

**RADIATION PROTECTION PROGRAMME
Progress Report**

1987

Contractor.

Contract no.: BI6-B-191-NL

Delta Institute for
Hydrobiological Research
Vierstraat 28
NL-4401 EA Yerseke

Head(s) of research team(s) [name(s) and address(es)]:

Dr. E.K. Duursma
Delta Institute
Vierstraat 28
NL-4401 EA Yerseke

Telephone number: 1131/1920

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.: R16-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.

Head(s) of project: Dr. E.K. Duursma, Dr. D. Eisma. Nederlands Instituut voor Onderzoek der Zee (Texel, The Netherlands)

Dr. J.M. Martin. Institut de Biogéochimie Marine (E.N.S. France)

Dr. J. Pentreath. Fisheries Hydrobiological Laboratory (Lowestoft, England)

Dr. Prof. R. Wollast. Université Libre de Bruxelles (Belgique)

Scientific staff:

Dr. D. Petit. Institut de Biogéochimie Marine (E.N.S. France)

J. Nieuwenhuize. Delta Instituut voor Hydrobiologisch Onderzoek (Yerseke, The Netherlands)

I. Objectives of the project:

Study of total dissolved and particulate Pu-238 and Pu^{+3} , Pu^{+4} and γ emitters (Co-60, Cs-137,...) in the Western Scheldt area.

Determination of Kd's as function of major physicochemical 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.

II. Objectives for the reporting period:

Sampling and analytical methods for measuring total Pu (suspended matters and waters) and redox Pu speciation(waters) have been tested in estuarine waters. The samples have been collected along the Western Scheldt estuary where specific sources additional to fallout Pu have been measured in suspended matter and sediments during a preceding cruise.

III. Progress achieved:

1. Methodology

Surface waters (about 200 l) and suspended matters from the Western Scheldt were collected in June, August and October 1987 on board R/V Luctor (DIHO, Yerseke, The Netherlands).

The samples collected during the first and the second cruises came from three monitoring stations located along the Western Scheldt (Rupelmonde, Doel and Schaar Van Spijkerplaat).

Suspended matter was recovered on the spot by continuous centrifugation. Dissolved water was obtained by pressure filtration on 0.4 μ m membrane filters. Recoveries were determined by the addition of yield monitors (Pu-242 or Pu-236). The samples were chemically separated and analyzed for total Pu according to the method given by Heterington (1976). Large volume samples (about 350 l) were collected in August 1987 for Pu redox speciation. These samples filtered on 0.4 μ m filter porosity and spiked with Pu-242 (III, IV) and Pu-236 (V, VI) were analyzed following the Fe (OH)₃ coprecipitation method given by Pentreath et al. (1985).

2. Results and discussion

2.1 Total Pu activities

The Pu activities of filtered surface waters and suspended matters from the December 1986, June and August 1987, respectively are given Table 1. As seen from these data, total dissolved Pu measured in June and August 1987 at the estuarine stations (Rupelmonde and Doel) were very low as compared with the samples taken at the same stations in December 1986.

Although the geochemistry of Pu in estuarine waters is not well documented, a recent paper of Sholkovitz et al. (1987), which has measured the activities of dissolved Pu in four estuaries on the north-east coast of the United States found very low Pu values in waters collected in the zone of turbidity maximum where salinities range from 0 to about 10 ‰. These dissolved Pu activities are very similar to our June and August 1987 cruises results.

The higher dissolved Pu values found in our estuarine stations during December 1986 cruise might be due to some artifacts like (1) increased fallout from Chernobyl accident (2) Pu contamination in the laboratory during chemistry samples processing or (3) change of filter pore size for iron hydroxydes recovery (in December 1986, we utilized 0.2 μ m porosity instead of 0.4 μ m which were normally used for all other cruises). Low Pu laboratory blanks measured during December sample analyses and Pu-238/Pu-239 activity ratios found in dissolved samples, which were very different from Chernobyl one's (Pu-238/Pu-239 = 0.4 - 0.5), excluded the first and the second hypothesis.

