RADIOCARBON, Vol 46, Nr 2, 2004, p 831–839

^{14}C SOURCES AND DISTRIBUTION IN THE VICINITY OF LA HAGUE NUCLEAR REPROCESSING PLANT: PART II—MARINE ENVIRONMENT

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ABSTRACT. Carbon dioxide partial pressure and radiocarbon activity were measured in air and seawater in the Bay of Seine and around the COGEMA-La Hague nuclear reprocessing plant (northwest France) during 3 cruises in 2000 and 2002. Results clearly show that the sea is a source of CO_2 and ^{14}C to the atmosphere. High ^{14}C concentrations in air and water related to the La Hague liquid waste are clearly recorded. For the restricted area of the Bay of Seine, CO_2 carbon and ^{14}C fluxes were estimated, indicating that less than 3% of the liquid ^{14}C release is introduced in the atmosphere.

INTRODUCTION

The COGEMA-La Hague nuclear reprocessing plant is located in the northwest of the Cotentin Peninsula, near Cherbourg (France). This nuclear plant releases radioelements in the atmosphere and in the English Channel. About 8.5 TBq.yr^{-1} of radiocarbon is released as liquid waste through a pipe a few km off the shore, west of the reprocessing plant (COGEMA data 2000). Recent studies in the peninsula (Fontugne et al., this issue) show anomalously high ^{14}C contents in vegetation near the coast which suggest a supplementary marine contribution through the degassing of the ^{14}C excess supplied by the liquid release of the nuclear plant.

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

MATERIALS AND METHODS

Methods

In order to estimate $^{14}CO_2$ fluxes across the surface seawater and the atmosphere interface, the partial pressure of carbon dioxide (pCO_2) was calculated using measurements of the 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 using Equation 1:

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

where K (m.s^{-1}) is the CO_2 transfer coefficient between seawater and the 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 a constant mean value of 367 µatm according to values published by Copin-Montégut (1996), Boehme et al. (1998), Frankignoulle and Borges (2001), and Keir et al. (2001). K is a parameter depending on wind speed; its values are available in Liss and Merlivat (1986), Tans et al. (1990), or Wanninkhof and McGillis (1999). As these K values are slightly different in these 3 studies, we present the 3 CO_2 flux estimates.

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Proceedings of the 18th International Radiocarbon Conference, edited by N Beavan Athfield and R J Sparks
RADIOCARBON, Vol 46, Nr 2, 2004, p 831–839

The exchange of CO_2 between the atmosphere and the surface seawater is an equilibrium process; the net 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 net ^{14}C flux is, once again, the difference. The expression for the net ^{14}C flux from the ocean surface to the atmosphere is given in Equation 2:

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

Regarding the constant factor due to the use of appropriate units, ^{14}C fluxes were calculated following Equation 3:

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

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.

Sampling and Analytical Procedures

Seawater and air samples were collected simultaneously during 3 cruises (TE-SEA cruise, 1–4 June 2000; TRANSAT 1 cruise, 24–28 February 2002; and TRANSAT 2 cruise, 27–31 August 2002) around the northern Cotentin Peninsula and the Bay of Seine (Figure 1). During these cruises, krypton-85 (^{85}Kr) was measured continuously at a frequency of 1 measurement.s^{-1} (Maro et al. 2002). 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. CO_2 in a few liters of air was trapped by bubbling air in sodium hydroxide solution. Sodium hydroxide was prepared a few hours before sampling to avoid contamination by sodium carbonate, generally present within sodium hydroxide tablets. In the laboratory, barium hydroxide was added to a sodium hydroxide solution to get a precipitate of barium carbonate. This carbonate was then rinsed with degassed distilled water and dried at 50 °C before reaction with orthophosphoric acid under vacuum to evolve CO_2. Water used to prepare the solution was previously degassed. Precipitation, filtration of precipitate, and rinsing were performed under a controlled nitrogen atmosphere. The blank was determined following this procedure on the same solution used for sampling.

