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Radionuclides transfer between water and atmosphere in the Loire estuary (FLORE project)

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Abstract. In estuaries, volatiles radionuclides (¹⁴C, ³H, ¹³¹I) originating from anthropogenic liquid waste release from nuclear reactor or hospitals are potentially transferable to the atmosphere. Due to the high biologic activity, the degradation of organic matter produce carbon dioxide fluxes to the atmosphere allowing transfer of ¹⁴CO₂ released by nuclear industry. Similarly tritium is transferred to the atmosphere through evaporation process. We present here, results obtained during FLORE-1 cruise in February 2003, a winter period when biological activity is supposed to be low. The first results of iodine 131 distribution and estimations of radiocarbon and tritium fluxes are presented.

1. INTRODUCTION

The behaviour of the toxic substances in the environment covers various fields of investigations like contamination by the radio-elements, heavy metals and organic compounds. The knowledge of the biogeochemical cycles of the radio-elements, basically their temporal and spatial distributions is essential to a better understanding of their biological effects. Estuarine environments present a major interest since they constitute accumulation areas of wastes and rejections of the majority of the anthropogenic activities. These transition zones between fresh waters and ocean, characterised by the change of the physico-chemical properties (pH, salinity, turbidity) allows a redistribution and the recycling of the radio-elements by their speciation or phase change thus modifying their bio-availability. The Loire River estuary receives the rejections of radio-elements coming from various sources like the nuclear thermal power stations (fourteen reactors with discharges of carbon-14, tritium) [1] [2], the hospital complexes (rejections of iodine 131).

The Loire estuary on the French Atlantic coast is 100 km long with a surface area of 102 km², and an average depth of 9 metres. The estuary is macrotidal, well mixed and highly turbid. Residence times of waters and suspensions are respectively 2-10 days and 1-2years [3]. The Loire river with an average discharge of 850 m³.s⁻¹ is highly eutrophic with chlorophyll-a exceeding 100 µg.L⁻¹ in summer.

This large biomass in the estuary is submitted to oxidation and microbial activity generating high concentrations of dissolved CO₂ and even precipitation of authigenic carbonate [4]. Such a pattern suggests clearly that estuary is a potential source of CO₂ to the atmosphere. Recent studies

around COGEMA La Hague nuclear reprocessing plant show that this area of high bacteriological activity generate high carbon dioxide flux marked by $^{14}\text{CO}_2$ originating from liquid waste released of the plant [5] [6]. Similarly in the Bay of Seine evaporating process results in ^3H flux from sea to the atmosphere [7]. This indicates that part of volatile radionuclides (^{14}C , ^3H) of liquid waste released are recycled in the atmosphere.

The aims of FLORE program are to study the distribution of these volatile radio-elements including ^{131}I and the processes of phase transfer (water-atmosphere) in this estuary especially in the mud plug area where the biochemical activity is intense. We present here, results obtained during FLORE-1 cruise in February 2003, a winter period when biological activity is supposed to be low. The first results of iodine 131 distribution and estimations of radiocarbon and tritium fluxes are presented.

2. EQUIPMENT AND METHOD

2.1 Sampling of seawater and air

Sampling performed between 15th and 20th February 2003 in the Loire estuary from Saint Nazaire city to Montjean sur Loire upstream of the dynamic tide influence. In the estuary the sampling was performed onboard of the R/V “Côtes de La Manche”.

Temperature and salinity of seawater were measured using a SBE 19-03 Seabird equipment and wind direction and speed were recorded. CO_2 partial pressure in surface sea water were calculated using pH and total alkalinity measurements following “Standard Operating Procedures SOP3 and SOP6” of the US Department of Energy [8].

^{14}C and ^3H activities in air and water samples were determined using the procedure defined by Maro *et al.*, [5], and Maro *et al.*, [7] respectively. ^{131}I concentration was measured by gamma spectrometry after precipitation of total iodine [9].