On the contrary, the last one cannot be ruled out. Previous studies have shown that "dissolved Pu" in estuaries might be removed from the dissolved phase by coagulation of colloidal particles originating from freshwater. As an example Shen et al. (1983) have showed, that the major part of "dissolved Pu" exists as colloids in the organic rich fresh-water end member of estuaries.

Particulate Pu did not follow the same trend and show activities which are almost constant for all the cruises (see Table 1.).

2.2 Pu redox speciation

Analyses of samples collected in August 1987 showed that, contrary to the first redox speciation experiment, made in December 1986, the separation of the reduced Pu-242 and the oxidized Pu-236 spikes were quite adequate. The degree of cross contamination was of the same order of magnitude (10 - 15 %) than the Lowestoft laboratory results found for marine waters contaminated by waste Pu effluents from Sellafield (Harvey and Lovett, 1984). Unfortunately, because of the very low activities found in the estuarine water samples (see Table 1) it has not been possible to measure Pu redox speciation in these samples.

Station	Date of sampling	Waters		Suspended matters	
		Pu-239-40	Pu-238/Pu-239 (fci/l)	Pu-239-40	Pu-238/Pu-239 (fci/g)
R*	December 1986	0.124±0.013	0.30±0.05	17.6±1.0	0.45±0.05
D*	"	0.098±0.009	0.27±0.05	19.4±0.8	0.35±0.03
S*	"	0.110±0.013	0.24±0.06	47.7±1.1	0.31±0.01
R	June 1987	0.005±0.002	-	15.2±0.4	0.40±0.04
D	"	0.007±0.001	-	12.0±0.9	0.37±0.05
S	"	0.081±0.005	0.39±0.04	41.9±1.6	0.29±0.03
R	August 1987	0.003±0.001	-	16.2±0.6	0.42±0.02
D	"	0.008±0.002	0.21±0.10	15.0±0.8	0.35±0.02
S	"	0.048±0.004	0.29±0.06	35.5±0.9	0.30±0.04

R*: Rupelmonde ; D*: Doel ; S*: Schaar Van Spijkerplaat.

Table 1. Results from the Pu 239-240 and Pu-238/Pu-239 activity ratio analysis in the water and suspended matters of the Scheldt estuary (errors are expressed as 1 standard deviation).

References

Harvey B.R. and Lovett M.B. (1984). Nucl. Instrum. and Meth. in Phys. Res., 223, 224-234.

Heterington J.A. (1976). Environmental toxicity of aquatic radionuclides: models and mechanisms, Miller M.W. and Standard J.N., Eds, Ann. Arbor Sci. Publ. Inc. Michigan, 81-106.

Lovett M.B. and Nelson D.M. (1981). Techniques for Identifying Transuranic Speciation in Aquatic Environments, 24-28 March 1980, Ispra, Italy, IAEA 27-35.

Pentreath R.J., Harvey B.R. and Lovett M.B. (1985). Speciation of Fission and Activation Products in the Environment, Bulman R.A. and Cooper J.R. Eds, Elsevier, London, 312-325.

Shen G.T., Sholkovitz E.R. and Mann D.R. (1983). Earth Planet. Sci. lett., 64, 437-444.

Sholkovitz E.R. and Mann D.R. (1987). *Estuarine, Coastal and Shelf Science*, 25, 413-434.

IV. Objectives for the next reporting period:

In order to locate more precisely the sources of Pu present in the Scheldt estuary, we have decided to analyse samples collected by centrifugation or sediment traps since July 1986 by the Brussels laboratory (ULB) in the Scheldt (Antwerp Hemiksem, Doel, Gent) and in some of its tributaries (Rupel, Dyle, Nethe). For the last cruise we project to complete our investigation of the Pu sources found in the Scheldt estuary by sampling waters and suspended matter samples from the Scheldt above the tidal intrusion at Gent and in various Scheldt tributaries. We also plan to conduct laboratory adsorption experiments made with Pu-237 ($T_{1/2} = 42$ d., γ emitter) on small estuarine waters volume (about 1 l) to test the stability of the reduced (III, IV) and oxidized (V, VI) forms of Pu in oxic and anoxic conditions.

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

VI. Publications:

