RADIATION PROTECTION PROGRAMME
Final Report

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. C. Heip
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.

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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:

Prof. Dr. C.H.R. Heip, Delta Instituut voor Hydrobiologisch Onderzoek
Yerseke, The Netherlands.
Prof. Dr. E.K. Duursma, Dr. D. Eisma, Nederlands Instituut voor Onderzoek
der Zee, Texel, The Netherlands.
Dr. J.M. Martin, Institut de Biogeochimie Marine, E.N.S., France
Dr. B. Harvey, Fisheries Radiological Laboratory, Lowestoft, England
Prof. Dr. R. Wollast, Université Libre de Bruxelles, Belgique

Scientific staff:

D.I.H.O. (Yerseke: J. Nieuwenhuize
N.I.O.Z. (Texel): J. Kalf, T. Schumacher
Inst. de Biog. Marine, ENS (Paris): J.M. Mouchel, A.J. Thomas, G.Corbière,
P. Prat
Fisheries Lab, Lowestoft: B.R. Harvey
Lab. d'Oceéan. Chim., ULB, Brussels: Hao Zhang, P- Regnier, M. Loijens
D. Mertens

I. Objectives of the project:

II. Objectives for the reporting period:

III. Progress achieved:

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

V. Publications:

Transfer Processes and Modelling of Plutonium Species and Gamma Emmitters in the Scheldt Estuary.

Participants in the programme:

1. **Delta Institute for Hydrobiological Research, Yerseke, The Netherlands**
   Egbert K. DUURSMA
   Carlo HEIP
   Joop NIEUWENHUIZE

2. **Institute de Biogéochimie Marine, Ecole Normale Supérieure, Paris**
   Jean-Marie MARTIN
   J.M. MOUCHEL
   Alain J. THOMAS
   G. CORBIERE
   P. PRAT

3. **Laboratorie d'Océanographie Chimique, Université Libre de Bruxelles**
   Roland WOLLAST
   Hao ZHANG
   Pierre REGNIER
   Michèle LOIJENS
   Dominique MERTENS

4. **Netherlands Institute of Sea Research, Texel, The Netherlands**
   Doeke EISMA
   Jaap KALF
   T. SCHUHMACHER

5. **Fisheries Laboratory, Lowestoft, England**
   B.R. HARVEY

I. INTRODUCTION

In a previous study (Duursma et al., 1985), it has been shown that radioactive contamination at low levels, in the Dutch Delta of the main European rivers Rhine, Meuse and Scheldt, may be due to two or three specific sources additional to fallout of radionuclides. The case of the Scheldt is particularly interesting: besides the systematic seaward increase of plutonium concentrations in the sediments indicating a marine source of this element. ^{238}Pu distribution in the Western Scheldt estuary is altered by additional inputs in the estuary itself. On the other hand, the study of the distribution of Co-60 allowed the identification of the area where the highest contamination by nuclear power plants effluents occurs. This area does not correspond with the peak of excess Pu-238 indicating that this Pu isotope originates partly or completely from another source located in the watershed of the Scheldt.

A complementary study of the radionuclides in the Scheldt was undertaken in order to have a better understanding of the sources and the behaviour of the radioactive material in this estuary. The Western Scheldt is a rather ideal system which has already been intensively studied for stable elements. It is characterized by a long residence time of water and particles in the brackish zone where almost permanent anoxic conditions prevail. It is thus possible to investigate in this system the influence of the redox conditions on the behaviour of the radionuclides and especially on Pu. Furthermore, the region of Antwerp receives an important load of organic matter which allows an in-situ study of complexation of radionuclides in water and on particulate matter. Finally, it appeared that the artificial radionuclides are valuable tools for studying estuarine hydrodynamic processes.

II. SAMPLING

Deposited sediments, water and suspended matter (SM) were collected on board R/V LUCTOR from D.I.H.O. in the estuary and its major tributaries from 1979-1984 (before the Chernobyl accident) and from 1986-1988 (Sampling began about 2 months after the Chernobyl accident.). On the whole, about 75 samples were collected. Sampling locations are identified by the distance (km) from the mouth of the estuary.

Particle size of suspended matter was determined with pipet analysis and Coulter Counter and related to the total concentration, salinity and biological activity as determined by ETS-measurements. The organic content of the suspended matter was determined by ashing at 500 °C for eight hours. The base exchange capacity in bottom sediments was determined for comparison by exchanging Ca-acetate and NaCl and determining the Ca in the percolate. A series of measurements were made of in-situ particle size with in in-situ suspension camera, which was used in April 1989 at a series of stations from Temse to Vlissingen in a salinity range from fresh water (0.08-0.19 o/oo S) to almost seawater (27 o/oo S). The photonegatives were analysed with a recently completed automated image analysis system.

Large volumes of surface waters (200 l to 500 l) were sampled by pumping and particulate matters were recovered by continuous centrifugation.
Water samples were then filtered by pressure filtration on membrane filters of

0.45 um and immediately spiked with Pu-242, after acidification to pH 1.5 with HCl.

Plutonium isotopes were coprecipitated with $Fe(OH)_3$ using NH_4OH at pH 9. Hydroxides were recovered by filtration and oven-dried at 105°C. Suspended matter and hydroxides were later dissolved with HCl and with a mixture of HF + HCl + $HClO_4$ respectively, for plutonium analysis according to classical methods (Talvitie 1971, 1972; Wong, 1971; Ballestra et al., 1979). Briefly, the solution was radiochemically purified using the anionic resin Bio-Rad AG1X8 of 50 - 100 mesh and the plutonium was finally electroplated and counted by alpha-spectrometry with 300 mm^2 Si-Au surface barrier. Gamma emitters were measured using a high purity Ge Gamma-ray detector (32% relative efficiency and 1.80 KeV resolution at 1.33 MeV) placed into a 1 m^3 low-level lead shield of 15 cm thickness. Counting times ranged from 1 to 7 days per sample. Measured emitters include Cs-137, Ru-106, Sb-125, Co-60, small amounts of Cs-134 and traces of Mn-54, Co-58, Zr-95, Nb-95 and Ce-144. Only the Cs isotopes, Ru-106 and Sb-125 will be discussed in this report.

