J. Nieuwenhuize. RIVM Report 248476004, August 1990 (in Dutch) Po-210 and other natural radionuclides in Dutch aquatic ecosystems; an reconnaissance investigation.

Head of Project 4: Dr. Galvão

II Objectives for the reporting period

In Portugal, a river/estuary, on which no industrial Po-210 emissions take place, will be studied to establish the natural background levels and their variation in this environment. In the Tagus estuary and adjacent coast the focus will be on the distribution of Po-210 and Pb-210 discharged by the phosphorus industry. The major emphasis will be on abiotic materials and to a lesser extent on bioindicators.

III Objectives for next period

The study on the distribution of Po-210 and Pb-210 in the same estuaries during summer conditions: low river flow, higher temperatures and different biological conditions. The whole of this research will alow the comparison between winter and summer conditions in abiotic and biotic components of both estuaries. The comparison of Po-210 and Pb-210 concentration levels in one estuary receiving P-plant effluent discharges and another estuary receiving no industrial discharges, will emmerge from this research.

IV Progress achieved including publications

1. Areas under study

The estuary of the Tagus receives the liquid wastes and undetermined amounts of phosphogypsum from a phosphate fertilizer plant located in the south margin and operating since 1951. The Tagus river drains a catchement area of 86 000 km2 and its average annual flow is of 1.3E10 m3. The estuary has 200 km2 of surface area and receives the industrial and urban effluents from a densely populated region.Its morphology fits the category of tidal lagoon estuaries.

The estuary of the Mira river, located some 200 km south of Lisbon, receives no industrial effluents. The Mira drains a much smaller catchement area, of 1580 km2, and flows across a region with no major towns. Besides the runoff from agricultural lands - agriculture is less intense than in the Tagus valley - it is an acceptable non-modified reference environment. The morphology of this estuary belongs to the funnel-shaped type.

2. Materials and methods

Sampling of phosphate raw materials, phosphogypsum and fertilizers was directly made in the factory and in the adjacent gypsum ponds and liquid wastes outlet.

The sampling of the Tagus and Mira estuaries was performed during high river flow (Jan - March), through the use of an inflatable rubber boat. Sediment samples were collected with a small box - corer and water samples were collected directly into plastic containers and filtered on shore. Biological samples - fish and shrimp - were taken in the Tagus estuary with a trawl net. Intertidal organisms - seaweeds, Balanus and molluscs - were colllected by hand on piers and in soft bottoms.

Po-210 measurements are made by alpha-spectrometry on Ag planchets, with the use of Po-209 as isotopic tracer. Pb-210 is calculated from a second Po-210 plating made 6 months later. A check

of the radioanalytical quality of the results was made through the participation in an intercomparison exercise.

3. Progress and status of the research

3.1. Results of the intercomparison exercise

The intercomparison was made with two IAEA sediment samples (Table I).

Table I - Results of the intercalibration exercise

Sample reference	number of aliquots analysed	Our result ^{210}Po (Bq/kg)	IAEA reference value (Bq/kg)
IAEA-SD-A1	6	71 ± 6	72 ± 2.5
IAEA-368	8	23.4 ± 1.4	24.3 ± 12.6 (a)

(a) Provisional results, ILMR, March 1991

3.2. Phosphorite, phosphogypsum and fertilizers

The source term of phosphatic materials released by the P-plant into the Tagus estuary is being adressed through the analysis of these materials (Table II).

The phosphogypsum collected in the ponds on the river bank of the Tagus estuary (Table II, indicated as A) displays much lower concentrations of uranium than phosphorite. However, the Ra-226 specific activity concentration is nearly the same as in the phosphorite, while Pb-210 and Po-210 have intermediate concentrations. Clearly the uranium series nuclides are fractinated during the ore processing and still important concentrations of Ra-226, Pb-210 and Po-210 remain in the gypsum. Most of the uranium and part of the Pb-210 and P0-210 are incorporated in the phosphoric acid produced. As the phosphoric acid is used in the manufacture of superphophate fertilizers, those nuclides are incorporated in those products. Furthermore, a linear relationship exists between the U contents of the fertilizer and its content in P2O5 (Carvalho, 1991).

3.3. The estuary of the Tagus river

During the sampling trips in January-March of 1991, about 40 surface sediment samples were taken, as well as 18 water plus suspended matter samples, and several biota samples, covering the whole estuary.

The analysis of these samples are being performed and results will became available throughout this year.

Table II - Specific activity concentrations (Bq/Kg) of uranium series radionuclides in phosphatic materials. Each value is the average of n samples. A designates samples from gypsum piles close to Tagus estuary; B designates other fertilizer plant.

		U-238	U-234	Ra-226	Pb-210	Po-210
PHOSPHORITE	(n = 4) •	1003	996	1406	1083	954
PHOSPHATE FERTILIZERS:						
18 % P_2O_5	(n = 2)	632	630	862	638	604
30 % P_2O_5	(n = 1)	941	917	608	630	679
46 % P_2O_5	(n = 2)	1867	1863	342	547	382
PHOSPHOGYPSUM						
A	(n = 6)	156	156	1043	----	586
B	(n = 2)	26	40	950	589	655

• Marocco and Syria

3.4. The estuary of the Mira river

The samples collected during the winter season comprise 18 water samples from the mouth of the estuary up to freswater, covering the entire range of salinity. Suspended matter and bottom sediments from several stations are currently being analysed.

4. Final remarks

The winter sampling programme has been sucessfully performed in Tagus and Mira estuaries. The whole of samples collected covers the abiotic and some biotic components of these ecosystems.

Reliable information about the phosphoric acid production since the start of the P-plant operation and about the disposal of gypsum in the past, was not yet made available by the industrial company. To evaluate the actual gypsum and liquid waste discharged into the Tagus it is foreseen to made repeated analysis of the outlet pipe discharges.

5. Publications

Carvalho, F.P.(1991). Adubos fosfatados e radioactividade natural (Phosphate fertilizers and natural radioactivity). Proceed. of the XII Nat. Symp. of Chemistry, Lisboa, 10-13 March 1991, pp.451-454 (in Portuguese)

Carvalho, F.P. (submitted). Radioactive wastes from industrial phosphate ore processing in the Tagus estuary. 5th Int. Symp. on the Natural Radiation Environment, Salzburg, 1991