Radionuclides in the Loire river estuary (France): Sources, transport and fate

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Abstract. Anthropogenic radionuclide inputs in the Loire estuary (French Atlantic coast) consist of radioactive releases from 14 nuclear reactors located along the Loire river basin, and of fallout from nuclear weapon tests and from the Tchernobyl accident. To estimate to what extent radionuclides associated with sediment accumulate in the estuary, three complementary approaches were used : field surveys, laboratory experiments and numerical modelling. Sampling of bottom sediments, water and suspended solids was carried out at 8 different dates over a 15 month-period. Analysis covered ^{14}C, ^{90}Sr, ^{3}H, the naturally occurring gamma-emitters (uranium and thorium decay chains, ^{7}Be and ^{40}K), and the artificial gamma emitters (mainly cobalt and cesium isotopes). Processes of radionuclide transport and exchange between dissolved and particulate phases were included in a previously developed estuary specific 2D-hydrodynamic model. Equations of sorption and desorption kinetics were derived from laboratory experiments conducted at different salinities. Simulations carried out for two river discharge conditions (low summer flow, high winter flow) allowed to follow radionuclide desorption in the estuary. For long term simulations, a simplified model was developed. It provided estimates of the amount of radionuclides expelled out of the estuary under dissolved and particulate forms, of the transit time for both forms and of the variations in radionuclides concentrations in the fluid mud. Based on computed results and observations, contributions from different origins (natural, military, industrial) to the inventory of radioactivity in the estuary are presented.

1. INTRODUCTION

The Loire river watershed is the greatest in France with a drainage area of about 120 000 km² representing one fifth of France surface area. With a mean annual discharge of 850 m³/s, it is one of the main riverine input to the Atlantic Ocean, in western Europe and stands as the most " nuclearized " river basin with 14 nuclear power plants (NPP) operating along the Loire river and its tributaries. The Loire river estuary exhibits the typical features of a macrotidal estuary : the mixing of freshwater with seawater creates a salinity and density gradient which is responsible for the formation of the turbidity maximum. With up to 1 million tons of suspended sediment trapped in the estuary, the Loire river estuary was identified as an important radionuclide accumulation zone and included in the " Loire and estuary radioecology " program, a global study of radionuclides transfer in the Loire river basin, initiated by Electricité de France.

To evaluate the residence times and accumulation of contaminant, it is essential to distinguish between dissolved and particulate forms since dissolved radionuclides are exported more rapidly to the ocean than particulate forms which undergo numerous episodes of deposition and resuspension. Although there is a general understanding of individual processes that affect the fate of particle-reactive contaminants in estuarine systems, it has been very difficult to quantify the partitioning between water and particles because of the complex suite of physical and biogeochemical reactions that take place when fresh water mixes with seawater in conjunction with the formation of turbidity maximum. Numerical modeling in combination with field surveys and laboratory experiments was the approach chosen to help in the quantification of accumulation in estuary and net exchange between rivers and the ocean.

2. SEASONAL INVESTIGATIONS OF RADIOACTIVITY IN THE ESTUARINE TURBIDITY MAXIMUM

Sampling of bottom sediments, water and suspended solids was carried out at 8 different dates over a 15 month-period . The survey strategy was composed to include various tide conditions from neap tide to spring tide at low and high river flows (Table1). Different depths in the water column were sampled, surface, intermediate and bottom. A total of 28 large water samples (300 to 2000 liters) were collected, along with 12 fluid mud samples and 11 bottom sediment samples. Analysis covered [14]C (dissolved and associated to particulate organic matter), [90]Sr (dissolved and particulate), [3]H (tritiated water and organic bound tritium), the naturally occurring gamma-emitters (uranium and thorium decay chains, [7]Be and [40]K), and the artificial gamma emitters (mainly cobalt and cesium isotopes) in the dissolved and particulate fractions.
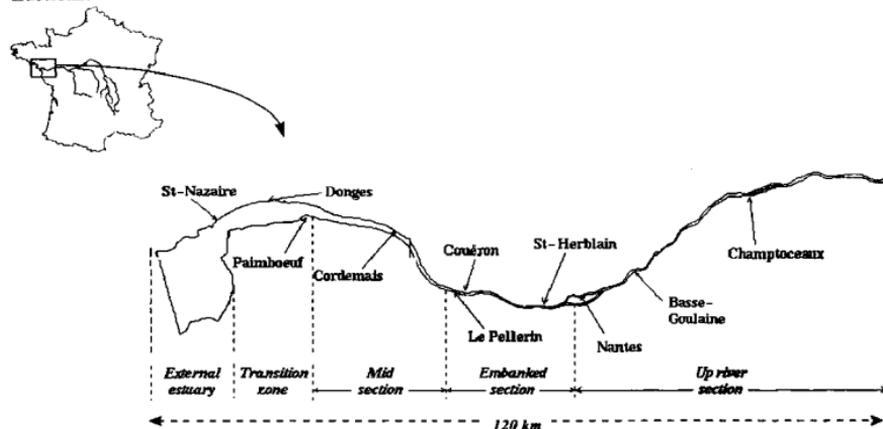