Aluminum content (2-6%) was analyzed in all S.M. and sediment samples and was used as an index of the abundance of clay minerals to normalize the concentrations (expressed in pCi/g Al) in order to distinguish activity variations controlled by grain size fluctuations from those due to other processes.

The major physicochemical parameters have been measured in each water sampling station (salinity, T, O_2, pH, DOC, POC, alkanility, Eh, dissolved iron and manganese, and suspended matter. Dissolved Co was analyzed by differential pulse cathodic stripping voltametry of its dimethyl glyoxime complex (Zhang et al., 1988).

III. SUSPENDED MATERIAL IN THE SCHELDT ESTUARY

Considerable variation in size of the suspended particles was found but no difference between freshwater and saline-water suspensions could be demonstrated. Maximum in-situ size of particles varied between 700 and 900 µm, median values were between 100 and 300 µm. Near the bottom particles tend to be somewhat larger. Particle size does not increase at the contact between fresh and saline water, salt flocculation does not appear to be an important process.

Coulter counter size measurements at stations with salinities higher than 4 o/oo S indicated large peaks of particles around 2 µm and around 10 µm. This clearly demostrates the destruction of the in-situ flocs by sampling and analysis; the in situ camera gives a more reliable estimate of particle size and surface area of the particulate matter in nature. Particle shape can also be analysed so that deviations from a spherical shape can be estimated, allowing a more precise estimate of surface area.

Variability in particle size seems to be regulated by local conditions of turbulence and particle settling. There is no relation with the organic matter content or the bulk composition. Changes in organic matter of the suspended material during transport through the estuary probably are due to a number of processes that may change the surface characteristics of the particles and thus alter their geochemical behaviour.

Mobilization of carbohydrates at low salinity, compositional changes from compounds of terrestrial origin to compounds of marine origin and changes in the isotopic composition may result in more porous, more surface active particles in the estuary than in both the freshwater or the sea.

At low salinities the particle size as measured with the pipet and Coulter Counter is smaller than in freshwater. The smaller size coincides with the area where carbohydrates are mobilized form the suspended material. They are probably present as polysaccharides or fulvic acids. Both types of organic compounds are very common in estuaries and are able to glue suspended particles together.

A turbidity maximum was present between Bath and Dendermonde, i.e. at low salinities and partly in the fresh water. Concentrations in the turbidity maximum reached 800 $mg.l^{-1}$ near the bottom and 200 $mg.l^{-1}$ in the surface waters. In the freshwater part up to Gent concentrations were between 40 and 60 $mg.l^{-1}$ and in the estuary downstream Bath between 25 and 60 $mg.l^{-1}$.

The organic matter content varied between 7.9 to 52.2 %. There is a general tendency for the organic matter content to be higher in the freshwater suspensions, but exceptions are frequent particularly because of primary production in the surface water. Because the automation of the scanning microprobe is not yet finished, the SEM analyses could not yet be carried out. From these data the origin of the suspended matter can be estimated.

IV. ORIGIN AND LONGITUDINAL DISTRIBUTION OF ARTIFICIAL RADIONUCLIDES

The distribution of artificial radionuclides will be discussed as a function of their major mode of introduction in the Scheldt estuary.

IV.1. The "marine" source : Sb-125, Ru-106, Cs-137 and Pu-239+240

The longitudinal distributions of Sb-125, Ru-106 and Pu-234-240 (fig.1) show a systematic seaward increase from about km 60, reaching a factor of 3 - 10 on a normalized basis. Cs-137 also increases seaward and Cs-134 was detected in the lower estuary with a constant but low Cs-134/Cs-137 activity ratio (about 0.05). This element will be discussed in more detail under section III.3 devoted to the Chernobyl accident.
These distributions suggest that the major source of Ru-106 and Sb-125, Pu 239+240 and to some extend Cs-137 is to be found in the contaminated coastal waters of the North Sea. Fixation of dissolved radionuclides in the saline waters by terrigenous Scheldt particles, or introduction of contaminated "marine" particles into the estuarine system may be considered.

The enrichment of artifical radionuclides in the North Sea has been directly related to the effluents released by the reprocessing plants of la Hague and Sellafield as previously discussed by DUURSMA et al., 1985. It must be added that near the mouth, dissolved Pu-239+240 and particulate Pu-239+240/Al ratio decreased by

30-50% from 1986 to 1988. These variations may correspond to a recent evolution of the contamination of the southern North Sea. Indeed Sellafield discharges have strongly decreased since a few years, but waters off the Scheldt mouth are essentially under the influence of Channel waters inputs and no recent data on plutonium releases at La Hague are available since 1985.

These results show that marine trace elements originating from the North Sea are introduced into the estuarine system and transported landwards up to km 60-90.

IV.2. Internal Sources : Co-60 and Pu-238

The longitudinal distribution of Pu 238/Pu 239+240 activity ratio and of Co-60 are given in figure 2. Both clearly indicates a maximum near km 60 for Co-60 and near km 100 for Pu-238+239 corresponding to the Doel power plant and the Rupel confluence respectively. These two sources would release a few mCi/y of Pu-238 and several hundred mCi of Co-60.