2.2 Fluxes calculations

2.2.1 ^{14}C fluxes

In order to estimate $^{14}\text{CO}_2$ fluxes across the sea surface water and the atmosphere interface the partial pressure of carbon dioxide (pCO_2) were calculated using measurement of total alkalinity and pH of water. According to Henry’s law the difference between pCO_2 in air and water indicates if seawater is a source of CO_2 to the atmosphere. Carbon dioxide fluxes were calculated following equation (1).

$$\Phi(\text{CO}_2) (\text{mole.m}^{-2}.\text{s}^{-1}) = K. S. \Delta\text{pCO}_2 \quad (1)$$

$K (\text{m.s}^{-1})$ is the CO_2 transfer coefficient between seawater and atmosphere, S is solubility of $\text{CO}_2 (\text{mole.m}^{-3}.\text{atm}^{-1})$ and $\Delta\text{pCO}_2 (\text{atm})$ is the difference between partial pressure in water and air. K is a parameter depending on wind speed and has been calculated by using studies of Liss and Merlivat [10], Tans *et al.*, [11] and Wanninkhof and McGillis [12]. As these K values are slightly different in these three studies we present the three CO_2 flux estimates.

The exchange of CO_2 between the atmosphere and the surface ocean is an equilibrium process, and the nett CO_2 flux is the difference between gas going from water to air and gas going from air to water. Both these fluxes carry ^{14}C at concentrations appropriate to the medium from where they originate, and the nett ^{14}C flux is, once again, the difference. The expression for the nett ^{14}C flux from surface ocean to the atmosphere should be of the form (equation 2).

$$\Phi(^{14}\text{C}) = [^{14}\text{C}]_{\text{O}} \Phi_{\text{OA}}(\text{CO}_2) - [^{14}\text{C}]_{\text{A}} \Phi_{\text{AO}}(\text{CO}_2) \quad (2)$$

Regarding constant factor due to appropriate units use, ^{14}C fluxes were calculated following equation (3).

$$\Phi(^{14}\text{C}) (\text{Bq.km}^{-2}.\text{d}^{-1}) = 10^9 ([^{14}\text{C}]_{\text{O}} \cdot \Phi_{\text{OA}} - [^{14}\text{C}]_{\text{A}} \Phi_{\text{AO}}) \quad (3)$$

where $[^{14}\text{C}]_{\text{O}}$ and $[^{14}\text{C}]_{\text{A}}$ are the ^{14}C concentrations ($\text{Bq.Kg}^{-1}\text{C}$) in the surface ocean and air, respectively, and Φ_{OA} and Φ_{AO} are the CO_2 fluxes ($\text{mole.m}^{-2}.\text{s}^{-1}$) from ocean to air, and air to ocean, respectively.

2.2.2 ^3H fluxes

To evaluate the transfer of ^3H between water and atmosphere due to discharge into the water by nuclear reactors, the flux of water vapour ($\text{L.m}^{-2}.\text{d}^{-1}$) is calculated first, using Rohwer's formula [13]:

$$\Phi(\text{H}_2\text{O}) = 0.372 (1 - 0.000374 P_a) (1 + 0.6 V_w) (e_s - e_a) \quad (4)$$

where:

$\Phi(\text{H}_2\text{O})$: Flux of water vapour ($\text{L.m}^{-2}.\text{d}^{-1}$),

P_a : Atmospheric pressure (mbar),

V_w : Wind speed (m.s^{-1}),

e_s : Saturated vapour pressure (mbar),

e_a : Vapour pressure in the atmosphere (mbar).

Then, knowing the concentration of ^3H in the water, the flux of ^3H ($\text{Bq.m}^{-2}.\text{d}^{-1}$) is determined using equation 5:

$$\Phi(^3\text{H}_2\text{O}) = \Phi(\text{H}_2\text{O}) [^3\text{Hw}] \quad (5)$$

where:

$\Phi(^3\text{H}_2\text{O})$: Flux of ^3H between water and atmosphere ($\text{Bq.m}^{-2}.\text{d}^{-1}$),

$[^3\text{Hw}]$: Concentration of ^3H in the water (Bq.L^{-1}).

3. RESULTS AND DISCUSSION

Results are presented in tables 1, 2 and 3 for ^{131}I , ^{14}C and ^3H respectively.

3.1 Iodine 131

^{131}I was detected in the fluvial part of the estuary (salinity 0 psu) between Montjean/Loire and Nantes cities. Activities range between 0.8 and 2 Bq.m^{-3} .

Table 1. ^{131}I concentrations in the fluvial part in Loire estuary.

Station	Date	Latitude (°)	Longitude (°)	Salinity (psu)	^{131}I (Bq.m^{-3}) water
1	02/15	47.235	-0.517	0	0.8
8	02/17	47.176	-2.016	0	0.9
13	02/18	47.168	-1.547	0	1.3
14	02/19	47.122	-1.344	0	2.0
16	02/19	47.178	-2.018	0	1.3

No measurement was performed for air samples. As iodine 131 is supposed to be absent in the atmosphere, degassing of this radionuclide and its transfer to the atmosphere is highly probable but has not yet been estimated.

3.2 Radiocarbon

Carbon 14 activities range between 230.8 and 400.9 Bq.kg⁻¹ C and 230.6 and 255.7 Bq.kg⁻¹ C for water and air samples respectively. As the post atmospheric nuclear test activity reference value is around 235 Bq.kg⁻¹ C in 2003, all samples excepted air sample at station 4 and water sample at station 14 are marked by ¹⁴C from the nuclear industry. These two samples may have been possibly affected by hard water effect originating from local dissolution of geological carbonate in water sample and a contamination of fossil fuel burning for air during sampling. ¹⁴C activity decrease slowly toward the mouth with increasing salinity. The measured pCO₂ values vary between 379 to 409 μatm (mean value of 391 μatm) and between 384 to 1767 μatm (mean value of 874 μatm) for air and water respectively. These indicate that Loire estuary is a source of CO₂ for the atmosphere.

CO₂ fluxes to the atmosphere are calculated from equation 1 using K transfer coefficient given in literature [10] [11] [12]. Carbon fluxes to the atmosphere range between 1000 kg C. km⁻².d⁻¹ (figure 1a) within the mud plug to nothing in oceanic water. For the high pCO₂ value in seawater, the difference between the three estimates seems high, nevertheless the relative differences are constant for high and low water pCO₂ values. As ¹⁴C fluxes given by equation 3 are proportional to the carbon dioxide fluxes, we observe similar difference between ¹⁴C fluxes estimates (figure 1b). The highest ¹⁴C flux is encountered in the mud plug at low salinity. The ¹⁴C fluxes vary between few to 3.1 10⁵ Bq.km⁻².d⁻¹.

Table 2. ¹⁴C concentrations in the fluvial part in Loire estuary (relative precision is better than 1%).

Station	Date	Latitude (°)	Longitude (°)	Water temperature (°C)	Salinity (psu)	Wind speed (m.s ⁻¹)	pCO ₂ Water (μatm)	¹⁴ C Water (Bq.kg ⁻¹ C)	¹⁴ C air (Bq.kg ⁻¹ C)
1	02/15	47.235	-0.517	4.5	0	4.0	1767	400.9	
4	02/17	47.047	-2.351	9.6	30.7	5.0	384	258.9	230.6
8	02/17	47.176	-2.016	4.57	8.3	6.0	840	304.9	255.7
11	02/18	47.114	-2.192	7.85	23.7	6.0	411	273.3	239.9
14	02/19	47.122	-1.344	3.38	0	5.0	1152	230.8	241.2
16	02/19	47.178	-2.018	3.47	0	7.0	870	238.6	241.9
18	02/19	47.179	-2.080	4.25	3.8	8.0	778	274.7	243.5
25	02/20	47.142	-2.154	5.7	7.5	4.0	790	249.2	240.2

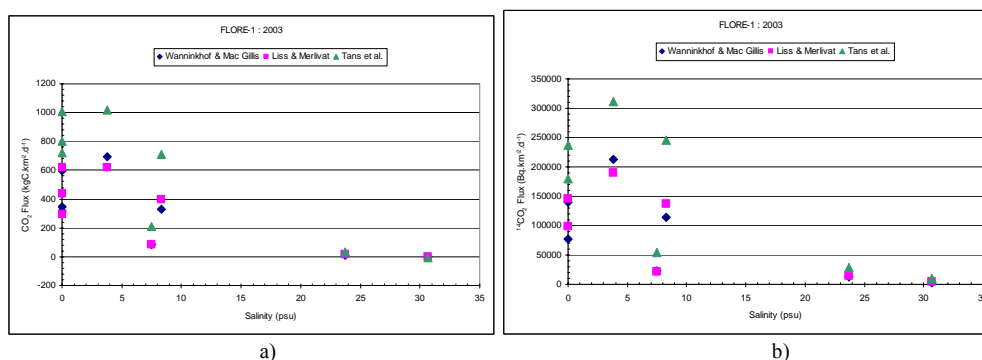


Figure 1. Variations CO₂ fluxes (a) and ¹⁴C fluxes (b) in surface seawater versus salinity during FLORE 1 cruise.

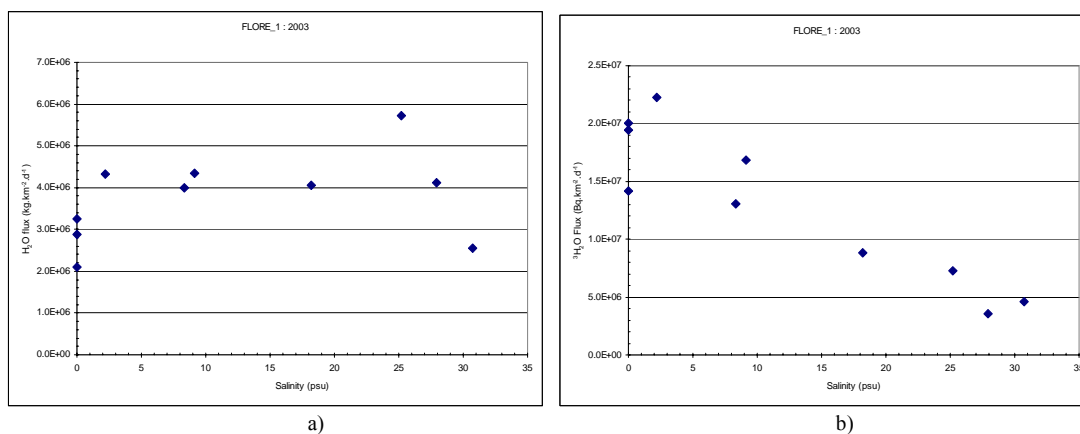
3.3 Tritium

Tritium activities vary from 1.0 to 6.9 Bq.L⁻¹ and 1.6 to 3.1 Bq.L⁻¹ for water and air samples, respectively. As the post atmospheric nuclear test activity reference value is less than 1.0 Bq.L⁻¹ in air and 0,15 Bq.L⁻¹ in water, all samples are clearly marked by ³H from the nuclear industry [7]. The activities in water decrease linearly with the salinity reflecting the dilution and the mixing of fluvial effluent into marine water.

Table 3. ^3H concentrations in the fluvial part in Loire estuary (relative precision is better than 30% at 1 Bq.L^{-1}).

Station	Date	Latitude (°)	Longitude (°)	Water temperature (°C)	Salinity (psu)	Wind speed (m.s ⁻¹)	^3H (Bq.L ⁻¹) water	^3H (Bq.L ⁻¹) air
1	02/15	47.235	-0.517	4.5	0	4.0	6.9	
2	02/15	47.219	-1.008	4.7	0	7.0	6.3	
3	02/15	47.155	-1.256	4.7	0	6.0	6.9	
4	02/17	47.047	-2.351	9.6	30.7	5.0	1.9	1.6
6	02/17	47.159	-2.118	5.8	9.1	6.0	4.0	
7	02/17	47.179	-2.021	4.7	2.2	6.0	5.3	
8	02/17	47.176	-2.016	4.6	8.3	6.0	3.4	2.9
10	02/17	47.105	-2.199	8.1	27.9	6.0	1.0	
11	02/17	47.114	-2.192	7.8	25.2	6.0	1.4	3.1
12	02/17	47.143	-2.145	7.2	18.2	5.0	2.3	2.5

The mean water vapour flux calculations obtained during these cruise vary between $2.1 \cdot 10^6 \text{ kg.km}^{-2} \cdot \text{d}^{-1}$ and $5.8 \cdot 10^6 \text{ kg.km}^{-2} \cdot \text{d}^{-1}$ (figure 2a). The corresponding variation of the flux of ^3H from water to atmosphere range from $3.6 \cdot 10^6 \text{ Bq.km}^{-2} \cdot \text{d}^{-1}$ to $2.3 \cdot 10^7 \text{ Bq.km}^{-2} \cdot \text{d}^{-1}$ (figure 2b).

**Figure 2.** Variations H_2O fluxes (a) and ^3H fluxes (b) in surface seawater versus salinity during FLORE 1 cruise.

4. CONCLUSIONS

During FLORE 1 cruise ^{14}C , ^3H et ^{131}I activities were measured in Loire river estuary. Results indicate clearly a contamination by iodine 131 in the fluvial part of the estuary. Measurements of ^{14}C and ^3H activities show the contribution of nuclear industry. Calculation of the radionuclide fluxes show that a significant part of the nuclear waste is transferred to the atmosphere even, if the winter period is characterised by low biological activity and low evaporation in the estuary.

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