Figure 1 : Location of study area

Table 1 - Sampling strategy

Survey number	Date	Tidal coef.	Loire river flow rate ($m^3.s^{-1}$)	Position of the turbidity maximum	Sampling type
1	03/07/1998	41	292	Cordemais	vertical profile at high tide
2	08/07/1998	71	270	Cordemais	variability over a tidal cycle : vertical profile at high tide, ebb tide, low tide , flow tide, and next high tide
3	15/09/1998	47	225	Le Pellerin	vertical profile at high tide
4	05/02/1999	78	1310	Donges	variability over a tidal cycle : vertical profile at high tide, ebb tide, low tide , flow tide, and next high tide
5	25/02/1999	51	3070	St-Nazaire	transect on the ebb tide
6	17/05/1999	107	663	Cordemais	vertical profile on the flood tide
7	12/07/1999	93	267	Le Pellerin	vertical profile on the flood tide
8	28/09/1999	101	354	Le Pellerin	vertical profile on the flood tide

A seawater sample was collected along the Atlantic coast near Le Croisic to serve as a possible reference. Furthermore, to investigate the extent of long-term radionuclide accumulation in this area, 8 sediment cores were sampled in the estuary, plus 2 cores on the sea shore near the river mouth. Results are presented in more details in [1] for ^{137}Cs and ^{90}Sr ,[2] for ^{14}C and [3] for sediment cores.

2.1. Particle associated radioactivity

Natural radioactivity in SPM and sediment was dominated by ^{40}K (above 600 Bq/kg) followed by ^{210}Pb (150 Bq/kg), ^{238}U and ^{232}Th families (50 Bq/kg) and ^{7}Be (30 Bq/kg). Anthropogenic radionuclides concentrations range from 10 Bq/kg for ^{137}Cs to below detection limit (0,1 Bq/kg) : the order of abundance was ^{137}Cs>^{14}C>OBT (organic bound tritium)>^{60}Co>^{134}Cs,^{110m}Ag,^{90}Sr. Radionuclides, such as ^{58}Co, ^{54}Mn, ^{131}I, although present in nuclear power plant discharges, were always below the detection limit in the estuarine particles.