A more detailed study of the distribution and behaviour of cobalt was performed during this study. Six longitudinal profiles of dissolved cobalt obtained under various flow conditions indicate that the concentration of the stable element in the fresh water part is strongly affected by the river discharge suggesting that there is a continuous source of this element more or less diluted by the river flow. At mean values of the river discharge, the longitudinal profile enhibits a maximum near km 60 (fig. 3) which may be due to a local input. Measurements of total Co in the suspended matter show that the distribution coefficient of this element between the dissolved and the particulate phase is remarkably constant over all the salinity range and is equal to 3×10^5. Only a small fraction of the dissolved Co was found to be complexed by organic matter. However, in most cases the relation between the concentration of dissolved Co and salinity exhibits a curvature suggesting that Co is partly scavenged in the area close to the input of this element (km 60). Besides the nuclear power plant, there are many industrial waste water discharges in this area but it is nevertheless striking to see that the maximum of stable Co in the water column corresponds also to the maximum of Co-60 in the suspended matter and sediments.

IV.3. The Chernobyl accident : Cs-134/Cs-137 activity ratios

A short time after the accident (June 1986), significant enrichments in Cs-134, Cs-137, Ru-106 and Sb-125 were found in fresh water particles collected in various Scheldt tributaries, as well as in the estuarine sediment traps. No obvious plutonium enrichment was found. A few months later, owing to mixing with the various sources mentioned above, Chernobyl impact was hardly detectable near the mouth, and became weak close to the terrigenous sources

We will discuss here only the distribution of Cs-134, Cs-137 and of the ratio of these two isotopes before and after Chernobyl. Figure 4 shows the longitudinal distribution of Cs in the suspended matter and in the sediments before Chernobyl and in the suspended matter only after Chernobyl. As expected, the signal is especially important for Cs-134. Our measurements in aerosols collected in Brussels during the maximum of Chernobyl deposition give a Cs-134/Cs-137 ratio close to 0.51, a value

identical to the ratio found in Paris (Thomas and Martin, 1986). This value will be used as a reference of the Chernobyl signature. Figure 5 shows the evolution with time of the Cs-134/Cs-137 ratio in the Scheldt river and estuary.
Scheldt river ratios at Gent exponentially decrease with time but with a shorter apparent half-life. In the S.M. collected near the mouth at Schaar, the ratios are always lower than in the river and decrease irregularly with time. Measuremement by other institutions (Gueguenait et al., 1988, Anonymous, 1987; Nies and Wedekind, 1987; Nies, 1990) in coastal and non-coastal unfiltrated waters of the southern North Sea (51-53°N) show that ratios are systematically higher near the coast than at a certain distance. This distribution suggests that the higher coastal ratios are certainly due to a higher content of terrigenous particles in the more turbid waters.

These results clearly indicate the predominant continental origin of Cs-134, and its mixture with a North Sea stock poorly affected by Chernobyl fallout (by the end of June 1986, and later). Moreover, the ratio decay, which differs from theoretical decay of Chernobyl deposition, may be interpreted in term of a progressive mixing of Chernobyl-contaminated soil particulates with an increasing proportion of the Cs-137 global fallout inventory.
It is possible to calculate with these data the fraction (F) of Chernobyl-derived Cs in a given S.M. sample. This fraction was 90% in June 1986 and was still 60% after 2.5 years.
Therefore, although an important proportion of Chernobyl deposition may have been early eroded before the beginning of our sampling in June 1986, total elimination of Chernobyl Cs isotopes from the Scheldt watershed will still take many years.

The results mentioned above allow to envisage the use of Chernobylderived Cs as a terrigenous tracer in the estuarine system. Relative variations (i.e. normalized with respect to the corresponding river value) of the fraction (F) of Chernobyl-derived Cs-137, calculated as described above, are shown in figure 6 for various sampling cruises.

This figure shows that penetration of the terrigenous Cs in the lower estuary (downstream km 60 approximately) is very limited during periods of low and intermediate river discharge (75-125 m^3/s), whereas the S.M. stock upstream km 80 seems rather homogeneous and essentially land-derived. This conclusion is consistent with the results obtained above using the penetraµtion of the "marine" radioactive tracers. It agrees also with the well known fact that most of the continental S.M. transported by the river is trapped in the area of Antwerp and does not reach the sea except during exceptional high floods.

During the March 1988 flood (average river flow - 339 m^3/s at Schelle), the contrast between the upper and lower estuary has disappeared and a more linear distribution is found (fig. 6). The low value at km 90 (Rupel confluence) is probably due to resuspension of deposited sediment less contaminated due to the high velocity of water during the flood event. Also, the high value near the mouth (F = 53%) may be interpreted as the result of a seaward flushing of the estuarine S.M. stock during the flood, showing that most of the estuarine stock of S.M. is land-derived under such hydrological conditions.

V. ESTUARINE BEHAVIOUR OF ARIFICIAL RADIONUCLIDES

V.1. Pu isotopes

Except during the December 1986 cruise, dissolved ^{239,240}Pu activities in samples collected in the Scheldt estuary (fig. 7) were very low (< 0.003 to 0.008 fCi/l), while the activities of most marine samples (collected near the mouth of the estuary) are at least 5 to 10 times greater and relatively constant (0.05 to 0.08 fCi/l).

The dissolved ^{239,240}Pu activities found in the Scheldt estuary are very similar to those found by Sholkovitz et al. (1987) in four northeastern United States estuaries. Pu activities in waters collected in the Scheldt without tidal influence (Gent) and in some of its tributaries (Rupel, Albert Kanaal) are also very low and similar to estuarine stations. Although the data collected during this study are scarce. It seems nevertheless that dissolved Pu might have been removed in the Scheldt estuary. The decrease could be attributed to enhanced scavenging due to the presence of high suspended particulate load in the estuary and to long flushing time (about 2 to 3 months) as suggested by Scholkovitz et al. (1987) for American estuaries.

Owing to the very low dissolved plutonium (0.001 - 0.0550 fCi/l) activities, the study of redox partitioning between Pu (III + IV) and Pu (V + VI) initially planned was not possible. It has been decided instead to investigate the variation of the distribution coefficient (K_d) in relation with dissolved oxygen and to carry out Pu-237 adsorption experiments. Results are discussed below.

Relation with dissolved oxygen

Whereas Pu-239+240 Kd (fig. 8) is rather constant ($6 \pm 2 \times 10^5$) in oxygenated waters (10 mg/l dissolved oxygen) collected near the mouth, it increases up to 5×10^6 in the estuarine oxygen-depleted waters (0.3 mg/l), with a few exceptions. These variations are due to a strong removal of dissolved Pu, attributed to a probable redox control. Pu coupling with Fe-Mn redox cycles, or redox transformation of Pu itself, has been found in reducing fjords where Pu depletion coincides with the 0_2-H_2S boundary (Sanchez et al., 1986) and in Pu-enriched deep anoxic estuarine waters (Sholkovitz et al., 1987). These authors have also shown that such depletion processes may be counter-balanced by later Fe-Mn oxide dissolution, and sorption inhibition by complexation with carbonate ions and dissolved organic matter. It seems that in the Scheldt Pu insolubilization in anoxic waters is the dominant process.

V.2. Sorption of radionuclides on suspended matter on short time scales

To investigate the sorption of the two main species of plutonium (Pu (III-IV) and Pu (V-VI)) as well as other important trace metals in oxic and anoxic conditions in the Scheldt estuary, a water sample of low salinity collected at Hemiksem in May 1988, was separated into four subsamples maintained under constant air or nitrogen bubbling during one week. Gas bubbling induced an increase of pH due to the desgassing of carbon dioxide. In each sample, a mixture of five trace metal isotopes (^{60}Co, ^{54}Mn, ^{65}Zn, ^{105}Cd and ^{134}Cs) was added in chloride form as well as Pu(IV) or Pu(VI) in nitric form, freshly prepared according to Lovett and Nelson (1981).

Aliquots were filtered at selected time intervals. Filters and filtrates were gamma counted.

For cobalt and cesium, a pseudo-equilibrium was rapidly attained, within less than four hours under oxic conditions. The distribution coefficient of cesium then increased slowly but significantly until the end of the experiment. Anoxic distribution coefficients were higher for cesium (compared to oxic distribution coefficients) and lower for cobalt.

In the case of manganese, as expected, the distribution coefficients were much higher and continuously increasing during the first hours in the oxic subsamples, while they were lower and reaching a pseudo-equilibrium in the anoxic subsamples. This evolution is likely due to the catalytic oxidation of Mn(II) into MnO_2 under oxic conditions or to the sorption of Mn(II) ions, under anoxic conditions.

Cadmium, zinc and surprisingly plutonium showed parallel evolutions. They reach an ill-defined pseudo-equilibrium after a few hours no systematic difference could be found between oxic and anoxic subsamples. We failed to notice any difference between the sorption behaviour of Pu (IV) and Pu(VI) in either oxic or anoxic conditions.

Data concerning the distribution coefficients K_d are summarized in fig. 9, together with former data obtained in December 1986 in the Scheldt estuary. Only the fresh water end member is considered here and only the K_d's after 3-4 hours incubation time have been plotted, i.e. after the establishment of the pseudo-equilibrium. Bars give the ranges of values for each series of samples. In December 1986, no bubbling was set, and the experimental medium initially anoxic remained anoxic.

The main significant difference between both series of data concerns manganese which was much more sorbed in May 1988, in oxic or anoxic conditions. Indeed, the December 1986 survey was carried out during strongly anoxic conditions, with high concentrations of dissolved iron and manganese. We argue that such important amounts of dissolved metals may have prevented manganese sorption during incubation by some kind of saturation effect. It is also possible that a strong anoxia might have dissolved iron and manganese oxides which are known to strongly bind Mn(II) ions and catalyze their oxidation.

The same trend is observed for cobalt. It is possibly due to the lack of manganese oxides in December 1986. These oxides are known to have a very high affinity for cobalt ions (Murray, 1975). A more detailed experiment of transfer of Co-60 along the Scheldt estuary has been performed in August 1988. The rate of transfer of this radionuclide from the dissolved to the particulate phase has been investigated over the whole salinity range. Figure 10 shows the distribution coefficient K_d obtained after an incubation of 15 hours. There is a pronounced maximum of K_d within the salinity range between 15‰ and 25‰. This salinity range corresponds also to the restoring of dissolved oxygen and the subsequent precipitation of Mn. This experiment confirms the very strong influences of redox conditions on the behaviour of trace elements and radionuclides in natural environments and the scavenging role of manganese for other trace elements.

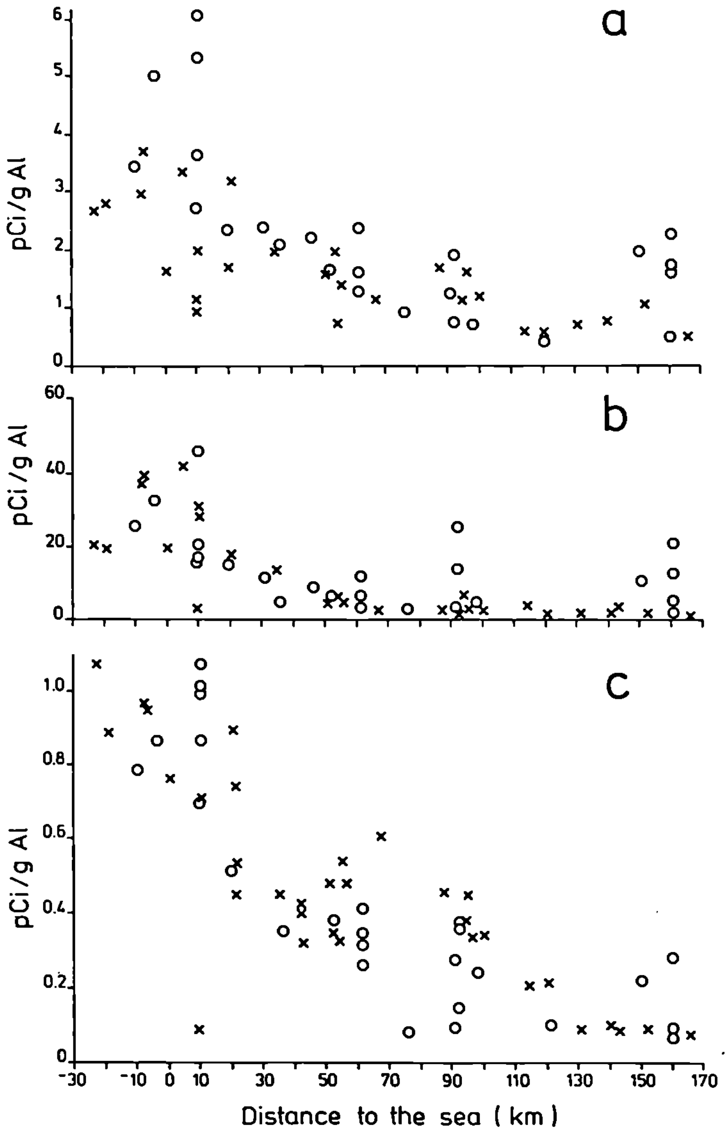

Fig.1 Longitudinal distribution of a) Sb-125, b) Ru-106, c) Pu 239+240 normalized with respect to aluminum in sediments and suspended matter of the Scheldt. X represents sediments and suspended matter collected before Chernobyl, and O denotes suspended matter collected after Chernobyl.

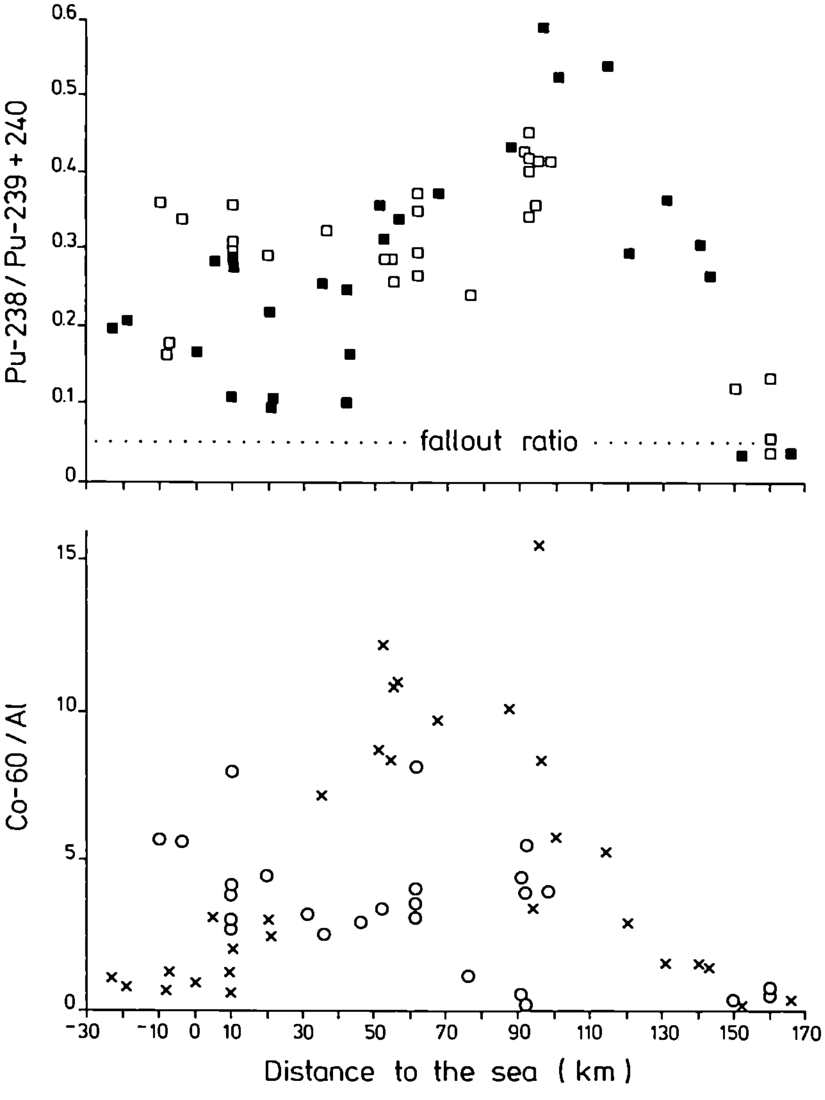

Fig.2 Longitudinal distribution of the Pu 238/Pu 239+240 ratio and of Co-60 normalized with respect to Al in the particulate matter and sediments of the Scheldt. ■ and □ for Pu refers to sediments and suspended matter respectively. Same symbols for Co as in figure 1.

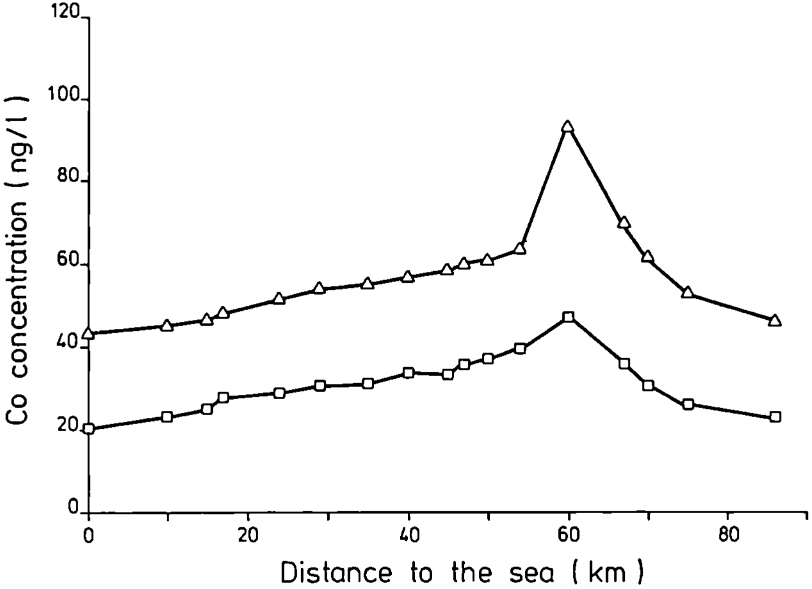

Fig.3 Longitudinal distribution of dissolved (□) and total (△) cobalt in the Scheldt for mean fresh water discharge (October 1988).

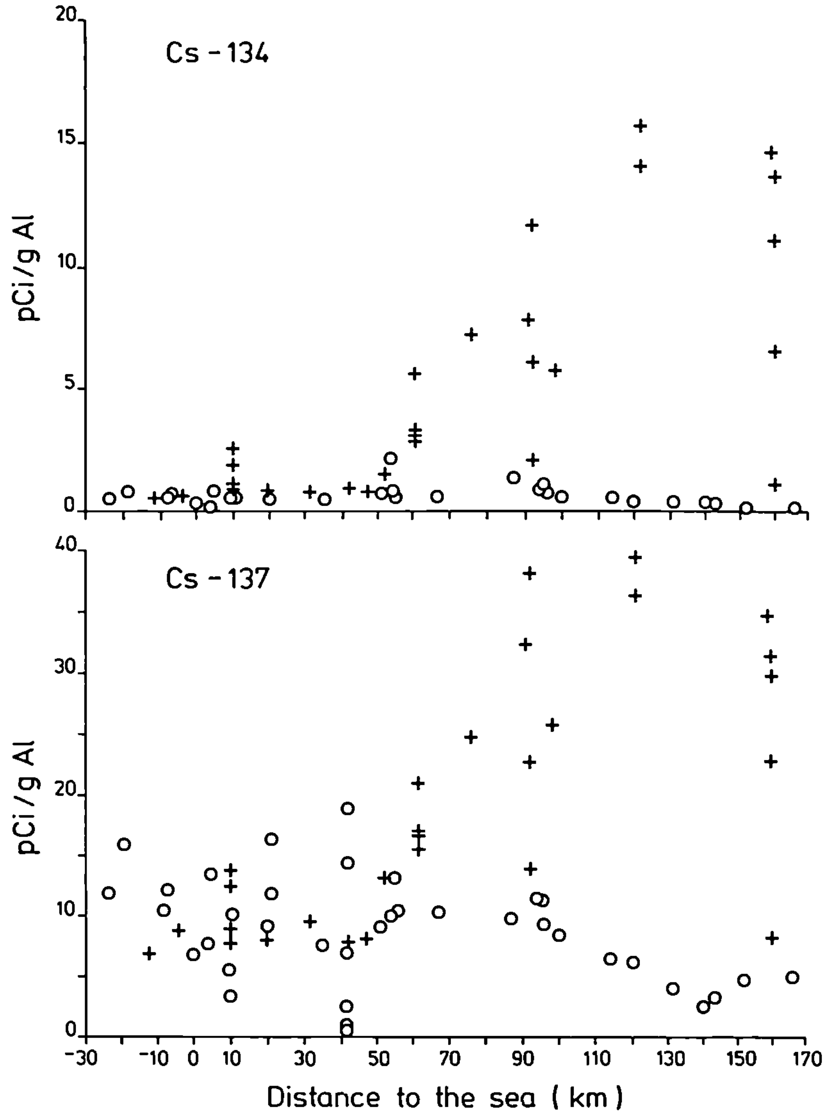

Fig.4 Longitudinal distribution of Cs-134 and Cs-137 normalized with respect to aluminum in the sediment and suspended matter of the Scheldt.

O represents sediments and suspended matter before Chernobyl and + denotes suspended matter after Chernobyl.

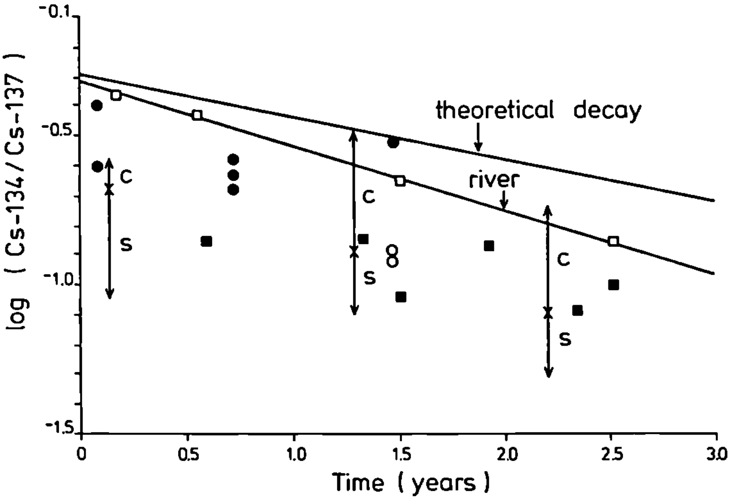

Fig.5 Cs-134/Cs-137 activity ratios versus time in the Scheldt river and estuary after the Chernobyl accident. Other measurements in unfiltered coastal and non-coastal Southern North Sea waters (51-53°N) are given for comparison

□ Scheldt river at Gent

■ Scheldt estuary near mouth

●,O Coastal and non-coastal sea water (Deutches Hydrographischer Institut, Hamburg).

C and S coastal and non-coastal sea-water (Laboratoire de Radio-ecologie Marine, La Hague)

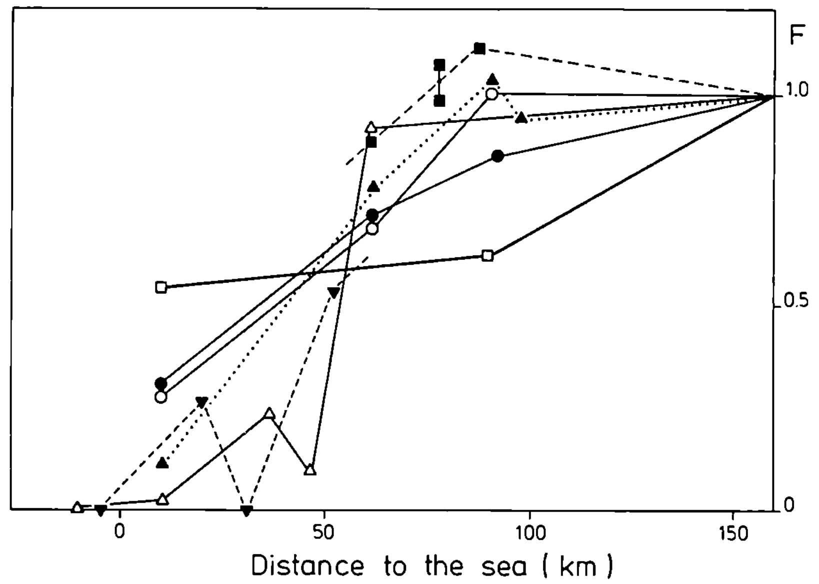

Fig.6 Fraction of the Chernobyl-derived Cs in the Western Scheldt suspended matter normalized with respect to the value observed at Gent.

■ July 1986, ● December 1986, ○ August 1987, ▲ October 1987, □ March 1988, △ August 1988, ▼ November 1988

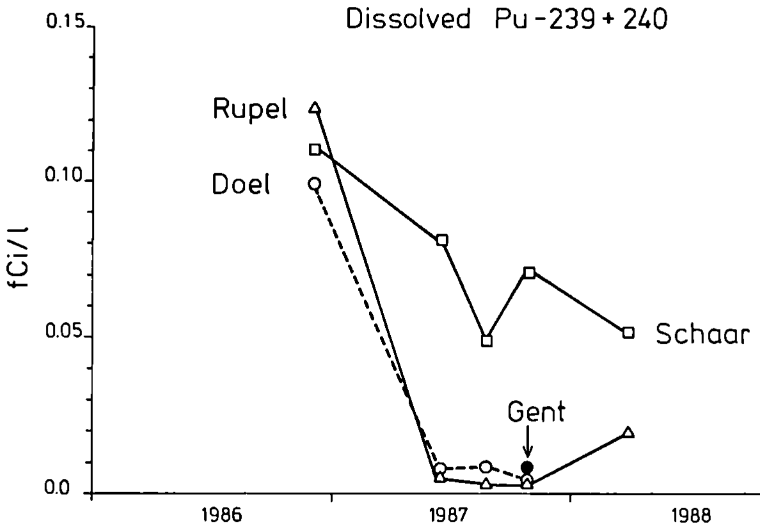

Fig.7 Activity of dissolved Pu-239+240 at Gent (km 160), Rupel (km 98), Doel (km 62) and Schaar (km 10) during the present study.

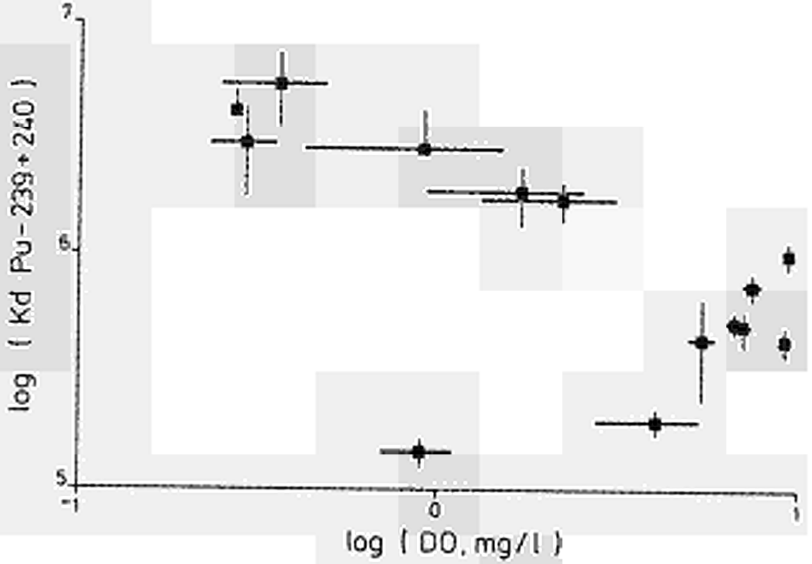

Fig.8 Distribution coefficient Kd of Pu-239+240 between the dissolved and particulate phases as a function of dissolved oxygen in the Scheldt estuary.

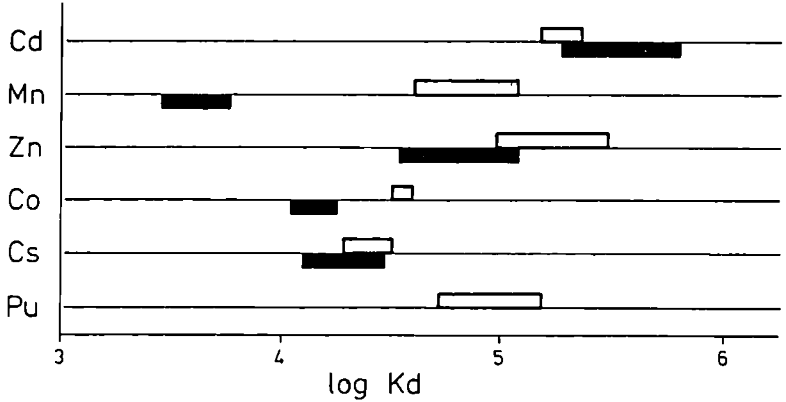

Fig.9 Fast distribution coefficients obtained during incubation of radionuclides after 4 hours with water samples of the Scheldt estuary in the fresh water part.

▬ December 1986, ▭ May 1988

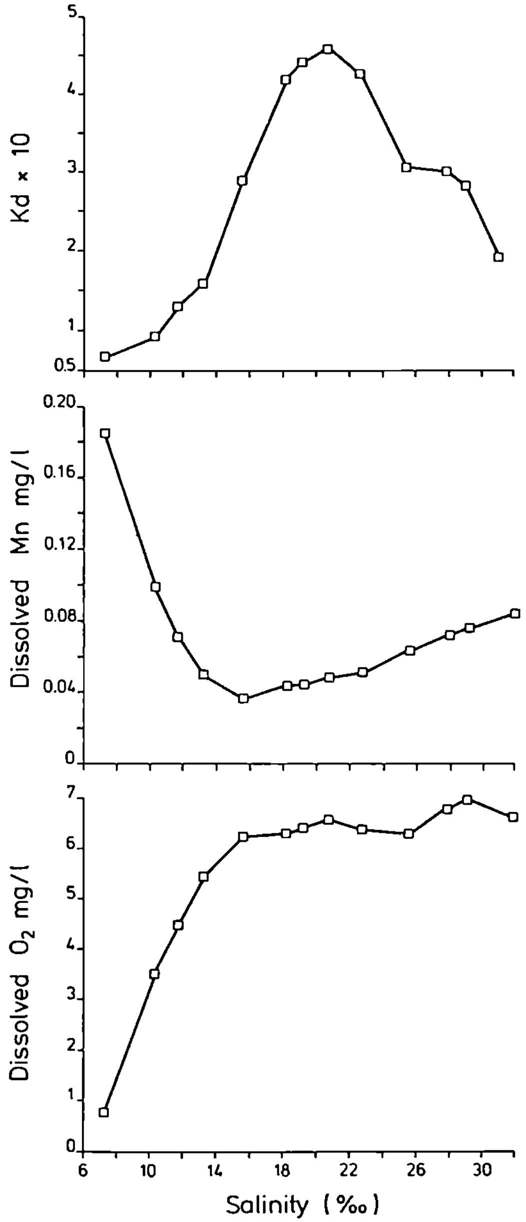

Fig. 10 Evolution of the distribution coefficient of Co-60 with salinity in the Scheldt estuary compared with dissolved oxygen and manganese, obtained in August 1988.

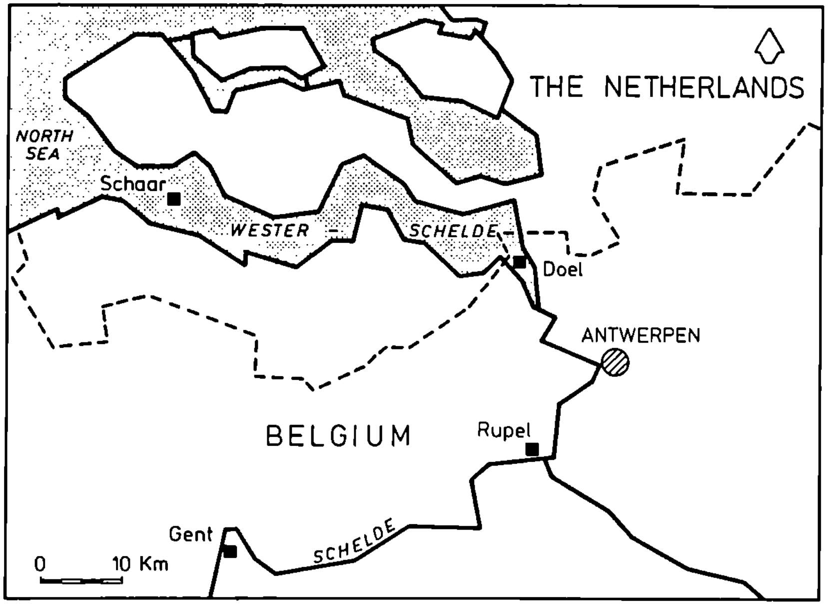

Fig.11 Map of the area