RADIATION PROTECTION PROGRAMME

Progress Report

1988

Contractor:

Contract no.: BI6-B-191-NL

Delta Institute for
Hydrobiological Research
Vierstraat 28
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Title of the research contract:

Transfer processes and modelling of plutonium species and gamma emitters in the Scheldt estuary ; redox and organic speciation in relation to aqueous and particulate fractionation.

List of projects:

1. Transfer processes and modelling of plutonium species and gamma emitters in the Scheldt estuary ; redox and organic speciation in relation to aqueous and particulate fractionation.

Title of the project no.: B16-B-191 NL

Transfer processes and modelling of plutonium species and gamma emitters in the Scheldt estuary; redox and organic speciation in relation to aqueous and particulate fractionation

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I. Objectives of the project:

Study of dissolved and particulate ^{238}Pu and ^{239}Pu, ^{240} and gamma-emitters (Co-60, Cs137...) in the Western Scheldt area;
Determination of Kd's as a function of major physico-chemical parameters such as dissolved oxygen, pH, Eh, salinity, DOC and POC.
Study of redox partitioning of dissolved plutonium (III + IV) and (V + VI) at selected locations of the Western Scheldt.
Study of the role of sediment particles as sorption substrate.

II. Objectives for the reporting period:

Field and experimental work to determine origin and fate of the studied nuclides. 1. Field measurements along the Western Scheldt estuary (Gent to Vlissingen): a) Measurement of major physico-chemical parameters: distribution of salinity, temperature, oxygen, total suspended matter, particle size and organic content of suspended matter, dissolved organic matter including amino acids, N- and P-nutrients, concentration of plankton and biological activity. b) Measurements of total Pu in suspended matter and water, redox Pu speciation in water and gamma emitters.

2. Experimental work: a) Determination of adsorption kinetics of plutonium and gamma emitters under oxic and anoxic conditions. b) Determination of the base exchange capacity of selected sediment samples.

III. Progress achieved:

Three cruises have been carried out along the Western Scheldt with the R/V Luctor from the Delta Institute in March, August and November 1988. During these cruises the major physico-chemical parameters have been determined. Surface water samples (200 l) and suspended matter were collected in a wide range of salinities from 2 - 32 ‰ . The separation of the particulate phase and coprecipitation of dissolved plutonium were made using the same procedures as in 1987. For adsorption experiments Scheldt water was spiked with ^{237}Pu (III + IV) or ^{237}Pu (V + VI) and maintained under oxic or anoxic conditions. Filtration of aliquot samples was performed as a function of time for subsequent gamma counting and K_D determination. Analyses of Co, Ni, Al and suspended matter were performed.

Normalized concentrations in the river samples beyond the tidal region and in the estuary do not differ much from previous observations and show a notable decrease from the mouth to the central part of the estuary. High $^{238}Pu/^{239+240}Pu$ ratios have been detected in the Bovenschelde and possibly in the Albertkanaal. These data confirm that the predominant source of $^{239+240}Pu$ is the North Sea.

The high activity ratios probably result from two different causes:
- the "Nete-anomaly" (also found with gamma-emitters) probably reflects reworking of contaminated sediments and/or nuclear effluents origination from the Mol/Eurochimic zones. This would explain the highest $^{238}Pu/^{239+240}Pu$ ratios in the Rupel area and confirms the existence of an industrial ^{238}Pu-source (1979-1984 study).
- high activity ratios (in the range 0.07-0.24) in the Boven Scheldt and Dijle and possibly the Albertkanaal are likely to represent a mixture of Chernobyl and pre-Chernobyl sediments. It is not understood at the moment why this ratio reached a maximum only 7 months after Chernobyl in the Dijle and 18 months in the Bovenscheldt.

Results for dissolved species are similar to the 1987 results. The difference with the much higher 1986 results is thus confirmed. The discrepancy has been attributed to the use of filters with different porosity. However, in December 1986 the pH was significantly lower in the estuarine zone than during the following 1987 surveys and even small pH changes may to a certain extent control Pu adsorption.

The $^{137}Cs/Al$ ratio in samples collected in 1986-1988 in rivers is higher by one order of magnitude than in the pre-Chernobyl samples. This large enrichment is still observed in the upper estuary but the ratio decreases to pre-Chernobyl values near the mouth. $^{134}Cs/^{137}Cs$ ratios reached maximum values in June 1986 (0.43 in the Bovenscheldt and 0.47 in the Dijle). Later measurements at Gent showed lower ratios decreasing with the ^{134}Cs half-life till October 1987. In the Nete sample the ratio is only 0.30.

A nearly linear decrease of the activity ratio with distance in the estuary was observed in 1986 and 1987. These data are very different from those collected in 1979-1984 which show an introduction into the estuary of ^{137}Cs associated to suspended matter from marine origin and a nearly constant ^{134}Cs background (activity ratio of about 0.06) probably due to Doel effluents. This difference obviously results from the Chernobyl input. When the ^{137}Cs due to Chernobyl is substracted most of the non-Chernobyl component falls into the range of the 1979-1984 measurements.

It would be interesting to model the ^{134}Cs ^{137}Cs ratio which decreases so regularly in

the estuary and essentially reflects the propagation of a terrigenous signal in the suspended matter stock. This would help understanding why the ^{137}Cs-content of the sediments near the mouth remained unaffected by the Chernobyl event. The development of a simple model should be envisaged; it could provide useful information and generalisation concerning the response of this estuarine system to an atmospheric poollutant input.

Only preliminary results on the adsorption experiments are available: oxic plutonium is more readily absorbed on particles than reduced plutonium but the difference decreases with time. Cobalt and Manganese are more soluble under anoxic conditions than expected. In one experiment in oxic conditions part of Pu, Cd and Mn were released from the particles: this mobilisation might be related to an important algal bloom.

Since Co is one of the major radioactive elements released by the nuclear power plant in Doel, special attention was devoted to the development of an analytical method able to describe its speciation in the estuary. The method is based on cathodic stripping voltametry and enables us to distinguish between free dissolved inorganic cobalt, organically complexed dissolved cobalt and easily available particulate cobalt. Several longitudinal profiles of these species in the Western Scheldt have been collected. They all show a systematic maximum of total Co in the area of Doel with a predominant contribution of the dissolved inorganic fraction. The total concentration observed at a given position is strongly dependent on the water discharge suggesting a source term of constant strength.

The rapid transfer of many contaminants form the dissolved to the particulate phase lead us to consider the possibility of developing a rapid method for the quantitative analysis of suspended matter in aquatic systems. The first part of the study concerned the direct analysis of small quantities (a few mg) of suspended matter collected on filter and resuspended in viscous slurries by atomic absorption. This method tested with certified international standards appeared to be very effective. The second aspect concerns the quantitative analysis of major elements in the same suspension. This information is essential to understand the origin and the behaviour of contaminants in the estuary. A method based on X-ray fluorescence is currently being developed.

Results from the sedimentological survey in December 1986 with the Luctor and the Jan Verwey from the Delta Institute are now available. Between Bath and Dendermonde a turbidity maximum with concentrations in suspended matter of 800 mg/l near the bottom was found. In the freshwater zone up to Gent the concentration of suspended matter was 40-60 mg/l and in the estuary downstream from Bath 30-55 mg/l. Relatively high numbers of particles larger than 16 µm exist in the freshwater part but not in the estuarine part. However, this may be an artifact due to a smaller stability of flocs in more saline waters.

The concentration of organic matter gradually decreased from 20-40 % in the freshwater part to 14-20 % in the estuary, with some exceptions. ETS measurements of biological activity show a regular decrease in the freshwater from Gent (22-30 µmol O_2/l/h) to Antwerpen (8-10 µmol O_2/l/h) which continues in the estuary. From Bath to Vlissingen the biological activity was very low (less than 2 µmol O_2/l/h. The lack of correlation between organic content, biological activity (mainly bacterial metabolism at this time of the year) and particle size indicates that particle concentration is not important. The base exchange capacity of sediments was found to be between 0.65 and 7.28 mval.

IV. Objectives for the next reporting period:

- In situ measurements of particle size and shape along the Schelde river with an in situ suspension camera system recently developed at NIOZ (Texel) with additional measurement of major physico-chemical parameters
- Scanning microprobe analyses of suspended particles to determine the origin of the organic matter
- Synthesis and publication of data obtained during the previous cruises including simple modelling of isotope distribution in the Scheldt estuary

V. Other research group(s) collaborating actively on this project [name(s) and address(es)]:

VI. Publications:

- Publication of the results is planned for 1989-1990