Comparison with radionuclide concentrations in the Loire river was possible using the CRESCENDO model results [4]. The CRESCENDO model calculates concentrations in the dissolved, particulate and sedimentary forms of radionuclides released by nuclear power plants. The results obtained in Montjean-sur-Loire, which is the limit of tidal incursion, were used for comparison. Observed ^{60}Co and ^{110m}Ag concentrations lay within one order of magnitude of the calculated Loire inputs (Figure 2), whereas observed ^{137}Cs and ^{90}Sr concentrations were respectively 20 and 100 times higher than the calculated values, demonstrating that the main origin for these two radionuclides was still weapon test fallout. Contribution from Chernobyl fallout in this part of France was not significant as suggested by the soil surveys conducted since 1980 in the framework of NPP radioecological monitoring programs.
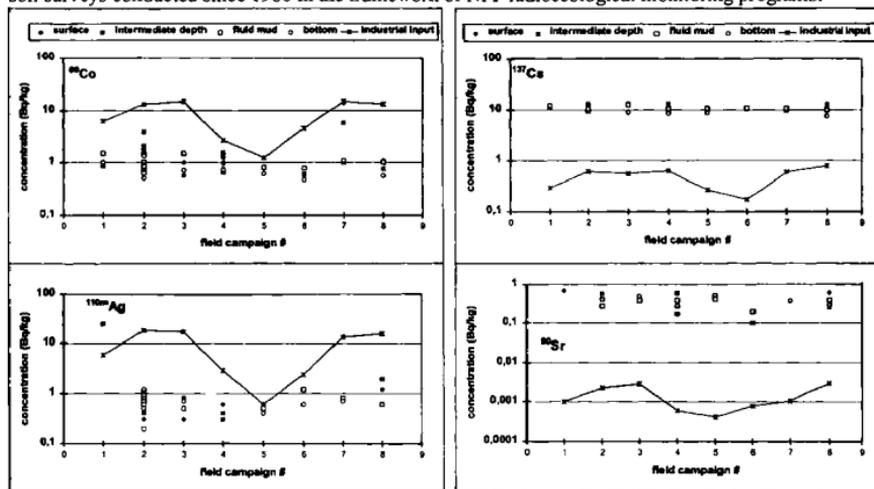

Figure 2 - Comparison between observed radionuclide particulate concentrations in the turbidity maximum and calculated values, in the Loire river, resulting from industrial releases
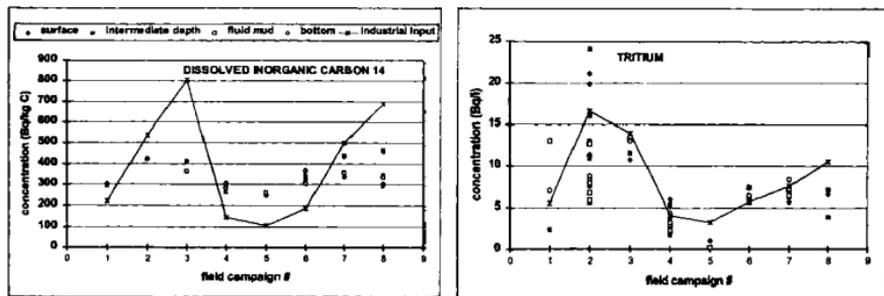
Figure 3 - ^{14}C and ^3H (free tritium) concentrations in the turbidity maximum and calculated values, in the Loire river, resulting from industrial releases

2.2. Dissolved radioactivity

Tritium was the most abundant radionuclide with a mean concentration of 7,6 Bq/l, closely followed by ^{40}K (2,7 Bq/l). ^{14}C, ^{90}Sr and ^7Be were lower by three orders of magnitude and ranged between 3 and 5 mBq/l. They were followed by ^{137}Cs (0,4 mBq/l). ^{60}Co was only detected in a few samples (0,01 mBq/l) ; ^{131}I was more frequent with an average of 0,05 mBq/l.

Variations in tritium concentrations coincided with calculated Loire industrial input (Figure 3). The same trend was observed for ^{14}C but variations in the Loire estuary were smaller than in the fluvial input. This could be due to an overestimation of ^{14}C industrial input since the CRESCENDO model considers ^{14}C as a conservative dissolved tracer. The presence of ^{14}C from natural sources at a concentration averaging 250 Bq/kg C in fluvial waters, in equilibrium with atmospheric CO_2, and 240 Bq/kg C in marine waters explains the elevated estuarine base level. At the opposite, background ^3H levels (less than 1Bq/l upstream of NPP and 0,5 Bq/l in the Atlantic Ocean) can be disregarded since they represent less than 10 % of the fluvial input to the estuary. Dissolved ^{137}Cs concentrations increased linearly with salinity [1] whereas ^{137}Cs particulate concentrations remained very stable along the salinity range, suggesting a combination of desorption and mixing with oceanic water enriched in ^{137}Cs .

3. MODELLING RADIONUCLIDE TRANSFER IN THE ESTUARY

To help in the understanding of radionuclide sorption and desorption processes in the estuarine environment where salinity and SPM concentrations are changing very rapidly, a multivariate transport model was developed, based on an existing hydrodynamic model of the Loire estuary. It represents tidal propagation, salt intrusion, transport of radionuclide and suspended sediment, sedimentation and erosion, as well as radionuclide exchange kinetics between dissolved and particulate forms. Laboratory experiments of the sorption and desorption kinetics of Co, Mn, Cs, Ag, and Sr were conducted with Loire river and Loire estuary waters. Based on their results, a kinetic model consisting of two successive exchange processes, the first one between liquid phase and weak sites on solids, the second one between weak and strong particulate sites, characterized by different salinity related time periods, was developed and calibrated [5]. It was included in the hydrodynamic and sedimentary model.
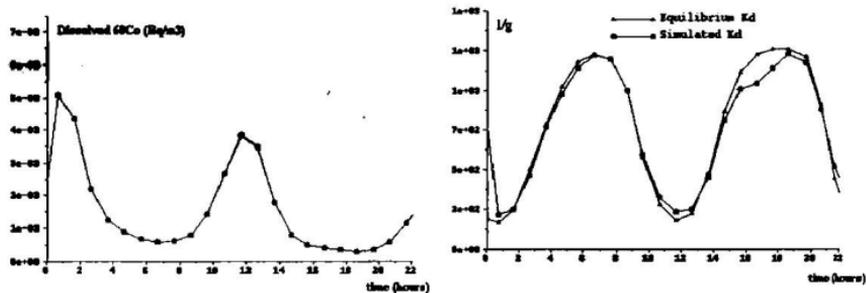
Figure 4 - Simulation of ^{60}Co behavior with the two-step kinetic model during two tides (simulation starts at high tide). Comparison between the ratio 'simulated particulate activity/ simulated dissolved activity' and the equilibrium Kd.

The objective of the simulations was to follow over a few tides the sorption and desorption processes [6]. As an initial condition, radionuclides were considered to be solely associated with particles. Results showed the same general trend for cesium, cobalt and silver . Desorption occurred immediately until the experimental Kd at a given salinity was reached (one hour after the beginning of the simulation) (Figure 4). Afterwards, dissolved and particulate forms respect the fluctuation of the Kd according to salinity. It thus appeared that taking into account exchange kinetics was not necessary and that equilibrium Kd as a function of salinity correctly represented partitioning between dissolved and particulate forms.

This detailed spatial hydro-sedimentary model could not be used for long term simulations because of numerical problems. For this purpose, a box-type model was developed (Figure 5) which considers that (i) contaminant entering the estuarine compartment is instantly mixed with the compartment water and exchange with solids according to Kd , (ii) the calculated concentration in the outflow to the ocean is the same as in the estuarine compartment , (iii) the net water flux to the ocean is equal to the river flow input, (iv) the rate of removal of particles and particle associated radionuclides is calculated by a function taking into account the Loire river flow during the 30 previous days. This relation was established by Ciffroy [7] using ^{7}Be to estimate particles age. The removal rate varied between 0,002 day^{-1} at low river flow and 0,02 at high flow. The input data from the Loire river are the results of the CRESCENDO model (river flow, SPM concentrations, dissolved and particulate radionuclide concentrations) which only takes into account the industrial releases of radionuclides.
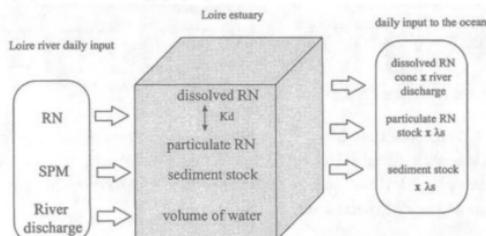

Figure 5 - Loire estuary box-model . λs is the apparent rate constant of sediment removal from the estuary

Model parameters values were taken from the results of the detailed spatial model and the laboratory experiments and checked with the field surveys data. In a first step the box-model dissolved contaminant transfer was compared to tritium measurements. Then it was checked for particulate contaminant against ^{60}Co field data. To improve the fit between predicted and observed values, from this study as well as from

other field studies of the solid load in the estuary [8], it was necessary to include in the model the *in situ* production of particles, through processes such as flocculation. The average *in situ* production rate was derived from Negrel [9] who estimated that half of the particles exported by the Loire river estuary were produced *in situ*. Simulation carried out over a six-year period showed that the resulting average sediment stock in the estuary was then 930 000 tons which is consistent with other published data. Simulated sediment export to the ocean varied between an average value of 2800 tons/day for river flows lower than the module, to 10 000 tons/day for river flows of 2000 m³/s. The sediment stock was completely exported to the sea at river flow above 5000 m³/s.
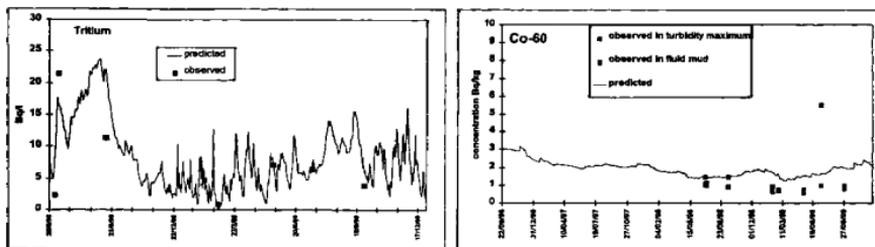

Figure 6 - Comparison between observed and box-model predicted radionuclides concentrations in the turbidity maximum

Once the model was calibrated (Figure 6), it was used to evaluate the radionuclide stock in the estuary and the flux to the ocean over a six-year period (Figure 7). Average ^{60}Co stock in the estuary was 1,7 GBq, it represents 37% of the total annual power plants radioactive releases. Export to the ocean amounted to approximately 4 MBq/ day and could reach 1GBq/day at very high river flows. The average residence time of ^{60}Co in the estuary was 133 days. For tritium, the average stock in the estuary was 2,2 TBq. When compared to NPP tritium discharge of 0,39 TBq/day, it allowed to calculate an average estuarine residence time for conservative dissolved pollutants of 5,4 days.
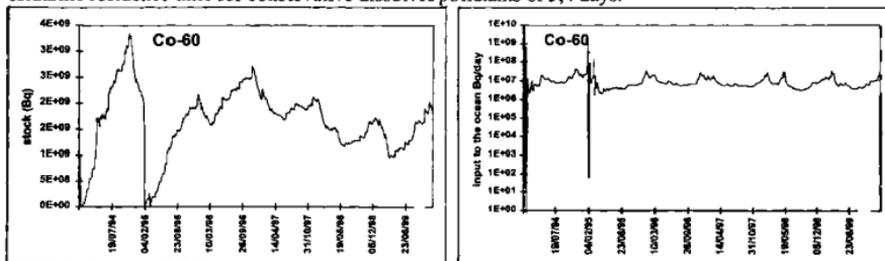

Figure 7 - Evolution of ^{60}Co estuarine stock and export to the ocean.

Similar calculations were conducted for ^{110m}Ag for which NPP radioactive releases represent the only source. For radionuclides with several origins, the concentrations in the estuary resulting from the radioactive releases were calculated with the box-model and compared to the observed concentrations to calculate the contribution of the industrial source.

4. CONCLUSIONS

Radionuclide accumulation in the Loire river estuary sediment is controlled by the sediment turnover rate. Although the total sediment stock is exported to the ocean, only for very high river flows (occurring every 5 year on average), particles residence times are much shorter (222 days) and particulate radionuclide residence times are even smaller (133 days for ^{60}Co) due to desorption and radioactive decay. While tritium originating from industrial releases dominates the dissolved radioactive inventory of the estuary,

natural radionuclides (^{40}K, ^{210}Pb, ^{7}Be, ^{238}U and ^{232}Th families) represent the largest contribution to the radioactivity present in the sediment with an average stock of ~1TBq. Nuclear power plants effluents are the only contributors to ^{60}Co and ^{110m}Ag inventories of ~2GBq, mainly associated with sediment. They contribute to 5% of the ^{137}Cs inventory (total ~ 9 GBq), the main source being fallout from nuclear weapon tests. Particulate ^{14}C inventory of ~ 7 GBq is due to natural sources (76%) and fallout ; industrial releases only contribute to the dissolved ^{14}C.

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