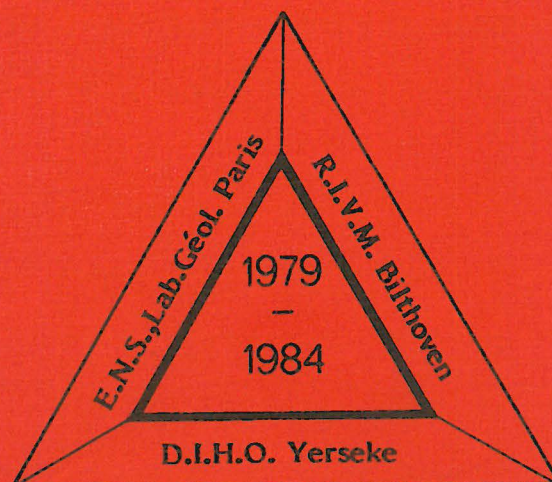
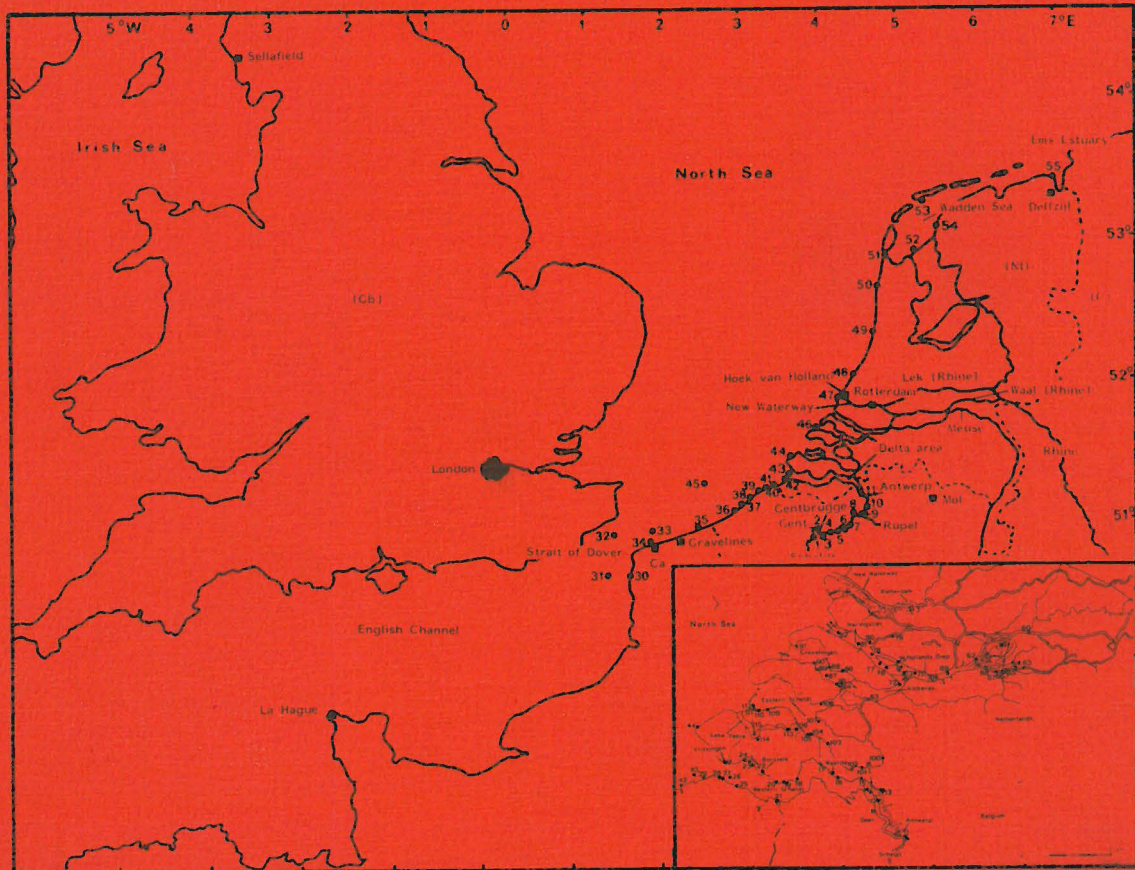


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**PLUTONIUM IN SEDIMENTS AND MUSSELS OF THE RHINE-MEUSE-SCHELDT  
 ESTUARY**





MS.

PLUTONIUM IN SEDIMENTS AND MUSSELS OF THE RHINE-MEUSE-SCHELDT  
ESTUARY (\*)

by

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## ABSTRACT

The Dutch Delta of the main European rivers Rhine, Meuse and Scheldt is a diverse system of estuaries, where river water meets North Sea water and where recently a number of estuarine branches have been enclosed by dams and barrages. Radioactive contamination occurs at very low level and is besides for gamma emitters measurable for the alpha emitter  $^{239+240}\text{Pu}$  and  $^{238}\text{Pu}$  in various substrates of this area

Potential sources of radionuclide contamination are those entering the estuaries through the North Sea from either the reprocessing plants of La Hague (F) or Sellafield (GB), radionuclides from nuclear power plants along the rivers Rhine, Meuse and Scheldt and fallout nuclides from earlier and recent bomb-test explosions.

Concentrations in deposited sediments and suspended matter average 12-21 pCi  $^{239+240}\text{Pu}$ /kg and 1.5-6 pCi  $^{238}\text{Pu}$ /kg (dry weight). These activities only represent 0.1 % of natural alpha radioactivity. In the soft parts of mussels, plutonium concentrations are one order of magnitude lower (also on dry-weight basis). Normalization of plutonium concentrations to aluminum, considered as an index of clay concentrations, allows some practical determination of the possible sources in the environment.

Clearly the whole Delta area receives plutonium isotopes from the North Sea, where  $^{238}\text{Pu}/^{239+240}\text{Pu}$  isotopic ratios are high due to the Sellafield and La Hague reprocessing plant effluents. In coastal sediments and mussels,  $^{239+240}\text{Pu}$  contamination decreases from La Hague to the north-eastern Dutch coast, where the influence of industrial effluents can hardly be distinguished from fallout background, contrary to industrial  $^{238}\text{Pu}$  contamination which is still detectable so far north.

Studies of the two estuarine systems of the Delta, the Rhine-Meuse-Eastern Scheldt and the Scheldt-Western Scheldt system, have shown a systematic seaward increase of plutonium concentrations in the sediments, thus confirming earlier findings in French estuaries. Uptake of marine plutonium is probably responsible for this general estuarine pattern.

$^{238}\text{Pu}$  distribution in the Western Scheldt estuary is altered by additional inputs in the estuary itself. The study of the distribution of  $^{60}\text{Co}$  allows the identification of the area where the highest contamination by nuclear power plant effluents occurs. This area does not correspond with the peak of the  $^{238}\text{Pu}/^{239+240}\text{Pu}$  ratios, showing that excess  $^{238}\text{Pu}$  originates partly or completely from another source, located in the watershed of a Scheldt tributary the Rupel river.



The occurrence of relatively high plutonium concentrations and isotopic ratios in the upper estuary, resulting from the landward transport of sediments, emphasizes the possibility of artificial radionuclides as valuable tools for studying estuarine hydrodynamic processes.

A tentative budget calculation for the Western Scheldt estuary is presented, giving an annual input of 'marine' plutonium of 21-24 mCi  $^{239+240}\text{Pu}$  and 5.8 mCi  $^{238}\text{Pu}$ . Radioactive contamination of mussels is far below the annual limit of consumption intake (ALI), being  $10^{-5}$  ALI for 50 kg mussels/yr.

## INTRODUCTION

The Dutch Delta in the southwest Netherlands (Fig. 1) is historically an important and complex estuarine system, through which three major European rivers the Rhine, the Meuse and the Scheldt are discharging their waters into the North Sea. Since the early sixties the Delta has been target of very expensive technical dam and barrage constructions as part of the Delta Plan 1956-1986, in order to protect the southwest Netherlands from severe storm floods.

Since a few decades, the Delta has been submitted to contamination by artificial radionuclides through atmospheric fallout and industrial discharges of radioactive effluents into the neighbouring seas, the rivers and the estuarine zone itself.

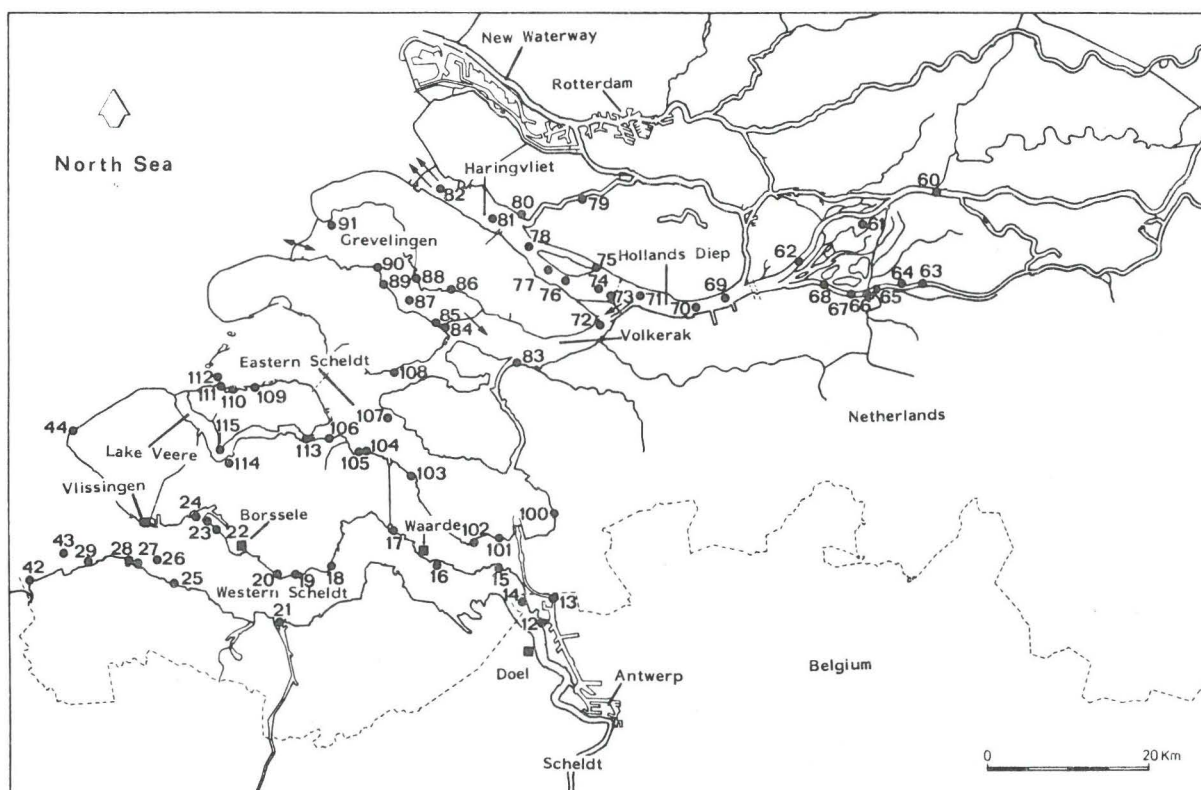


Fig. 1. Map of the Dutch Delta, and sampling stations.

With support of the Commission of the European Communities, DG XII, a cooperative research programme has been set up in 1979 to study the presentday artificial radioactivity in the Delta. The major objectives of this programme were: (i)- to assess the overall distribution of the artificial radionuclide concentrations in sediments and biota of the different basins and adjacent sea; (ii)- to identify possible sources of radioactive contamination; and (iii)- to make a first assessment on the radionuclide behaviour of the various estuarine systems.



