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Carbon 14 transfer from seawater to the atmosphere through degassing processes in the Bay of Seine (North-West of France)

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Abstract. COGEMA La Hague nuclear reprocessing plant is located in the North West of Cotentin peninsula near Cherbourg (France). This nuclear plant releases radioelements in atmosphere and in the English Channel. About 8.5 TBq.year^{-1} of radiocarbon are released as the liquid wastes through a pipe a few kilometres off sea shore, West of the reprocessing plant. Recent studies in the peninsula show anomalous higher radiocarbon contents in vegetation near the coast that have suggested a supplementary marine contribution through the degassing of the ^{14}C excess supplied by liquid releases of the nuclear plant. Carbon dioxide partial pressure, ^{14}C activities were measured in air and sea water in the Bay of Seine and around the COGEMA-La Hague nuclear reprocessing plant during three cruises in 2000 and 2002. Results show clearly that sea is a source of CO_2 and ^{14}C to the atmosphere. Higher ^{14}C concentrations in air and water related to the La Hague liquid wastes are clearly recorded. The aim of this paper is to show results of these oceanographic campaigns. Flux between seawater and atmosphere are calculated in the North-West Cotentin and in Bay of Seine.

1. INTRODUCTION

COGEMA La Hague nuclear reprocessing plant is located in the north west of Cotentin peninsula near Cherbourg (France). This nuclear plant releases radio-elements in atmosphere and in the English Channel. Radiocarbon is released to the environment as CO_2 through a 100 metres high chimney and as liquid waste few kilometres off sea shore, west of the reprocessing plant. Atmospheric ^{14}C releases are estimated to 19 TBq.year^{-1} [1].

The carbon dioxide is assimilated by plants through photosynthetic processes. Consequently, the ^{14}C activity of vegetation constitute an integrated record of COGEMA La Hague emissions, during the vegetative period (spring to fall). During 3 years (1997, 1998 and 1999) ^{14}C measurements in air and in furzes were performed. Measurements of ^{14}C activity in the chimney plume show a rapid dilution from about 7200 Bq.kg^{-1} C near the chimney to values ranging between 400 and 900 Bq.kg^{-1} C at a distance of 4 to 6 km [2]. Outside periods of release ^{14}C residual value is around 270 Bqkg^{-1} C. Vegetation around the nuclear plant record these period of release, concentration in bio-indicators like furzes ranging between once and twice the present atmospheric background [2] [3]. Higher ^{14}C concentrations are observed at the coast suggesting a supplementary marine contribution though the degassing of the ^{14}C excess supplied by liquid release (8.5 TBq.year^{-1}) through a pipe few kilometres off sea shore, west of the reprocessing plant [1].

The aim of this study is to estimate the ^{14}C fluxes between seawater and atmosphere in the north-west Cotentin and in the Bay of Seine.

2. EQUIPMENT AND METHOD

2.1 Strategy

In order to estimate $^{14}CO_2$ 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).

$$\Phi(CO_2)\ (mole.m^{-2}.s^{-1}) = K.\ S.\ \Delta pCO_2 \qquad (1)$$

K ($m.s^{-1}$) is the CO_2 transfer coefficient between seawater and atmosphere, S is solubility of CO_2 ($mole.m^{-3}.atm^{-1}$) and ΔpCO_2 (atm) is the difference between partial pressure in water and air. pCO_2 in air was considered as constant mean value of 367 µatm [4] [5] [6] [7]. K is a parameter depending on wind speed and has been calculated by using studies of Liss and Merlivat [8], Tans *et al.,* [9] and Wanninkhof and McGillis [10]. 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).

$$\Phi(^{14}C) = [^{14}C]_O\ \Phi_{OA}\,(CO_2) - [^{14}C]_A\ \Phi_{AO}\,(CO_2) \qquad (2)$$

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

$$\Phi(^{14}C)\ (Bq.km^{-2}.d^{-1}) = 10^9\ ([^{14}C]_O\ .\Phi_{OA} - [^{14}C]_A\ \ \Phi_{AO}) \qquad (3)$$

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

This method usable if the samples are collected out of the influence of the chimney plume which is easily detectable by the krypton 85 (^{85}Kr) content. During ^{14}C sampling ^{85}Kr was measured continuously at a frequency of 1 measurement.s^{-1} [11]. Consequently the detection of ^{85}Kr emitted from the chimney of the reprocessing plant allows air to be sampled for ^{14}C measurements free of direct contamination coming from the plume of the chimney.

2.2 Techniques

Sea water and air samples were collected simultaneously during two cruises (TRANSAT 1 cruise, February 24-28th, 2002 and TRANSAT 2 cruises, August 27-31st, 2002) around north Cotentin peninsula and Bay of Seine (figure 1).

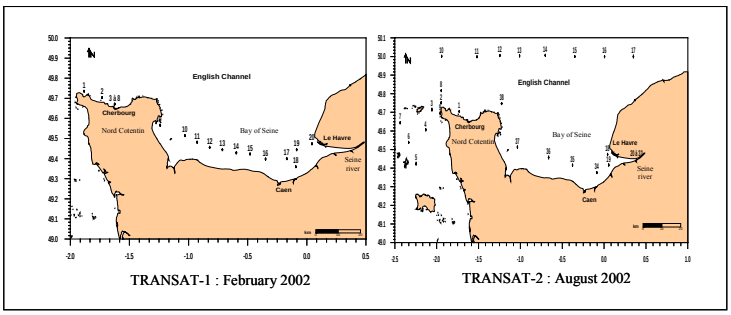


Figure 1. Location of sampling stations during TRANSAT 1 and TRANSAT 2.

Temperature and salinity of seawater were measured using a SBE 19-03 Seabird equipment and wind direction and speed were recorded. Only for TRANSAT cruises, 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 [12].

^{14}C activity in air samples were determined using the procedure defined by Maro *et al.*, [13].

Water samples were collected in glass bottle and poisoned with mercury chloride. In the laboratory, total CO_2 (ΣCO_2) was extracted from seawater following the procedure described by Bard *et al.,* [14] and Leboucher *et al.,* [15].

The radiocarbon activity was measured at Laboratoire de Sciences du Climat et de l'Environnement using the Gif Accelerator Mass Spectrometry (AMS) facilities. Results are expressed in $Bq.kg^{-1}$ C (100 pMC is equivalent to 226 $Bq.kg^{-1}$ C). The relative precision varies between 0.5 and 2%.

3. RESULTS AND DISCUSSION

Results are presented in table 1.

Table 1. Distance from the pipe outlet, wind speed at 10m high, surface seawater temperature (SST), salinity and CO_2 partial pressure in sea surface seawater, ^{14}C activity in seawater and air, during TRANSAT cruises.

Station TRANSAT 1	Distance (km)	Wind speed (m/s)	SST (°C)	Salinity (pm)	pCO2 (µatm)	[14C]water (Bq/kg C)	[14C]air (Bq/kg C)
1	15	12	9.7	33.91	373.4	587.8	238.8
2	22	11	9.8	33.86	378.6		
3	29	12	9.5	33.49	377.1	410.2	239.4
4	30	11	9.5	33.61	386.3		
5	30	10	9.6	33.55	384.1		
6	30	10	9.6	33.42	386		
8	30	10	9.6	33.63	373.5		
9	58	8	8.7	33.01	387.5	378.4	237.1
10	74	12	9.2	33.43	378.5	379.5	239.3
11	82	9	8.8	33.05	402.8		
12	91	9	8.7	32.88	400.7	353.3	236.4
13	99	9	8.6	32.41	416.8		
14	107	10	8.5	32.35	415.3	331.0	236.2
15	115	10	8.5	32.31	419.9		
16	125	10	8.5	32.17	430.3	324.8	241.3
17	138	10	8.5	32.37	421		
18	144	10	8.4	31.26	441.2		242.7
19	143	10	8.4	31.65	448.6		
20	151	10	8.1	25.63	613.6	286.3	236.2
Station TRANSAT 2	**Distance (km)**	**Wind speed (m/s)**	**SST (°C)**	**Salinity (pm)**	**pCO2 (µatm)**	**[14C] water (Bq/kg C)**	**[14C] air (Bq/kg C)**
1	22.40	7.3	17.9	34.78	465.7	342.5	226.4
5	33.7	6.2	18.0	35.10	422.7	270.7	222.2
7	34.4	3.4	16.7	35.10	424.0		
9	3.6	3.4	17.8	34.89	462.9	706.7	346.4
10	37.7	4.1	17.1	35.06	438.0	281.6	240.9
13	83.4	3.4	17.7	34.90	442.5		
17	175.4	1.8	18.6	34.56	452.0	343.6	262.6
18	151.3	3.1	19.6	29.01	759.0	258.3	243.5
19	152.7	3.9	19.5	22.40	1407.6		
34	144.4	5.5	19.4	31.66	464.3		
36	101.7	4.8	19.6	33.30	402.0		
37	74.0	4.6	18.7	34.35	441.0	351.5	262.2

3.1 pCO_2 and ^{14}C activities

pCO_2 values vary from 373 to 614 µatm for the TRANSAT 1 cruise data, and between 402 and 1408 µatm for TRANSAT 2 cruise data. pCO_2 measurements in water show similar high values compared to air during the winter and summer cruises and increase toward Seine River estuary. This indicates CO_2 flux to the atmosphere since mean atmospheric pCO_2 value is 367 µatm. This results are easily predictable because coastal and shelf and estuarine areas exhibit high biological activity due to the nutrient input near the river mouths and organic matter recycling in the water column [16]. This heterotrophic activity resulting in high degradation rates at the sediment surface and in the water column produces high dissolved CO_2 concentrations [17].

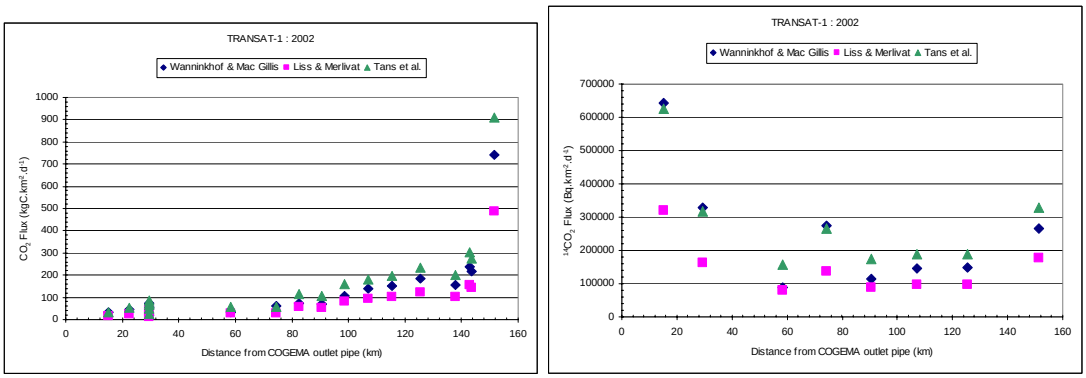
During TRANSAT cruises, ^{14}C activities in surface water vary between 258.3 to 706.7 $Bq.kg^{-1}$ C. The highest value corresponds to a station within the plume of the liquid waste near the pipe outlet. All these values are higher than the reference value, 239 $Bq.kg^{-1}$ C (year 2002). During TRANSAT 1 winter cruise atmospheric values are near the reference value mainly due to the stormy meteorological conditions that induce a greater mixing of the atmosphere. During the TRANSAT 2 summer cruise, ^{14}C activities in air present a positive correlation with ^{14}C in surface water, confirming previous results [3][13] and the transfer from the sea.

3.2 Carbon dioxide and ^{14}C fluxes

3.2.1 TRANSAT 1

CO_2 fluxes to the atmosphere are calculated from equation 1 using K transfer coefficient given in literature [8] [9] [10]. Carbon fluxes range between few to 911 kg C. $km^{-2}.d^{-1}$ (figure 2a). For the high pCO_2 value in seawater, the difference between estimates is high nevertheless the relative differences are constants for high and low water pCO_2 values.

As ^{14}C fluxes given by equation 3 are proportional to the carbon dioxide fluxes we observe similar difference between estimates (figure 2b). During TRANSAT 1, the highest ^{14}C flux is encountered near Cherbourg City and the lowest between Cherbourg city and the Seine river estuary. Maximum flux are 6.4 10^5 $Bq.km^{-2}.d^{-1}$ for TRANSAT 1.

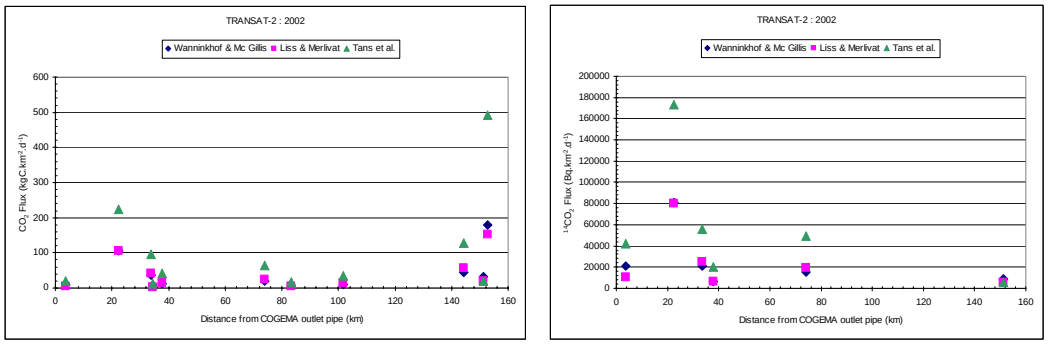


a) b)

Figure 2. Variations CO_2 fluxes (a) and ^{14}C fluxes (b) in surface seawater versus distance from pipe outlet during TRANSAT 1.

3.2.2 TRANSAT 2

Carbon fluxes range between few to 493 kg C. $km^{-2}.d^{-1}$ (figure 3a).



a) b)

Figure 3. Variations CO_2 fluxes (a) and ^{14}C fluxes (b) in surface seawater versus distance from pipe outlet during TRANSAT 2.

Although water pCO_2 are higher during this cruise the carbon dioxide fluxes are smaller due to the weak wind speed. During this cruise maximum ^{14}C fluxes values were encountered near Cherbourg city and minimum values near Seine river estuary (figure 3b). Maximum flux are 1.7 10^5 $Bq.km^{-2}.d^{-1}$ for TRANSAT 2.

3.2.3 Annual flux estimate for the Bay of Seine

Following estimates derived from Tans *et al.* model, the mean flux in the Bay of Seine due to COGEMA La Hague liquid wastes would reach 2.3 10^5 and 3.9 10^4 $Bq.km^{-2}.d^{-1}$ for TRANSAT 1 and 2 respectively. A rough annual estimation would give 216GBq for the 4400 km^{-2} of the Bay of Seine, representing less than 3% of the liquid release from COGEMA La Hague nuclear reprocessing plant.

4. CONCLUSION

Simultaneous measurements of CO_2 partial pressure and ^{14}C activity in air and sea water indicate that the English Channel and Bay of Seine are a source a carbon dioxide to the atmosphere in good agreement with previous studies. ^{14}C activities decrease from the west to the east according to the dilution of the waste plume of the plant. Estimations of CO_2 and ^{14}C flux show that a minor part of the ^{14}C liquid release by industrial activity is recycled to the atmosphere. These estimates are not very accurate due to the variation of CO_2 transfer coefficients propose by different models. However, the ^{14}C releases in Bay of Seine could provide a good opportunity to perform new experiments in order to get better estimates of CO_2 transfer coefficients between water and atmosphere.

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