The results presented in this paper are essentially restricted to the study of plutonium isotopes in sediments and mussels, being collected from 100 different locations in the Delta (Fig. 1) and the adjacent coastal areas (Fig. 2).

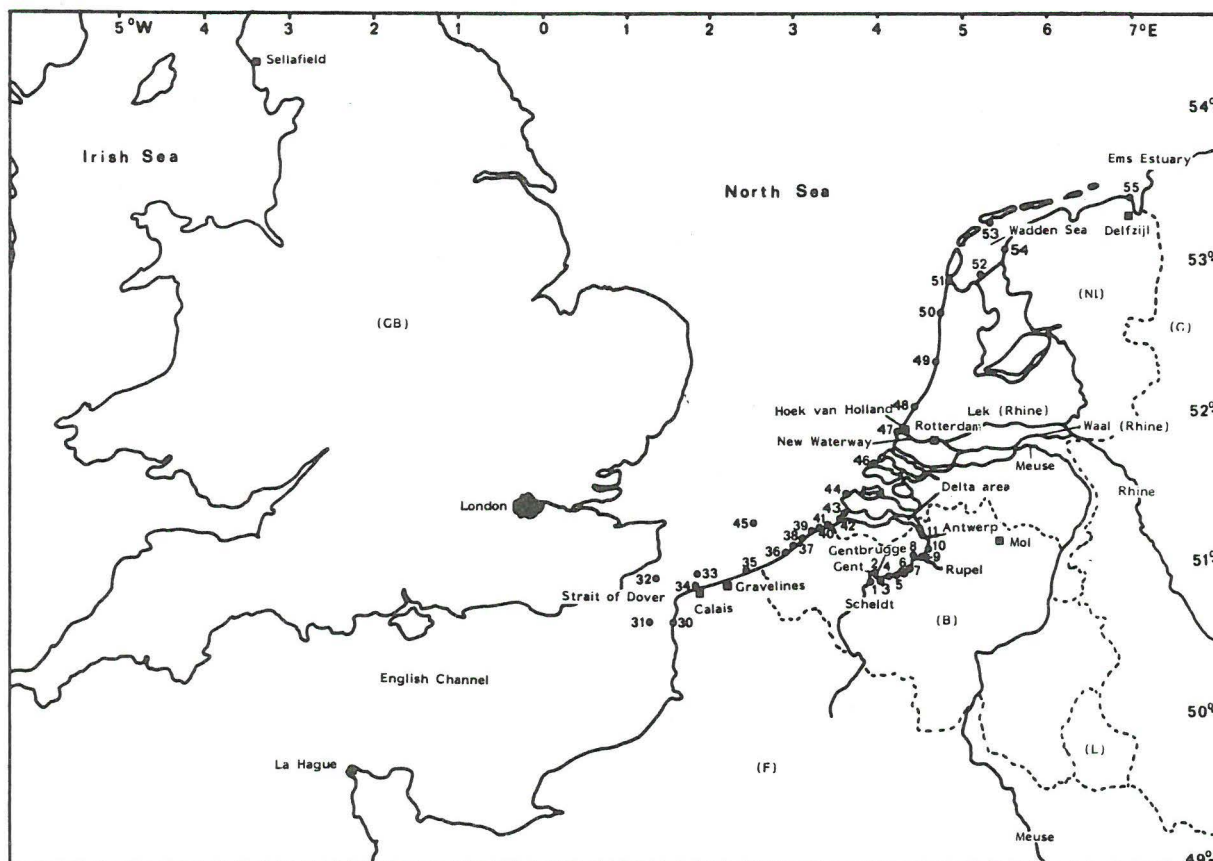


Fig. 2. Map of southern North Sea, and sampling stations.

### AREA OF INVESTIGATION

In its present situation, the Delta includes two major estuarine systems and a number of completely and partially enclosed basins. The hydrographical data, reflecting the actual conditions during the study period (1979-1984) are summarized in Table I.

The Western Scheldt estuary in the southern part of the Delta is an estuary in open connection to the North Sea, receiving freshwater from the Scheldt River in quantities of  $100 \text{ m}^3/\text{s}$ . The tidal amplitude at Antwerp reaches  $\pm 5 \text{ m}$ . The estuary has been an object of comprehensive sedimentological and biochemical studies (1, 2, 3 and 4). Salt intrusion under average conditions reaches 160 km from the inlet (the zero km reference is taken at Vlissingen), whereas tides are propagated 180 km landward until Gentbrugge sluice, where the amplitude still reach 2 m. This point represents the landward limit of the estuary.

Table I. Hydrographical data of the Dutch Delta

Basin	Salinity ‰	Enclosed	Tide Amplitude	Annual Average Discharge
Rhine	-	-	0-2 m (at mouth)	2200 m <sup>3</sup> /s
Meuse	-	-	0-0.5 m (at mouth)	330 m <sup>3</sup> /s
Scheldt	-	-	2-5 m	100 m <sup>3</sup> /s
Lake Veere	15-20	1961	-	-
Haringvliet	-	1970	0.5 m	irregular
Lake Grevelingen	27-29	1971	-	small exchange in winter with North Sea
Eastern Scheldt	8-30	1986 open storm- surge barrier	3.5 m	(50 m <sup>3</sup> /s inflow freshwater)
Western Scheldt	0-30	-	2-4 m	-

The estuarine systems in which both the Rhine and the Meuse rivers discharge is more complex. Natural discharge patterns of these rivers have been altered through history and most of the freshwater now reaches the North Sea through the New Waterway of Rotterdam harbour (which has not been included in the present study) with an overflow in wet seasons through the Haringvliet sluices. A release of 50-100 m<sup>3</sup>/s of freshwater through sluices and shiplocks from the Hollands Diep into the Volkerak still ensures estuarine conditions in the Eastern Scheldt. Tidal intrusion through the Rotterdam harbour reaches the freshwater upstream area of the Hollands Diep, where both the rivers Rhine and Meuse are interlinked by a series of communicating canals. (The Rhine branches in the Netherlands are called Waal and Lek). It is very unlikely that any sediment, originating from brackish waters may be transported landward (except to Rotterdam) and reach the area of investigation, despite the occurrence of a significant tidal movement. The samples collected there will be referred to as riverine material.

The Haringvliet-Hollands Diep basin is closed off since 1970, the Grevelingen became a stagnant lake in 1971, while Lake Veere is a small enclosed brackish basin, which was separated from the Eastern Scheldt in 1961.



Table II. Nuclear power plants discharging liquid effluents into the rivers of the Dutch Delta. After Luykx and Fraser (8).

River	Country	Location	Reactor type	Max. output capacity MWe	First grid connection	Activity released in 1980 <sup>1)</sup> (Ci)
<u>W. Scheldt</u>						
	NL	Borssele <sup>2)</sup>	PWR	450	1973	0.12
	B	Doel 1 <sup>2)</sup>	PWR	395	1974	2.64
		" 2	"	395	1975	
		" 3	"	900	1980	
		" 4	"	1000	1983	
<u>Rhine</u>						
	NL	Dodewaard	BWR	52	1968	0.48
	G	Karlsruhe (MZFR)	PHWR	52	1966	0
		Obrigheim	PWR	328	1968	0.095
		Biblis A	PWR	1146	1974	0.10
		" B	PWR	1240	1976	0.24
		Philippsburg	BWR	864	1979	0.12
	F	Fessenheim 1	PWR	890	1977	7.1
		" 2	PWR	890	1977	
<u>Meuse</u>						
	B	Tihange 1	PWR	870	1975	1.36
		" 2	"	900	1980	?
		" 3	"	1000	1983	?
	F	Chooz	PWR	305	1967	0.26

PWR = pressurized water reactor

PHWR = " heavy water reactor

BWR = boiling water reactor

1) = liquid effluents, excluding <sup>3</sup>H

2) = direct discharge into study area

## POSSIBLE RADIONUCLIDE SOURCES

Radionuclides have been initially supplied to the Delta area from the major nuclear weapon tests of the years 1954-1962 and smaller tests later, through direct deposition from the atmosphere and land run-off. These include the long-lived  $^{238}\text{Pu}$ ,  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  isotopes (half lives, 86, 24000 and 6600 yr, respectively, total 400 kCi). Launching failure of SNAP-9A satellite in 1969 has added on world scale 17 kCi of  $^{238}\text{Pu}$  to the atmosphere (5). As a consequence of these various inputs, the  $^{238}\text{Pu}/^{239+240}\text{Pu}$  concentration (by activity) ratio in fallout averaged 0.036 in the Northern Hemisphere in 1970-1971 (6). This value did not change much later on (7).

A number of nuclear power plants discharge radioactive effluents in the Rhine and Meuse river systems (Table II), but most of them are located relatively far upstream from the Delta. There is no nuclear plant in the Scheldt river (canal) upstream of Gent, these are located at Doel (Belgium) and Borssele (Netherlands). These powerplants discharge directly into the Western Scheldt estuary.

The composition of these liquid effluents has been summarized by Luykx and Fraser (8).  $^{60}\text{Co}$  is an activated corrosion product which may be present in effluents of PWR reactors (gamma emitter; half life 5.2 years), but no reports are available concerning transuranic nuclides.

Nuclear fuel reprocessing plants are at present the major sources of artificial radionuclides in the marine environment. The Delta may receive from the North Sea radionuclides originating from the reprocessing plant at La Hague (English Channel) and from that at Sellafield (Irish Sea). As can be seen in Fig. 3, the Delta obtains a large marine influence from sea water originating from the English Channel. Contaminants from both reprocessing plants should reach this area mainly by this way.

As will be indicated later, the isotopic plutonium composition of sediments contaminated by the effluents of reprocessing plants shows a significant  $^{238}\text{Pu}$  enrichment as compared to fallout. Therefore the  $^{238}\text{Pu}/^{239+240}\text{Pu}$  ratio can be used as a tracer for the origin of the contamination.

Other potential artificial radionuclide sources must also be taken into account, such as effluents of the CEN nuclear research centre at Mol (Belgium) and associated industrial plants. These plants are located in the watershed of the Rupel River, a tributary of the Scheldt.

Because of the occurrence of these multiple potential radionuclide sources, a complex distribution pattern of plutonium isotopes in the Delta was expected. To



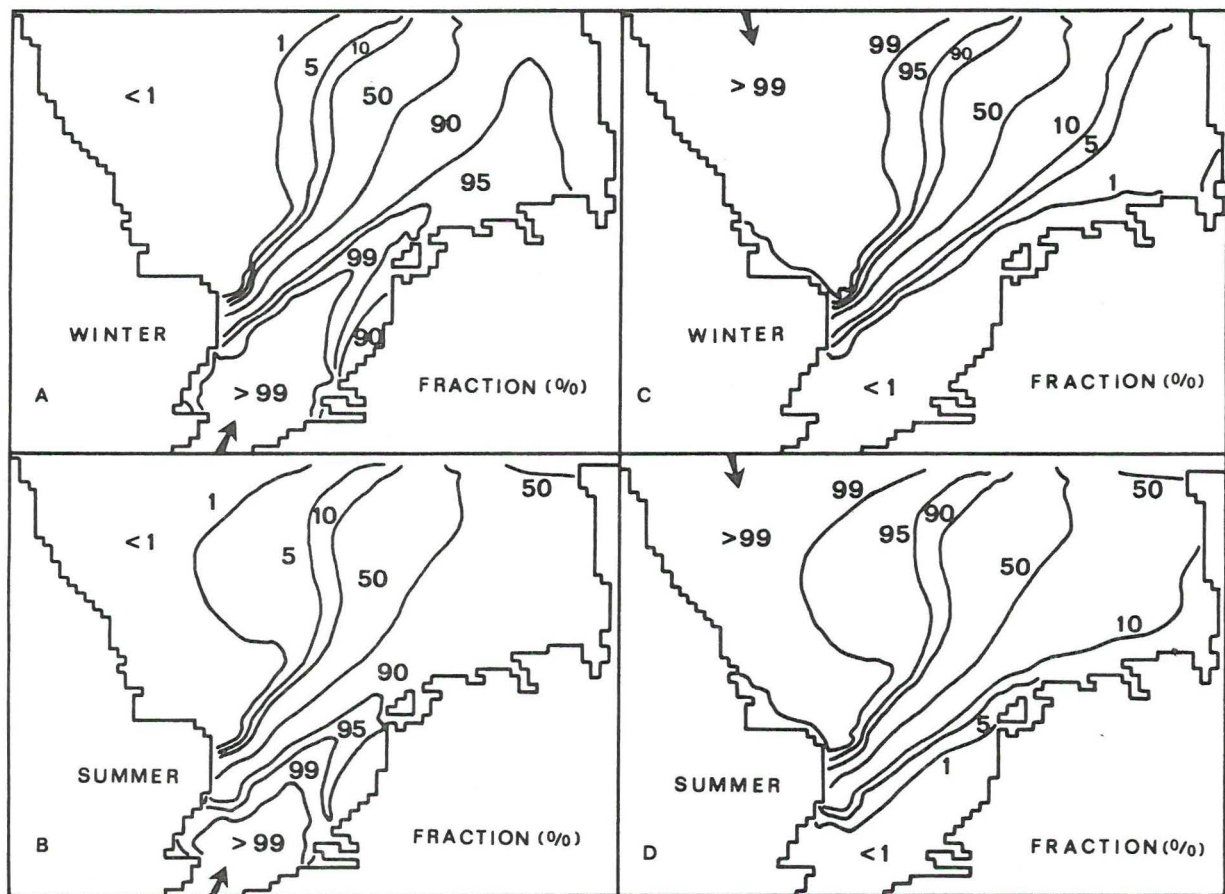


Fig. 3. Computed distribution of English Channel water into the southern North Sea. A: in winter, B: in summer; equally the computed distribution of North Atlantic water into the southern North Sea. C: in winter, D: in summer. Figure reproduced with permission from 'Concept "The Ecology of the North Sea", Part 2: Analysis. Study report for the water-quality plan of the North Sea. Delft Hydraulics Laboratory, Delft, and Environmental dept. Deltadienst-Rijkswaterstaat, Middelburg.'

help identifying the sources, comparisons are made with available data of several French areas (rivers, estuaries and coastal waters), which only receive plutonium from weapons-testing fallout. like the Arcachon basin, the Gironde estuary and the Loire river upstream of the nuclear power plants.

## SAMPLING AND ANALYSIS

### Sampling

Surface aquatic bottom sediments were sampled with a Van Veen grab, from which load the top 0-3 cm layer was selected. A few cores of a length of 1 m were taken in the Haringvliet and the Western Scheldt by divers, while salt-marsh sediments were collected by hand-coring until 20 cm deep.

In order to collect a sufficient quantity of suspended material in waters of sometimes low turbidity, particulate material was recovered by continuous centrifuge-

gation. In this aspect the help of the research vessels "Delta" of the Dutch Rijkswaterstaat and the "Mechelen" of the Belgian Navy was highly appreciated. All sediment samples were oven-dried at 80°C for 7 days, and subsequently grinded and homogenized.

Mussels (Mytilus edulis) were collected by hand near the low tide level of the brackish areas and along the coast. In a few cases, samples were collected from mussel beds of the aquaculture areas in the Eastern Scheldt. In order to facilitate dissection, mussels were shortly cooked for a few minutes. The flesh was subsequently freeze-dried and grinded.

### Analysis

#### Plutonium isotopes

Two slightly different methods were used. At the E.N.S. laboratory (Paris), dried samples were spiked with  $^{242}\text{Pu}$  and  $^{243}\text{Am}$ , and ashed at 550°C during 16 hours. Subsequently radiochemical extraction was carried out according to the procedure of Wong (9), Talvitie (10,11) and Ballestra et al. (12). At the ITAL-RIVM laboratory (Wageningen-Bilthoven),  $^{236}\text{Pu}$  was used as a yield monitor while the analytical steps were essential identical.

After electroplating on stainless steel discs, the samples were measured by alpha spectrometry with Si-Au surface-barrier detectors.

Various intercalibrations with IAEA sediment material SD-N-1 (actually originating from the Western Scheldt) and duplicate analysis of mussel samples by the two laboratories were realized. Observed differences were comparable to errors resulting from counting statistic ( $\pm$  one standard deviation).

#### Gamma emitters

Dried samples were measured at the E.N.S. laboratory (Paris) by non-destructive gamma spectroscopy with a high-purity Ge detector (1.8 KeV resolution and 32% efficiency), placed inside a 1x1x1 m lead shielding of 15 cm thickness, and coupled to a 8000 channel analyzer. All errors reported for radionuclide concentrations are within one standard deviation error

#### Total alpha

In order to determine the background alpha radioactivity in the total samples, caused by mainly the available natural alpha emitters, dried samples were counted by the direct scintillation technique of Hallden and Harley (13). This was carried out at the laboratory at Yerseke.

#### Other parameters

Various basic sedimentary and geochemical parameters were measured in the sediment samples by conventional methods. These include the determination of the



clay fraction, defined as the fraction smaller than 16  $\mu\text{m}$ , carbonates, P.O.C., and Al. Results of the analysis of this latter element were checked using available international standards.

Table III. Range and average concentrations of  $^{239} + ^{240}\text{Pu}$  and the isotopic ratios of  $^{238}\text{Pu}/^{239+240}\text{Pu}$ , as determined in the Dutch Delta and in comparable other region as (average  $\pm$  one standard deviation; number of data (n) in brackets; 1 pCi = 37 Bq).

		$^{239+240}\text{Pu}$		$^{238}\text{Pu}/^{239+240}\text{Pu}$				
	Period	range	average	(n)	range	average	(n)	
1. DUTCH DELTA								
Sediments		0.1 - 63			0.037-0.59			
suspended matters			21 $\pm$ 12	(15)		0.28 $\pm$ 0.13	(14)	
bottom sediments			12 $\pm$ 11	(43)		0.21 $\pm$ 0.14	(40)	
marsh sediments			17 $\pm$ 13	(35)		0.11 $\pm$ 0.09	(29)	
Mussels								
soft parts		0.15- 4.4	1.2 $\pm$ 1.1	(32)	0.12 -0.42	0.26 $\pm$ 0.07	(30)	
shells		0.03- 0.27	0.1 $\pm$ 0.06	(13)	<(0.2-0.3)	-		
2. FALLOUT AREAS (40-50°N)								
Sediments		1978-1983						
French rivers (a)		2 - 7	6.7 $\pm$ 3.3	(34)	-	$\leq$ 0.035	( 3)	
French coasts		1 - 32	16 $\pm$ 10	( 9)	0.036-0.06	0.044 $\pm$ 0.008	( 9)	
Mussels (soft parts)								
SW France (b)		1975						
Mediterranean (c, g)		1976-1977	1 - 5	2.0 $\pm$ 1.6	( 6)	0.035-0.079	0.054 $\pm$ 0.019	( 4)
W coast USA (d)		1977-1978	0.3 - 4.6	0.8 $\pm$ 0.5	(16)	0.03 -0.10	0.058 $\pm$ 0.026	( 7)
3. LA HAGUE AREA ( $\pm$ 100 km)								
Sediments		1980-1984						
coarse		1 -130	24 $\pm$ 41	( 9)	0.15 -0.44	0.29 $\pm$ 0.09	( 9)	
fine		17 -113	55 $\pm$ 35	(12)	0.16 -0.30	0.24 $\pm$ 0.05	(13)	
Mussels		1978-1980						
soft parts (e)		2 - 20	11 $\pm$ 5	(11)	0.28 -0.73	0.48 $\pm$ 0.12	(11)	
4. SELLAFIELD AREA (Irish Sea) (f, g)								
Sediments		1979-1982						
sands		100 -500	-		0.18 -0.22	-		
silts		10 <sup>3</sup> - 10 <sup>5</sup>	27000	(27)	0.21 -0.27	0.23 $\pm$ 0.02	(26)	
Mussels		1979-1982						
soft parts		(0.7-3.2) $\times$ 10 <sup>4</sup>	(2 $\pm$ 1) $\times$ 10 <sup>4</sup>	( 5)	0.24 -0.26	0.25 $\pm$ 0.01	( 5)	

(a) Loire river, upstream nuclear power plants (15)

(b) Guary & Fraizier (total Pu) (16)

(c) after Ballestra (17)

(d) after Goldberg et al. (18)

(e) after Germain et al. (depurated) (19)

(f) after Hunt (20)

(g) assuming wet/dry weight = 8

## RESULTS

### General characteristics of sedimentary material

The sediment samples, collected in the Delta, consisted purposely of fine-grained material, except those from areas where only sandy sediments were available. Except for the afore mentioned samples, the concentration of the clay fraction in these samples averaged from 25 to 35% for the bottom sediments and around 45% for the suspended material. Carbonates, indicating a mixture of marine and riverine sediments (14), were present in all types of samples ( $10 \pm 5\%$   $\text{CaCO}_3$ ). P.O.C. (particulate organic carbon) averaged between 3 and 4% (5.7% in suspended matter), but higher values were found in riverine sediments, especially in those of the Rhine and Meuse (5 to 9%). The aluminum averaged between 3.4 and 3.8% for the fine-grained samples.

With the exception of one sample from the Wadden Sea, the coastal sediments collected north of Hoek van Holland towards the north-east, were mainly sands, having lower concentrations of clays (below 6%), P.O.C. (0.1-2%) and Al (1-2%).

The salinity of the interstitial waters were for riverine sediments around 0.5‰, increasing in seaward direction to 30‰. There was a general tendency of higher salinities in the interstitial waters than as observed in the overlying waters. The pH of the interstitial waters showed little variations, from 7.0 to 7.3 in the Scheldt and Rhine-Meuse area to about 8.2 for the coastal regions.

### Average plutonium concentrations

The results of all plutonium isotope measurements in the Dutch Delta and coastal areas are summarized in Table III-1, along with comparable data from other regions as found in the literature (Table III-2 to 4).  $^{239+240}\text{Pu}$  concentrations in sediments are rather scattered due to the wide diversity of sampled sedimentary material. Concentrations in sandy deposits are systematically lower than those in fine-grained sediments. Nevertheless it was possible to find even for these concentrations (not yet normalized to aluminum) some trends. For bottom, salt-marsh, and suspended sediments, the average values are higher than those of mussels. The values of the flesh of mussels are one order of magnitude higher than of the shells (Fig. 4).

$^{238}\text{Pu}$  concentrations in the suspended matter, bottom sediments and salt-marsh sediments averaged around  $6.0 \pm 3.8$ ,  $2.8 \pm 3.7$  and  $1.5 \pm 1.0$  pCi/kg, respectively. French river and coastal sediments, collected in areas where  $^{238}\text{Pu}$  only originates from atmospheric fallout, have a mean concentration of  $0.69 \pm 0.66$  pCi/kg, all for the same period of 1979-1984. Since both  $^{238}\text{Pu}$  and  $^{239+240}\text{Pu}$  are supposed to

have the same behaviour, a comparison of data between different areas is better understood using their concentration ratios. These ratios decrease from 0.26-0.28 in suspended matter and mussel flesh to 0.21 in bottom deposits and 0.11 in salt-marsh sediments and cores until 20 cm depth (Fig.4).

A few older sediment samples of the Eastern and Western Scheldt, Lake Veere, the Haringvliet and the original Grevelingen estuary have been collected between the years 1961 and 1968. Their  $^{238}\text{Pu}/^{239+240}\text{Pu}$  ratios are lower (0.081 are confirmed by measurements of the  $^{238}\text{Pu}/^{239+240}\text{Pu}$  ratios in the sub-surface sediments of two cores (20-40 cm depth) of the Haringvliet basin and the Western Scheldt estuary at Waarde. The ratios range from 0.04 to 0.09 and are thus identical to the ratio of "older" sediments.

Total alpha radioactivity has been measured in most of the sediment samples. No significant difference is observed for the various types of sediments, and an average value could be determined of  $(6 \text{ to } 9) \times 10^3 \text{ pCi/kg}$ . This specific radioactivity is approximately 3 orders of magnitude higher than that of both plutonium isotopes, and has to be attributed to isotopes of the uranium and thorium series.

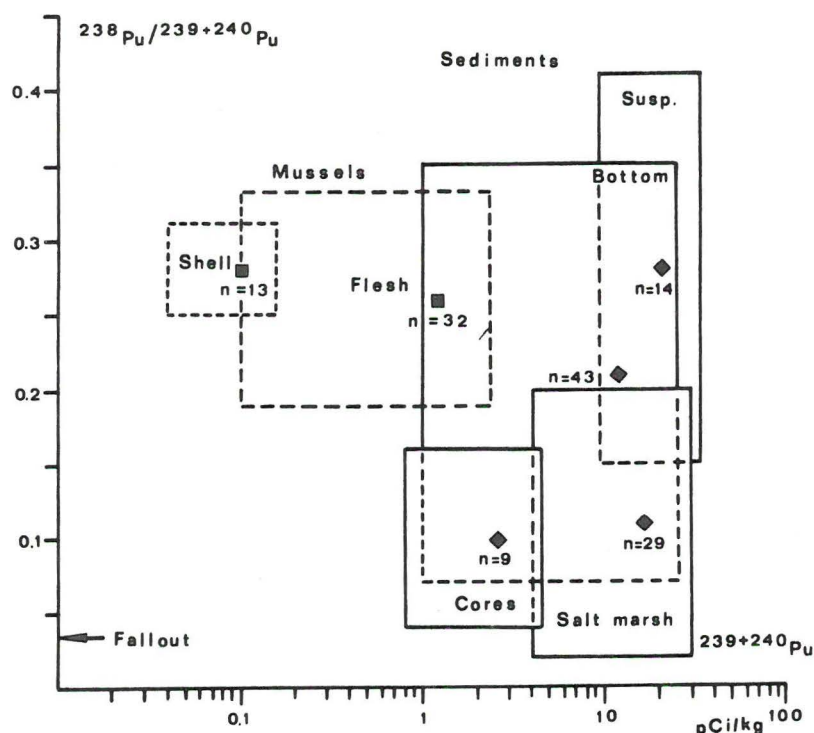


Fig. 4. Average data of plutonium isotopic ratio as related to  $^{239+240}\text{Pu}$  concentration in sediments and mussels (*Mytilus edulis*) in the Dutch Delta. Dimensions of each box is average  $\pm$  one standard deviation; n = number of samples analyzed. (1979 - 1984).



### Normalization of concentrations

It is known that the concentration of trace metals in sediments correlates well with that of clays or clay minerals. This general statement is, however, not always supported if a detailed investigation is carried on this behaviour of natural trace metals in ocean sediments. Duursma et al (21) showed that for 18 trace elements and 33 major ocean sediments some significant correlations existed, but there were equally element specific correlations also with other components than only clay minerals. Nevertheless in terms of pollution research, where adsorption proceeds incorporation, it might be convenient to normalize the concentration relative to the clay fraction. Instead of using the clay content as a parameter, this can also be done by normalizing the concentrations to an element like potassium or aluminum, which for a number of sediments significantly correlate with the clay fraction.

The use of Al as a tracer of the clay fraction has been discussed by Elbaz-Poulichet et al (22), and a correlation between plutonium and aluminum has been found in various French estuaries (23,24). Also in the Dutch Delta bottom sediments the Al contents clearly correlate with the clay percentages and the Al/clay ratio is rather constant ( $0.12 \pm 0.03$ ; %/%).

The correlation between Pu and Al concentrations can only be established in an area where the Pu input is rather constant in time and where the major exchange processes between the particulate and dissolved phases are in some sort of equilibrium. Fig. 5 shows the results obtained with freshwater fine-grained bottom and suspended sediments, sampled from 1979 to 1982 in the Delta. Despite obvious scatter of the data, a significant correlation is observed.

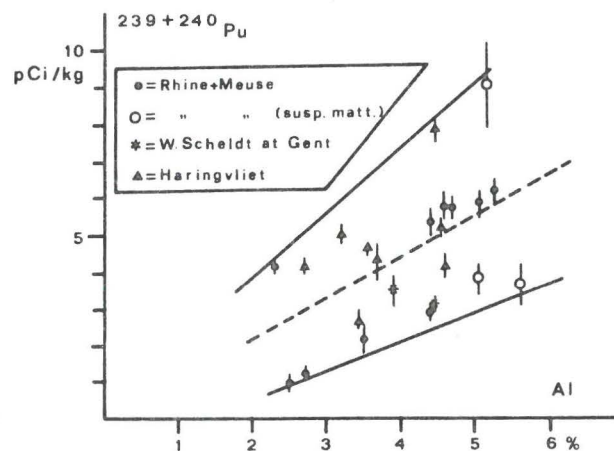


Fig. 5. Correlation of  $^{239+240}\text{Pu}$  with Al concentrations in freshwater sediments of the Dutch Delta (1979 - 1982).  
 ----- = regression line  $\text{Pu} = f(\text{Al})$ , ————— = range.

Therefore the use of the Pu/Al ratio instead of absolute Pu concentration is of great help to differentiate the concentration variations, resulting essentially from the variations of sediment composition, from those due to other causes like local input of Pu and other radionuclides. Referring to the above-mentioned information, it might be clear that the use of such normalization does not mean that plutonium is necessarily fixed on or inside of the aluminum-silicates. The prevailing association of Pu with clay minerals does not yet allow an identification of the particular fraction of the particles to which Pu is associated, neither to determine the exact nature of the association(s).

#### Plutonium in river sediments

The average  $^{239+240}\text{Pu}$  concentration in the Rhine-Meuse river system is  $4.0 \pm 2.6$  pCi/kg. The concentrations remain identical in the downstream sediments of the Hollands Diep and the Haringvliet. Similar results have been determined in the Scheldt river near Gent (km 152-160), 3.1-3.5 pCi/kg. The average  $^{239+240}\text{Pu}/\text{Al}$  ratio in all these samples is  $112 \pm 43$  pCi/kg Al.

The  $^{238}\text{Pu}/^{239+240}\text{Pu}$  ratio in the upper Scheldt is 0.038, whereas the ratio in the Rhine-Meuse system is higher ( $0.14 \pm 0.07$ ).

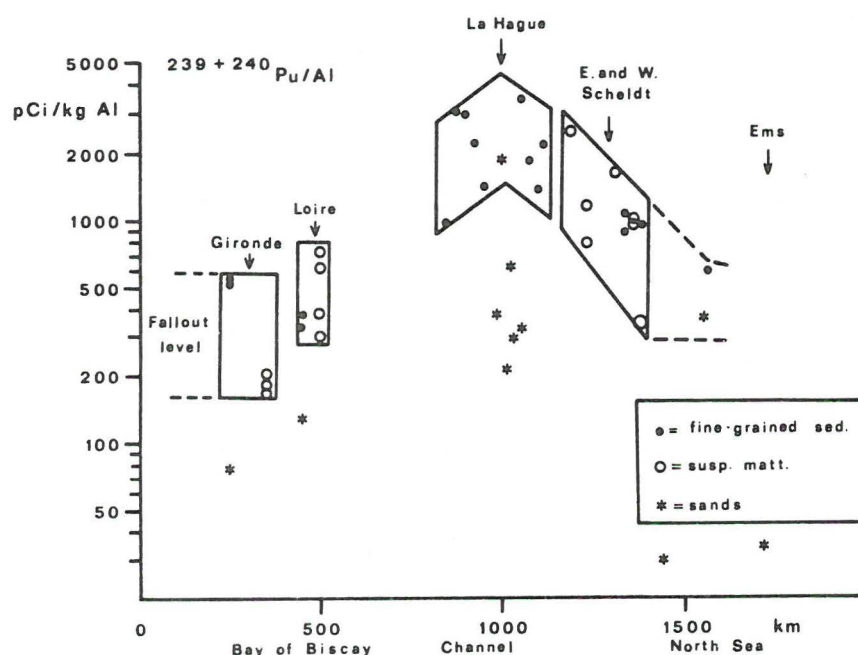


Fig. 6. Normalized Pu concentrations in coastal sediments of north-west Europe (1978 - 1984). (This study and 15).

### Plutonium in estuarine and coastal sediments

In fine-grained bottom sediments and marine suspended matter of the Delta and adjacent coast, both the absolute and normalized  $^{239+240}\text{Pu}$  concentrations are systematically higher than in the rivers :  $30 \pm 10$  pCi/kg, and  $1150 \pm 600$  pCi/kg Al, respectively. It is interesting to examine these results at a larger scale, considering a gradient in the plutonium distribution along the coast of north-western Europe (Fig 6). Normalized  $^{239+240}\text{Pu}$  concentrations in the sediments of south-west France, where Pu originates from fallout only, were the lowest. An increase by one order of magnitude is observed in the English Channel, followed by a rather regular decrease along the Dutch coast. As indicated, Pu concentrations in sands are much lower, but the  $^{239+240}\text{Pu}/\text{Al}$  ratio showed a similar pattern, from 80-130 pCi/kg Al in south-west France to 200-2000 pCi/kg Al near La Hague and scattered values averaging 150 from Hoek van Holland to the Ems estuary.

The distributions of  $^{239+240}\text{Pu}$  in the soft parts of the mussels are not essentially different (Fig. 7). The only available value in south-west France is not very different from the values reported from other fallout areas in the world (Table III). Again a ten fold increase is observed near La Hague, followed by a rapid decrease in the North Sea.

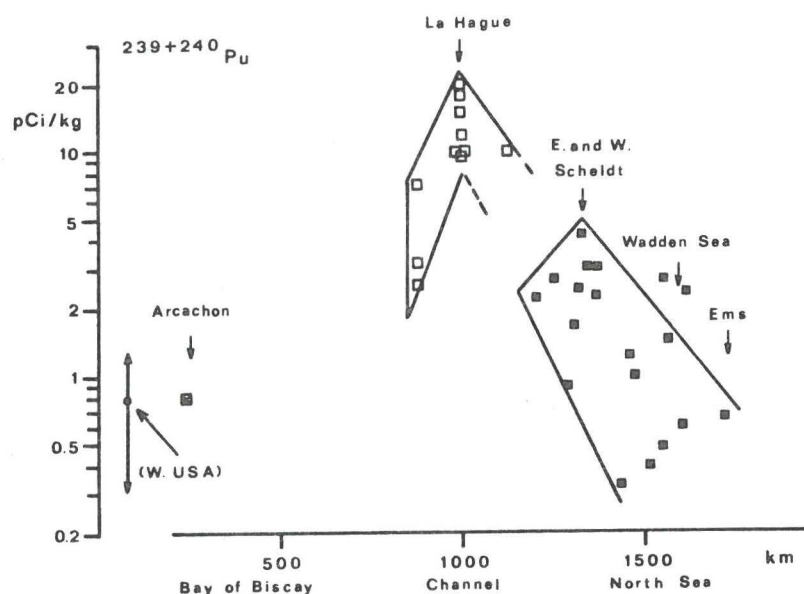


Fig. 7.  $^{239+240}\text{Pu}$  concentrations in flesh of mussels (*Mytilus edulis*). At Arcachon from Guary and Fraizier (16) as total Pu. La Hague values are from Germain et al (19) (depurated samples). Average concentration and standard deviation in mussels from the western USA coasts are given for comparison (after Goldberg et al (18)).



$^{238}\text{Pu}/^{239+240}\text{Pu}$  ratios in sediments are presented in Fig.8. Comparing the data of south-west France and those of La Hague clearly show the nuclear contamination of the English Channel, but, contrary to the  $^{239+240}\text{Pu}$  concentrations, this ratio decreases very slowly towards the North Sea. In mussel flesh the Pu isotopic ratio is higher than in coastal sediments, but the north-east decrease is similar.

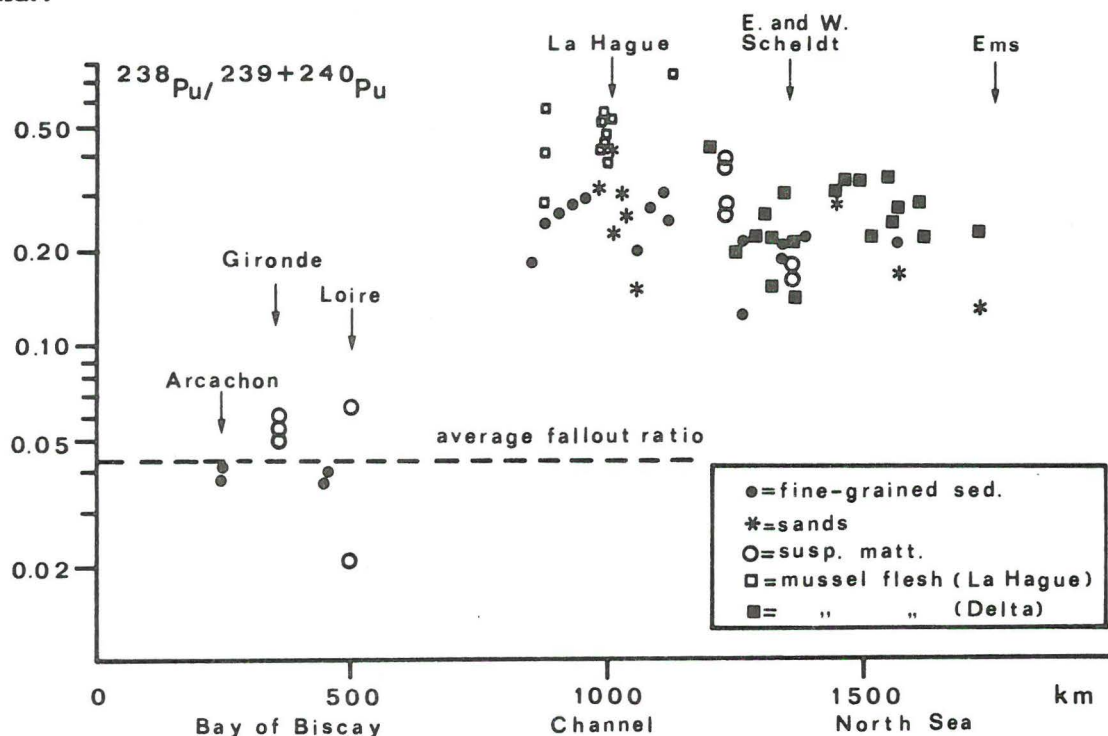


Fig. 8. Isotopic  $^{238}\text{Pu}/^{239+240}\text{Pu}$  concentration ratios (by activity) in coastal sediments and mussel flesh of north-west Europe (1978 - 1984).

### Gamma emitters

Although a variety of gamma emitters has been systematically analysed, in this paper only attention is given to the distribution of  $^{60}\text{Co}$  in sedimentary material of the Western Scheldt. The  $^{60}\text{Co}$  data are essential for understanding the plutonium distribution, in particular with reference to its possible sources. So far the  $^{60}\text{Co}$  data are presented in Fig. 13, later on in this paper.

### DISCUSSION

#### Plutonium-239+240, average concentrations

Average  $^{239+240}\text{Pu}$  concentrations in the sediments of the Rhine-Meuse-Scheldt delta and coastal regions north east to the Ems estuary are low, (12-21 pCi/kg), very low as compared to the natural alpha radioactivity background, which is a factor  $10^3$  higher (6 to 9) $\times 10^3$  pCi/kg). Both the range and average values of

$^{239+240}\text{Pu}$  in the Delta sediments do not seem to present a clear evidence of nuclear industrial contamination. This is, however, different if the  $^{239+240}\text{Pu}$  concentrations are normalized to aluminum. Then there are significant differences which lead to other conclusions. The normalized concentrations, found in the sediments of the mouth of the Western and Eastern Scheldt estuaries are about three times higher than those of the sediments in south-west France, where plutonium can only be attributed to weapons-testing fallout. Even higher values were determined in the suspended matter collected near the Strait of Dover Fig. 6). At the north-east limit of the study area, normalized  $^{239+240}\text{Pu}$  concentration in a mud sample of the Wadden Sea was still slightly higher than the average fallout value of the south-west France sediments.

These data show that with respect to fallout, there should be one or more additional sources of  $^{239+240}\text{Pu}$  for the Delta, the importance of which being at least equal to the fallout input. Further north-eastwards, the impact of these additional sources decreases and becomes nearly undetectable. The distribution of  $^{239+240}\text{Pu}$  in sand confirms this conclusion. A similar pattern is observed with concentrations in mussel flesh, although the decrease is more pronounced. This difference might result from the ingestion by mussels of coarser sediments with low plutonium contents in the north-eastern part of the Dutch Coast.

#### Plutonium-239+240 in rivers

When freshwater sediments are considered, the  $^{239+240}\text{Pu}$  of the Rhine-Meuse system, the Haringvliet and Hollands Diep basin and the Scheldt near Gent show a great deal of similarities. The corresponding average  $^{239+240}\text{Pu}/\text{Al}$  ratios ( $112 \pm 43$  pCi/kg Al) are very close to the average fallout values found in France in the suspended matter of the Garonne and Loire for the period 1978 to 1983 ( $93 \pm 35$  pCi/kg Al) (15). Thus on a statistical basis,  $^{239+240}\text{Pu}$  transported by rivers to the Delta is mainly land run-off fallout plutonium.

#### Average values of plutonium isotopic ratios

The average  $^{238}\text{Pu}/^{239+240}\text{Pu}$  ratios found in recently deposited sediments and mussels of the Delta and the North Sea coast, are higher than those of material only contaminated by fallout (Table III). The highest ratios were found in suspended matter of the Strait of Dover (0.40). Lowest values were determined in salt-marsh deposits with ratios of 0.11. Studies undertaken in 1975 by Murray and Kautsky (25) have shown that the  $^{238}\text{Pu}/^{239+240}\text{Pu}$  ratios in waters off the Dutch Delta were much lower than the present data ( $0.15 \pm 0.04$ ). These data are in agreement with



those of some 'old' Delta samples, collected in the period 1961 to 1968. However, these samples had systematically slightly higher ratios (0.08) than fallout, but lower than those of the recently collected samples of the period 1979-1984.

It is therefore likely to conclude that the sediments with intermediate ratios (bottom and salt-marsh sediments) are formed by mixing of recent and older deposits. This is particularly true for the salt marshes. In the river sediments, the Pu isotopic ratio in the Scheldt river near Gent is identical to the fallout value, but the ratio is significantly higher in the Rhine-Meuse system.

All these average data indicate that there is a recent input of  $^{238}\text{Pu}$  into the Delta region from the North Sea, while additionally a limited amount of  $^{238}\text{Pu}$  is introduced by the Rhine-Meuse rivers, reflecting the presence of various nuclear installations in their upstream system, (Table II). Riverine  $^{238}\text{Pu}$  is partially trapped in the Hollands Diep-Haringvliet basin, where in spite of discharge to the sea in wet seasons, sedimentary material is not mixed with material of marine origin, (the Haringvliet sluices only discharge at low tide). The isotopic ratios are here  $0.15 \pm 0.05$ , (Fig. 11).

The distribution of  $^{238}\text{Pu}$  along the North Sea coast (Fig. 8) indicates a contamination of the English Channel by nuclear reprocessing plants. Although high isotopic ratios in Fig. 8 were actually measured in sediments and mussels, collected at a few km distance from La Hague and therefore are directly related to the effluent composition of the reprocessing plant of La Hague, the possibility that further north-eastwards part of the  $^{238}\text{Pu}$  may also originate from the Sellafield reprocessing plant cannot be disregarded. As given in Fig. 3, the main watermass transport in the south-west North Sea is regulated by the input of Channel water, while the water of Atlantic origin reaches increasingly the northern coastal regions. The major pathway of Sellafield radionuclides to the North Sea is by the northern Irish Sea and around Scotland (26), but the actual amount of plutonium escaping the Irish Sea, in particular southwards to the Channel is still poorly documented. Even if the return flow southward out of the Irish Sea is 'very small and probably sporadic' (26), a small percentage of Sellafield radionuclides entering eventually the Channel would not be obviously negligible as compared to the much smaller discharges by the La Hague plant. The  $^{238}\text{Pu}/^{239+240}\text{Pu}$  ratio in sediments in the vicinity of both reprocessing plants are very similar (Table III) and it cannot be used to distinguish both sources in the study of environmental samples.

Contrary to the  $^{239+240}\text{Pu}$  distribution, the decrease of  $^{238}\text{Pu}$  contamination in sediments and mussels is rather small between the English Channel and the Ems estuary. The northwards distribution of  $^{238}\text{Pu}$  along the coast of the North Sea is



difficult to distinguish. Older studies ( 25, 27 ) have concluded that in the year 1975 the  $^{238}\text{Pu}$  in the German Bight was due to atmospheric fallout. We have seen, however, that the situation has evolved since, at least along the Dutch North Sea coast. Measurement in the Kattegat (28) did not show an influence of transuranics from reprocessing plants, while equally the  $^{239+240}\text{Pu}$  concentrations in unfiltered seawater collected between Norway and Spitzberg could be solely explained as being caused by fallout (29). Recent studies in the North Sea have shown that  $^{238}\text{Pu}/^{239+240}\text{Pu}$  ratios in (unfiltered) sea water collected off the Norwegian coast range from 0.12 to 0.17 (30), allowing the authors to conclude that at  $61^{\circ}30' \text{ N}$  latitude still 38% of  $^{238}\text{Pu}$  could be attributed to contamination by Sellafield reprocessing plant effluents. This result is consistent with a northwards extrapolation of the data presented in Fig. 8.

### Plutonium behaviour

The significant differences of plutonium concentrations between river and coastal sediments raise questions concerning the behaviour of this radionuclide in estuarine systems. The plutonium distribution in the two major estuarine systems of the Delta will therefore be examined in more detail.

The common feature is a regular increase of the normalized concentrations in recent sediments and in suspended matter in the range from river to sea (Fig. 9 and

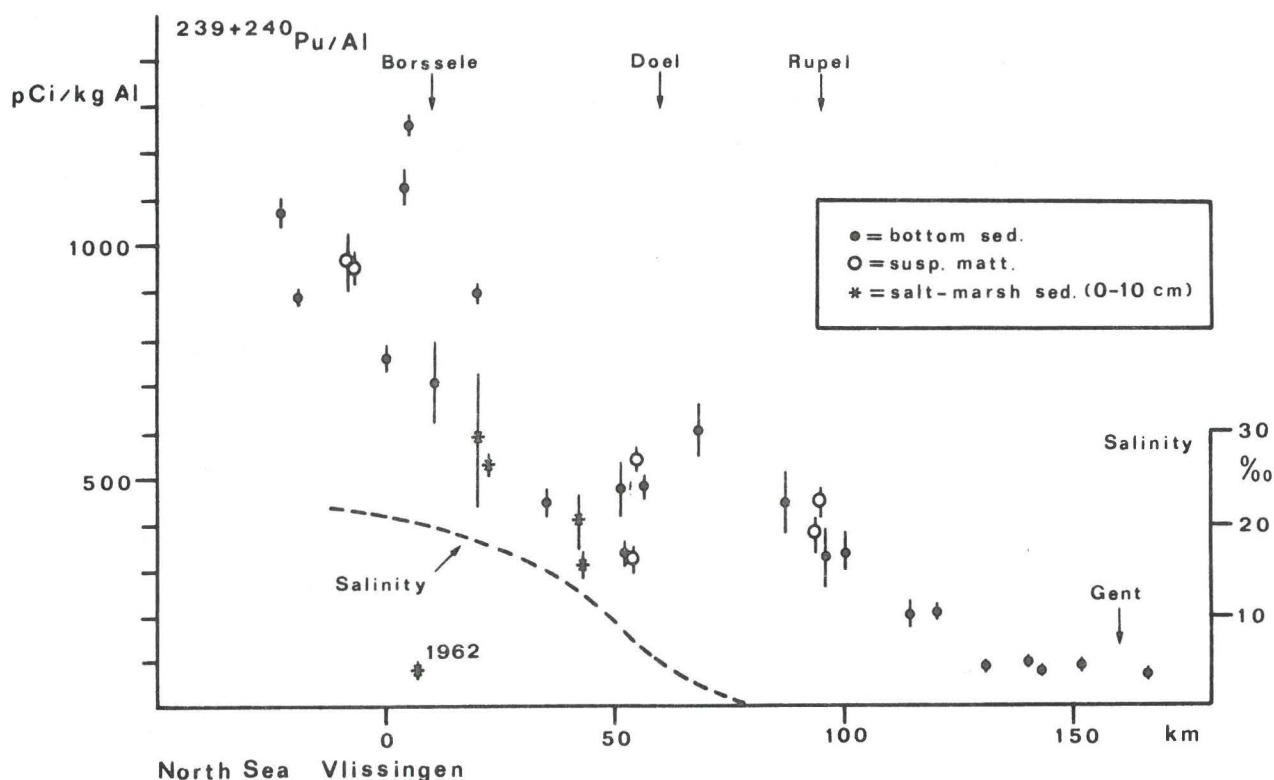


Fig. 9. Normalized Pu concentrations versus distance to sea in recent sediments of the Western Scheldt estuary (1979 - 1984). The salinity is the average concentration in interstitial water. Salt-marsh sample near Vlissingen was collected in 1962.

10). This result confirms earlier findings in the Gironde and Seine estuaries (23, 24) and recent measurements in the Loire estuary. Thus seaward increase of normalized plutonium concentrations is probably a general pattern in partial to well-mixed estuaries.

In the Rhine-Meuse-Eastern Scheldt estuary (Fig. 10), this concentration increase is observed in the brackish-water sediments of the Eastern Scheldt, but data are missing in the lower salinity region up to the Hollands Diep.

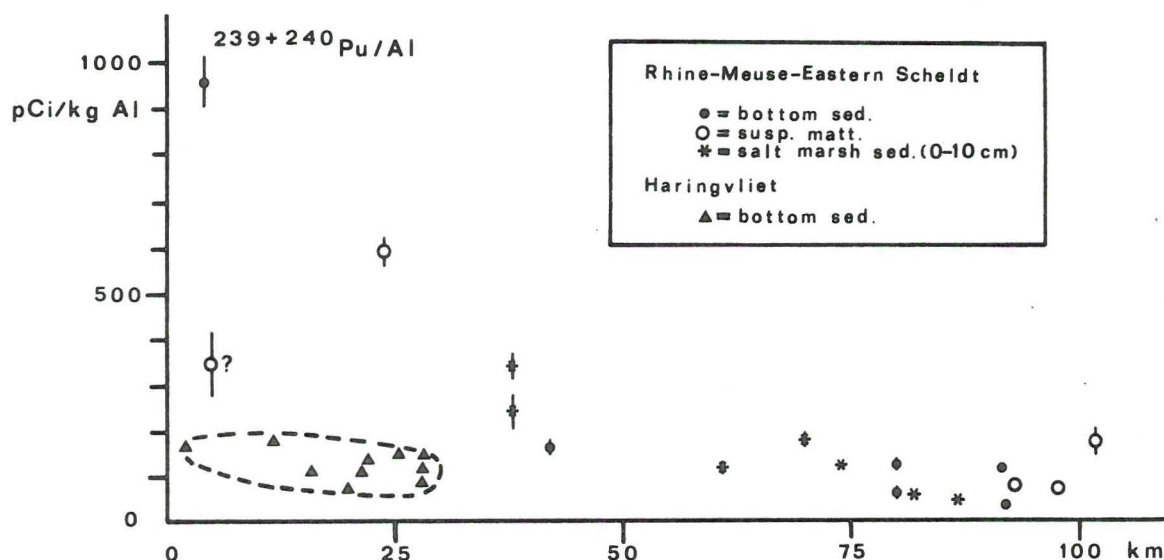


Fig. 10. Normalized Pu concentrations versus distance to the sea in recent sediments of Rhine-Meuse-Eastern Scheldt estuary (1979 - 1984). Data from the freshwater enclosed basin Haringvliet are given for comparison.

Particular attention has to be given to the Western Scheldt estuary, which is better documented and sampled than the Rhine-Meuse-Eastern Scheldt system. The increase of  $^{239+240}\text{Pu}$  normalized concentrations is first observed in the freshwater sediments (near km 120) and then continues through the area near km 80, where a permanent dissolved oxygen depletion usually is observed (30), until the coastal waters are reached. Concentrations in the Strait of Dover are still higher ( $1600 \pm 800$  pCi/kg Al). This distribution is likely to be explained by an input of enriched marine sediment into the estuary. Whether this marine sediment is completely of marine origine is another point, since Salomons and Mook (31) determined by  $^{13}\text{C}/^{12}\text{C}$  ratios of P.O.C. large fractions of continental organic matter in fine-grained material of the Western Scheldt mouth and adjacent coast.

Sediment mass balances (1, 2) have underlined the importance of landward transport of particulate matter from the outer reaches of the estuary towards the zone near Antwerp (km 60-85), where a net sedimentation is observed. This process has been confirmed by hydrodynamical modelling by Nihoul and Smitz (30, this volume). Further confirmation is obtained with  $^{15}\text{N}$  studies by Mariotti et al (31),

which show that in the winter period the suspended matters consist of a mixture of terrigenous and marine particles up to km 70, (continuous dredging is required to keep the gullies at a certain depth). Almost all samples analyzed for plutonium, were in fact collected during this winter period (Febr. to April). Our data show that plutonium-enriched particles may be transported much further landward, well into the freshwater zone up to km 120.

The exact enrichment process is still unknown. In the absence of a significant input of particles like in the Gironde estuary, a plutonium increase has there been ascribed to the uptake of marine dissolved plutonium by the brackish-water suspended matter (22, 23, 24). In the Western Scheldt estuary, it is not known if the particles which 'scavenge' dissolved plutonium are the detrital particles supplied by the river (and later retransported landward) or the 'marine' particles of the North Sea.

Dissolved (by filtration) marine  $^{239+240}\text{Pu}$  concentrations in the La Hague region are 1.3-6.8 fCi/l (19). In the water of the North Sea in front of the Delta, average total (particulate + dissolved) concentrations were  $0.81 \pm 0.34$  fCi/l in 1980-1982 (34). All these concentrations are higher than those of the coastal waters of the Bay of Biscay (0.1-0.2 fCi/l; dissolved) near the Gironde estuary (23). The seaward increase of normalized  $^{239+240}\text{Pu}$  concentrations in the Western Scheldt sediments is by a factor 10, whereas it is only 2.5 in the Gironde estuary. This plutonium enrichment of marine fine-grained sediments probably reflects the dissolved concentrations, as might be expected.

#### Origin of plutonium $^{238}$

In the Rhine-Meuse-Eastern Scheldt estuary,  $^{238}\text{Pu}/^{239+240}\text{Pu}$  ratios increase seaward, reaching 0.22 in sediments and 0.31 in mussel flesh (Fig. 11). The Western Scheldt estuary shows a different pattern with a pronounced peak near km 100 (Fig. 12), where this ratio reaches 0.5-0.6, a value nowhere observed in the Delta region. These data clearly point to the occurrence of an additional  $^{238}\text{Pu}$  source. Potential sources of artificial radionuclides are only nuclear installations at Mol, Doel and Borssele. In the Western Scheldt estuary sediments are transported over a long distance so that the location where the maximum radionuclide concentration occurs, does not necessarily need to correspond with the area where effluents are discharged in the system. In order to clarify this problem, attention has been given to  $^{60}\text{Co}$ , a major component of PWR power plant effluents.

This gamma emitter has been supplied to the Western Scheldt since 1973 at Borssele and 1974 at Doel (8). Assuming that  $^{60}\text{Co}$  did not escape from the estuary,



the total activity after decay correction ( half-life 5.2 yr) would amount to about 11 Ci in 1981, most of which supplied by the power plants of Doel. Recent  $^{60}\text{Co}$  discharges near Mol in a small tributary of the Rupel river amounted 0.22 and 0.27 Ci in 1979 and 1980, respectively (after De Clerq-Versele et al, (35) this volume) and Metayer-Piret et al (36). During this period a total of 1.3 and 0.9 Ci of  $^{60}\text{Co}$  has been discharged into the Western Scheldt estuary by the three mentioned sources, 62-70% being attributed to the Doel power plant.

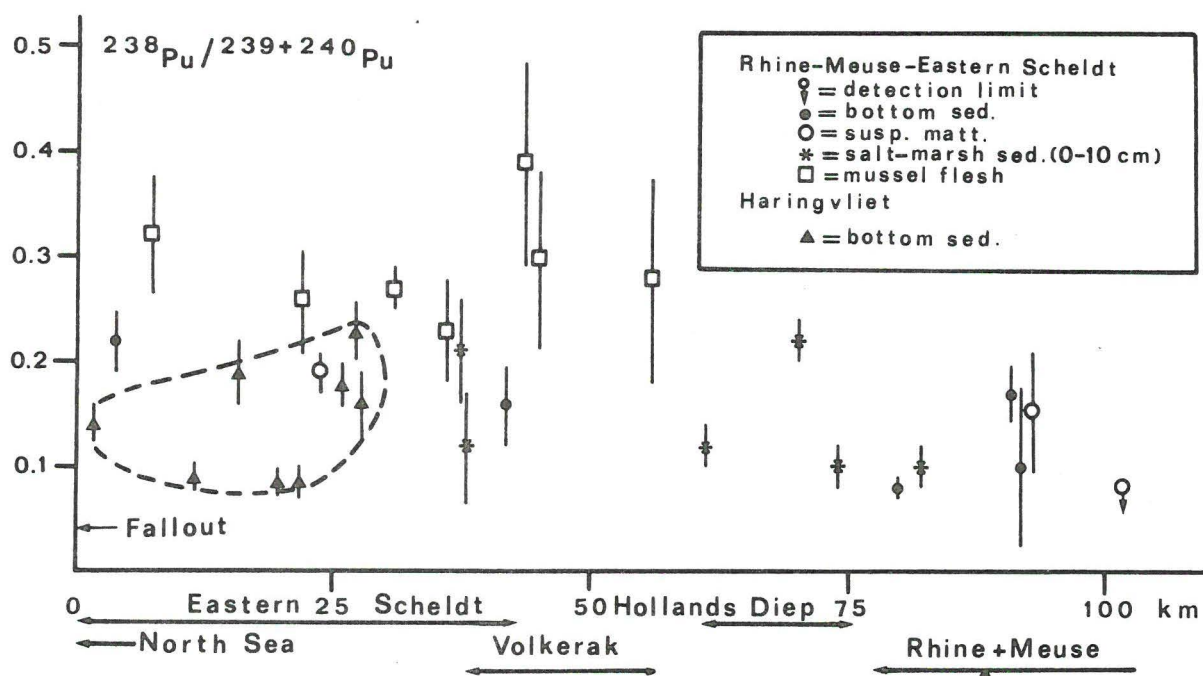


Fig. 11. Isotopic  $^{238}\text{Pu}/^{239+240}\text{Pu}$  concentration ratios in recent sediments and mussels (only *Mytilus edulis* from brackish regions) from the Rhine-Meuse-Eastern Scheldt estuary. Haringvliet data are given for comparison.

The  $^{60}\text{Co}$  distribution (Fig. 13) shows a prominent peak near km 60 (at Doel), where concentrations reach 12000 pCi/kg Al. They decrease in both landward and seaward directions. The sediments of the English Channel show a variable  $^{60}\text{Co}$  contamination level, due to effluents from reprocessing plants and a number of nuclear power stations. Normalized concentrations in suspended matter of the Strait of Dover are  $800 \pm 460$  pCi/kg Al.

Locally these concentrations might reach 2200 pCi/kg Al as in the Aa estuary near Gravelines power plant. The concentrations in the Dutch Delta are, however, always very low ( $80 \pm 50$  pCi/kg Al), so that input from the sea towards the Western Scheldt is very limited. These data indicate that the peak near km 60 can essentially be attributed to the discharge of the Doel plants.

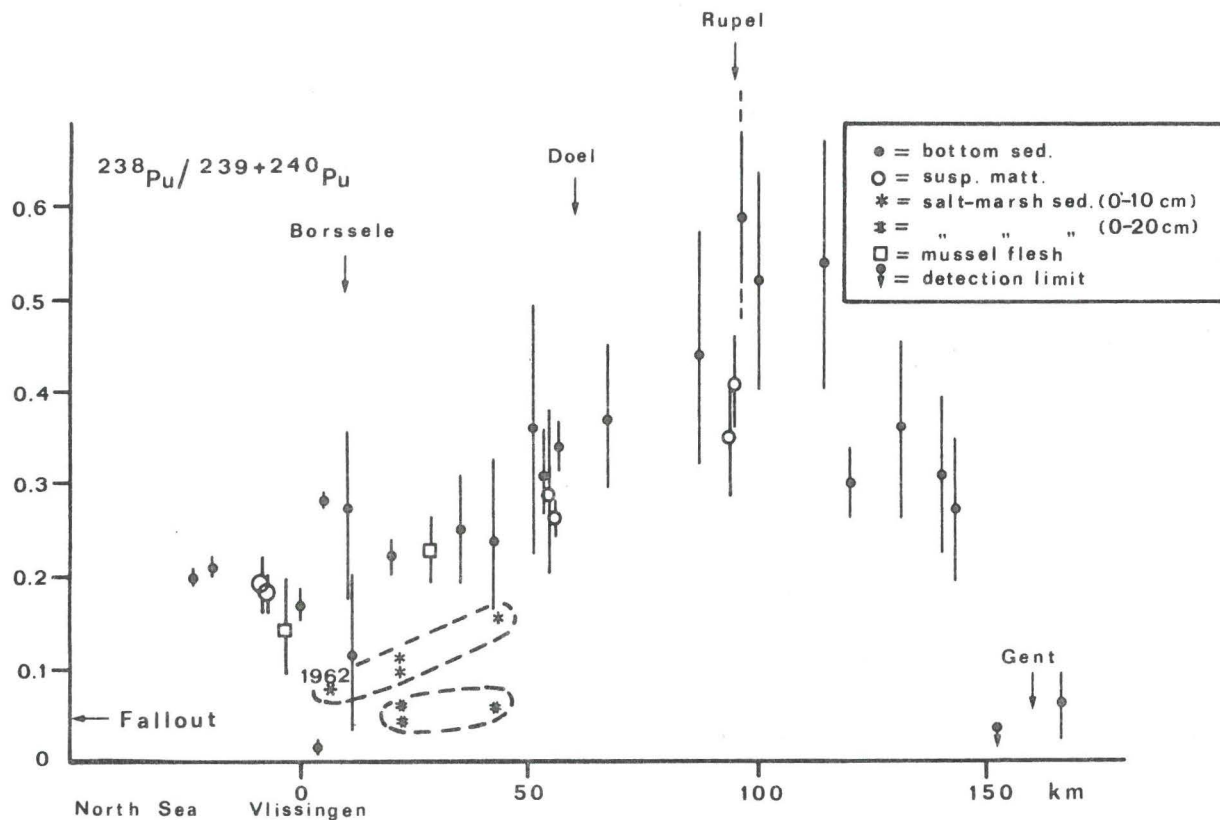


Fig. 12. Isotopic  $^{238}\text{Pu}/^{239+240}\text{Pu}$  concentration ratios in sediments and mussels of the Western Scheldt estuary.

Although the location of the  $^{60}\text{Co}$  peak in the bottom sediments is not sharply defined, it does not correspond with the highest  $^{238}\text{Pu}/^{239+240}\text{Pu}$  ratios. In consequence, the likely major source of excess  $^{238}\text{Pu}$  is probably not the Doel power-plants effluent, but the nuclear installations at Mol, its drainage entering the Scheldt at km 100 through the Rupel river.

#### Estimated sources and quantities of plutonium in the Western Scheldt

A tentative estimate is made of the annual input of plutonium isotopes in the Western Scheldt estuary (Fig.14), assuming that: (i) the concentrations measured between km 50 and km 100 in the surface layer of the bottom deposits and in the suspended matter are representative of the sediments entrapped in this major shoaling area, (ii) these concentrations are not biased by reworking with old sediments and (iii) plutonium is fixed rapidly by sediments and post-depositional migration in the estuary is negligible, (37,38). In fact, several samples of salt-marsh sediments were collected in 1961-1962 in the Haringvliet basin and Lake Veere, having low interstitial water salinities (0.3-3 ‰). Normalized  $^{239+240}\text{Pu}$  concentrations in these samples ranged from 17 to 370 pCi/kg Al, which is of the same order of magnitude as those of sub-surface layers in two cores taken in the Haringvliet and Western Scheldt. These values are similar to those found in recent

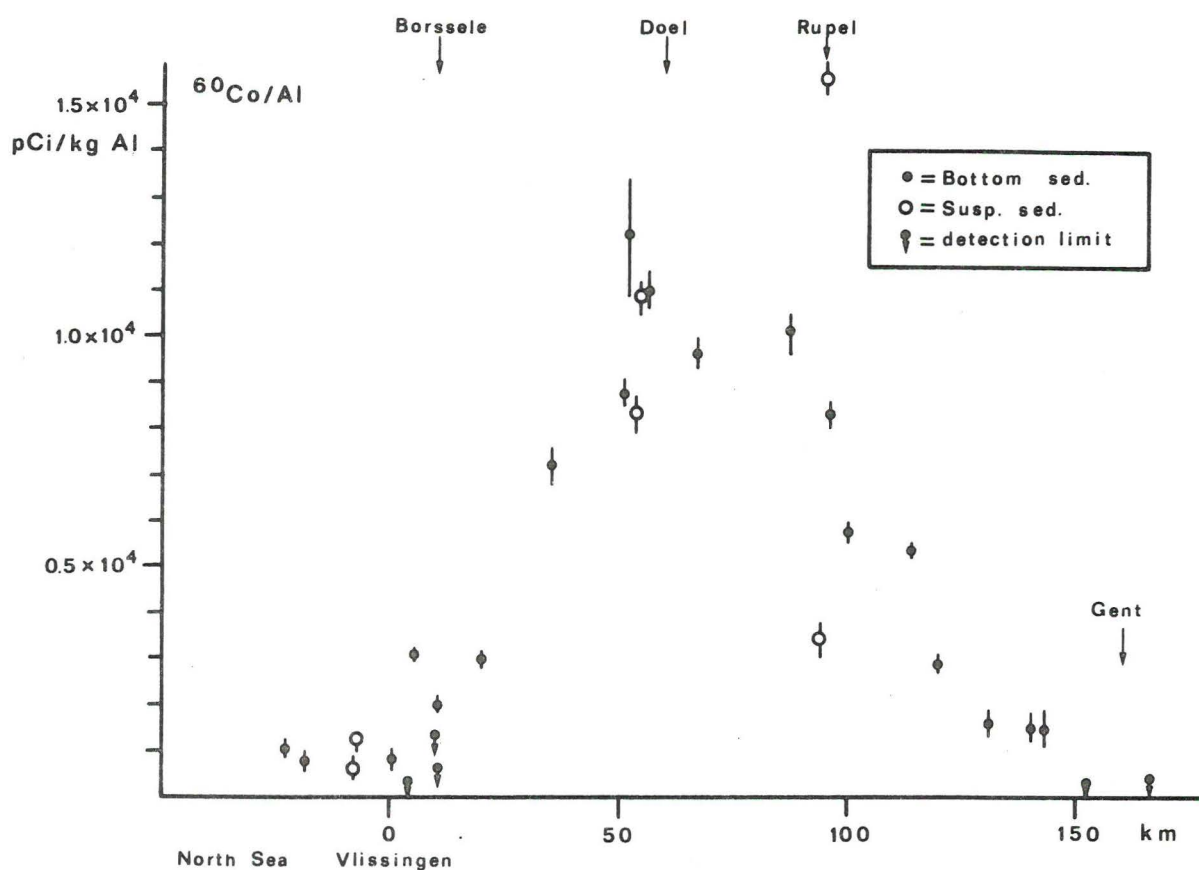


Fig. 13. Normalized  $^{60}\text{Co}$  concentrations in recent sediments of the Western Scheldt estuary (1979 - 1984).

freshwater sediments and no evidence has been found of any occurrence of old sediments with higher plutonium content in the Delta.

According to a net sedimentation of  $2 \times 10^6$  tons/yr between km 50 and 100 in the Scheldt (1,2), and taking into account the average concentrations of plutonium measured in that area ( $^{239+240}\text{Pu}$ : 16 pCi/kg and  $^{238}\text{Pu}$ : 6.5 pCi/kg), the quantities of  $^{239+240}\text{Pu}$  and  $^{238}\text{Pu}$ , which are associated to these sediments are 32 and 13 mCi/yr, respectively (Fig. 14). Input by fallout includes river input in particulate and dissolved form and direct fallout by rain over the estuary. Using a Scheldt solid and liquid discharge of  $1.52 \times 10^6$  tons/yr and  $2.8 \times 10^9$  m<sup>3</sup>/yr, respectively, the particulate and dissolved plutonium inputs can be calculated. Taking the particulate plutonium measured near Gent, the particulate input of  $^{239+240}\text{Pu}$  and  $^{238}\text{Pu}$  is 5 and 0.2 mCi/yr, respectively. Dissolved river concentrations may be estimated using an average distribution coefficient of  $7 \times 10^4$ , as measured in French rivers (24). If calculated on this basis, the dissolved input seems to be negligible as compared to the particulate input, (dissolved input of  $^{239+240}\text{Pu}$ : 0.13 mCi/yr and of  $^{238}\text{Pu}$ : 0.005 mCi/yr).

$^{239+240}\text{Pu}$  fallout at Milford Haven (G.B.) from 1979 to 1982 was smaller than



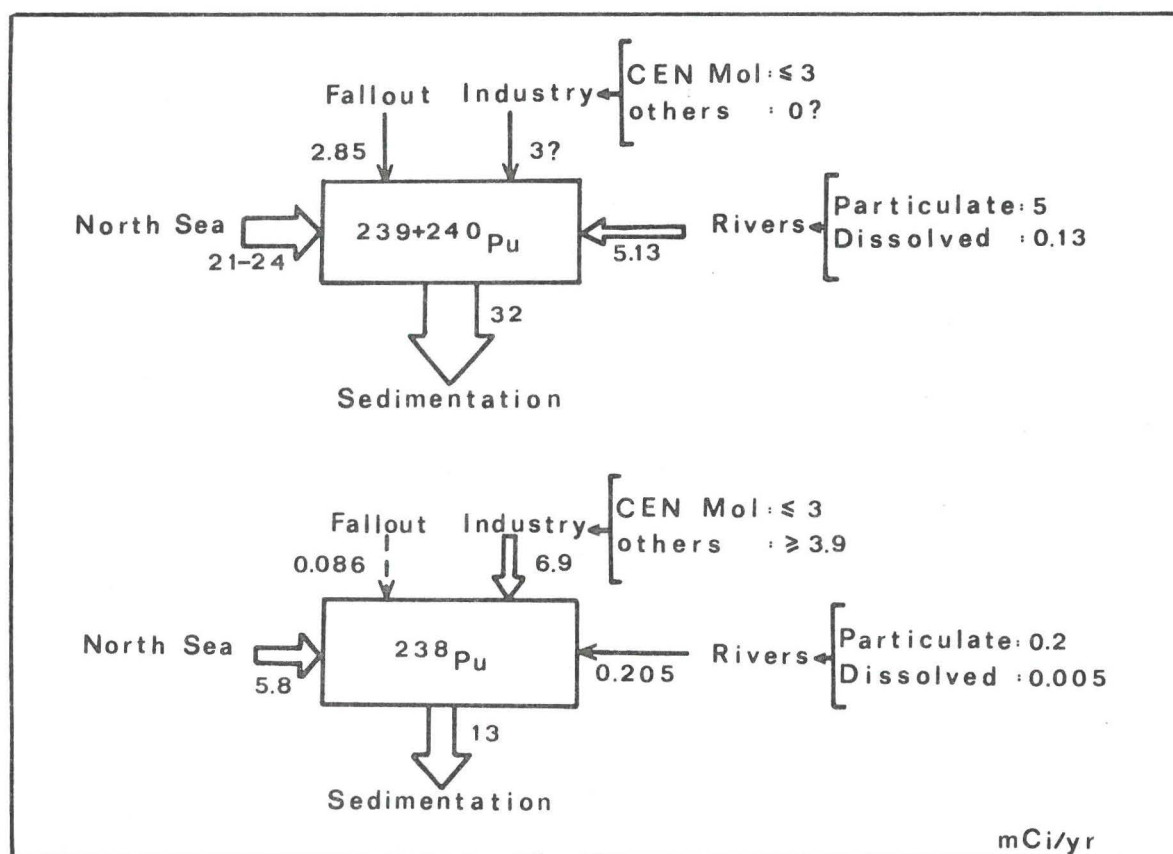


Fig. 14. Tentative budget of average plutonium isotopes annual sources and sinks of the Western Scheldt estuary in the major shoaling area of sediments near Antwerp (between km 50 and 100). All data are in mCi/yr.

$5.7 \mu\text{Ci}/\text{km}^2$  (39, 40), and this allows to calculate a maximum input of 2.85 and 0.086 mCi/yr for  $^{239+240}\text{Pu}$  and  $^{238}\text{Pu}$ , respectively, over the entire Western Scheldt estuary (surface  $500 \text{ km}^2$ ). Hence, the total input by fallout amounts to 8 and 0.3 mCi/yr for these isotopes.

The contribution of the remaining, non-fallout sources is then estimated at 24 mCi/yr for  $^{239+240}\text{Pu}$  and 12.7 mCi/yr for  $^{238}\text{Pu}$ . This remaining or 'excess' plutonium may originate from the North Sea and from contributions of local nuclear effluents. The distribution of  $^{239+240}\text{Pu}$  (Fig. 9) does not allow, however, to envisage these contributions to be of great importance and the input from the North Sea amounts probably entirely to the 24 mCi/yr.

Taking an isotopic ratio of 0.24 at the mouth of the Western Scheldt, the marine input of  $^{238}\text{Pu}$  is then approximately 5.8 mCi/yr. Since as afore mentioned the input other than fallout was 12.7 mCi/yr, an additional source of 6.9 mCi/yr is required for the Western Scheldt estuary. Part of it may be covered by the CEN at Mol, where in 1979-1980 the release was of 3 mCi total Pu/yr (35,36). This leaves at least 3.9 mCi/yr to be accounted for. In principle nuclear power plants should not release any  $^{238}\text{Pu}$ , but as observed in the Loire river sediments the isotopic

$^{238}\text{Pu}/^{239+240}\text{Pu}$  ratio increases from 0.035 upstream of nuclear power plants to 0.25-0.42 downstream (15). Thus, in view of these findings, the occurrence of  $^{238}\text{Pu}$  releases by other sources like nuclear power plants in the Western Scheldt cannot be definitely discarded.

Concerning the Borssele nuclear power plant, the average radioactive effluents discharged per year amount to  $\pm 5000 \text{ m}^3$ , containing an alpha activity of 1 to 4  $\text{kBq/m}^3$ , from which 10% is attributed to  $^{238}\text{Pu}$  (41). This presents a quantity of 0.01 to 0.05  $\text{mCi/yr}$ . For the Doel power plants, the value is less than 1  $\text{pCi/l}$  total alpha for about  $5000\text{-}10000 \text{ m}^3/\text{yr}$  (42), which accounts for less than 5-10  $\text{mCi}$  total alpha/yr. If  $^{238}\text{Pu}$  is again 10%, the figure is 0.5-1  $\text{mCi } ^{238}\text{Pu/yr}$ . Thus, both Borssele and Doel cannot be alone responsible for the remaining 3.9  $\text{mCi/yr}$  to be accounted for. This would be better if the used figure for the net sedimentation as given at  $2 \times 10^6 \text{ tons/yr}$  is lower, as is suggested by the Rijkswaterstaat, Vlissingen on the basis of dredge-spoil data for the period 1964-1983 (43), however denied by recent Belgian recalculations (44) which give the same figure.

Nevertheless, even for a lower sedimentation value of f.e.  $1 \times 10^6 \text{ tons/yr}$  (the dredge-spoil amount), the effect on the  $^{238}\text{Pu}$  budget (Fig. 14) is that 4.3  $\text{mCi/yr}$  is to be supplied by industry (instead of 6.9  $\text{mCi/yr}$ ), which leaves 1.3  $\text{mCi/yr}$  at the account of other sources than the C.E.N. at Mol, like the mentioned nuclear power stations. Such inputs are, however, small compared to the controlled releases of the La Hague (6.5  $\text{Ci}$  total  $\text{Pu/yr}$  in 1977 (45)) and Sellafield (170  $\text{Ci } ^{238}\text{Pu/yr}$  in 1979-1983 (46)) reprocessing plants.

In conclusion, the preceeding estimates only represent a first tentative assessment of plutonium inputs in the Western Scheldt estuary, which obviously requires additional experimental work and modelling. Although a number of uncertainties still subsist, these estimates confirm that the marine input is the major source of plutonium contamination being more than 70 % for the  $^{239+240}\text{Pu}$  and approximately 45 % for the  $^{238}\text{Pu}$  accumulation in this estuary.

On the contrary,  $^{60}\text{Co}$  is essentially supplied by industrial effluents directly discharged in the estuarine zone. The same calculations as above allow us to estimate  $^{60}\text{Co}$  sedimentation to 700  $\text{mCi/yr}$ . Average annual input by CEN at Mol in 1979-1980 is 245  $\text{mCi/yr}$ , to which must be added the discharges by nuclear power plants. According to Luykx and Fraser (8), 740 and 125  $\text{mCi/yr}$  were supplied by the Doel and Borssele power plants, respectively. River input by particulates is negligible (smaller than 18  $\text{mCi/yr}$ ) since the radionuclide is not found in fallout. Thus total nuclear input averages 1110  $\text{mCi/yr}$ . This value is not significantly different from the quantity entrapped within the sediments, but raises the question



of a possible partial mobilization from anoxic sediments.

Concerning the hazards of mussel consumption, it has to be remembered that only 0.1 % of all alpha radioactivity is contributed by the total plutonium activity. Additionally a consumption of 50 kg mussels per year is still  $10^{-5}$  of the ALI (annual limite of intake for people involved with the nuclear industry).

## CONCLUSIONS

-Measurable plutonium contamination has been detected in all sedimentary material as well as in marine biota (mussels) in the entire Dutch Delta area and coastal regions north-eastwards to the German border. The total alpha activity of plutonium isotopes is very low and only represents 0.1 % of the alpha radiation caused by natural radionuclides of the uranium and thorium series.

-Contamination of coastal environments of the Delta by  $^{239+240}\text{Pu}$ , originating from nuclear industrial sources (reprocessing plants), is at least equal to the supply of plutonium by atmospheric fallout, including drainage-fallout. This industrial influence is hardly detectable in the north-eastern part of the Dutch coast.

- $^{238}\text{Pu}$  is a very sensitive tracer for nuclear industrial releases, which on the whole exceeds the input by fallout by one order of magnitude. Although  $^{238}\text{Pu}$  concentrations tend to decrease north-eastwards, the industrial contamination by  $^{238}\text{Pu}$  is still obvious near the German border and probably can be followed furtheron.

- $^{238}\text{Pu}$  contamination in the Delta area is of recent origin, as is shown by an increase of the  $^{238}\text{Pu}/^{239+240}\text{Pu}$  ratio during the last ten years. This effect is primarily noticeable in regions where recent sediments accumulate, contrary to the salt-marsh deposits in which deposition is slower and mixing with reworked older sediments occurs.

-The major sources of plutonium contamination are the effluents released by the nuclear fuel reprocessing plants of La Hague and Sellafield, the relative contribution of each cannot be simply evaluated. Input of plutonium from the North Sea (probably essentially contaminated along the Dutch coasts by inputs of Channel water) to the Delta is observed in coastal and brackish-water environments. It is obvious that landward transport due to specific estuarine hydrodynamic processes is most likely occurring. Thus contamination may spread up into the freshwater environment of the estuary.

-Part of the  $^{238}\text{Pu}$  concentrations measured in the sediments of the Rhine and Meuse rivers cannot be attributed to fallout, but suggest the existence of small nuclear industrial inputs in the upstream system.



-Local effluents do influence the general pattern in the Western Scheldt estuary, where additional industrial inputs of  $^{238}\text{Pu}$  are present at levels equal to the quantity originating from the North Sea.

-Estuarine distribution of plutonium isotopes is characterized by a seaward concentration increase. This result confirms earlier studies in fallout environments and is likely to be observed in any other well or partially mixed estuarine system.

-The seaward increase is partly governed by an uptake of marine dissolved plutonium by estuarine sedimentary particles. The exact location where such uptake occurs is unknown. The occurrence of a large proportion of detrital terrigenous components in the fine-grained marine fraction of the sediments of the Delta, as well as an important reintroduction of such 'marine' material in the estuarine zones does not permit a simple answer to that question.

-Whatever may be the true enrichment process, the estuarine zones are able to accumulate plutonium from the sea and deposit it in bottom sediments.

-A large question remains how these processes of accumulation will extend into the future, and whether at some time a steady state equilibrium will be reached where an input into the estuary is counterbalanced by an output, probably 'again' to the sea.

-A practical consequence of interest is the possibility to use particulate plutonium, and probably also other long-lived artificial radionuclides discharged by effluents, as convenient tracers for studies of the sedimentary dynamics in estuaries. Application to the Western Scheldt has shown that landward sediment transport almost reached the limit of tidal intrusion.

-The hazard for mussel consumption is far below the ALI (annual limit of intake), like  $10^{-5}$  ALI for the consumption of 50 kg mussels/yr.

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