Water samples were collected in glass bottles 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. (1988) and Leboucher et al. (1999).

The temperature and salinity of seawater were measured using SBE 19-03 Seabird equipment, and wind direction and speed were recorded. For the TRANSAT cruises, CO_2 partial pressure in surface seawater was calculated using the pH and total alkalinity measurements following the "Standard Operating Procedures SOP3 and SOP6" of the US Department of Energy (DOE 1994).

The ^{14}C activity was measured at the 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 = 226 $Bq.kg^{-1}$ C). The relative precision varies between 0.5 and 2%.

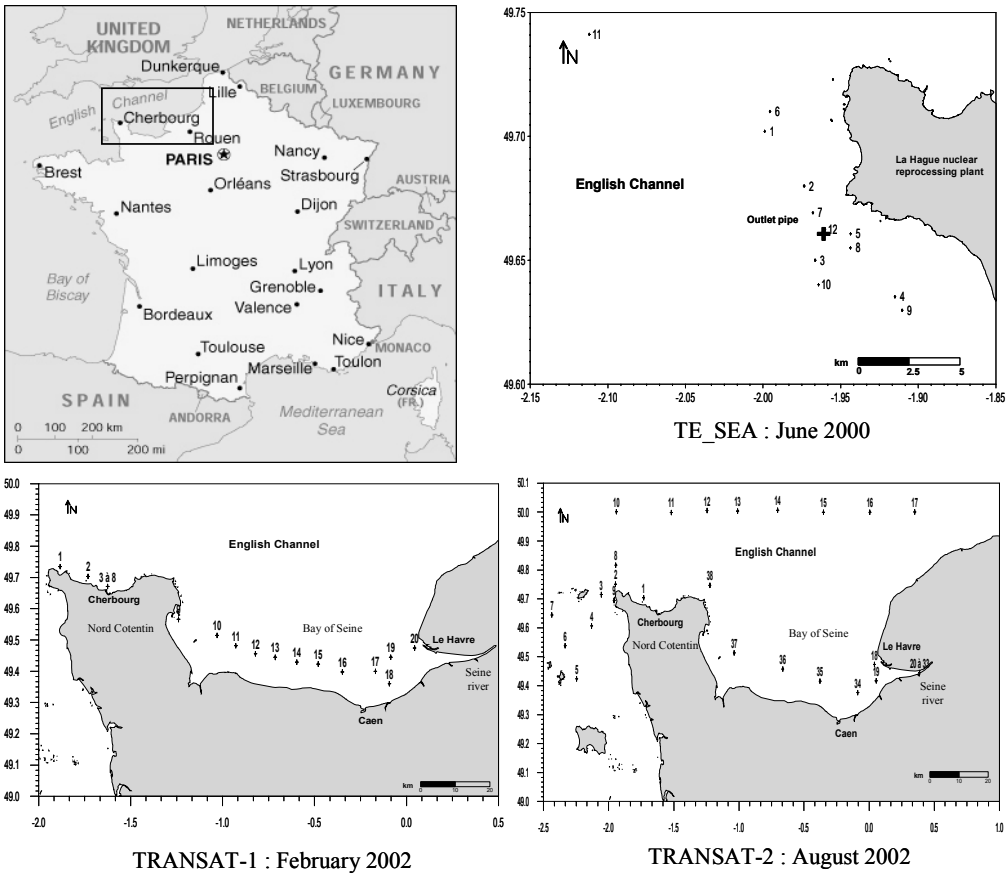

Figure 1 Location of sampling stations during the TE-SEA, TRANSAT 1, and TRANSAT 2 cruises

RESULTS AND DISCUSSION

Carbon Dioxide Flux

pCO_2 values (Figure 2 a, b) vary from 373 to 614 µatm for the TRANSAT 1 cruise data, and between 423 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 the Seine River estuary. This indicates CO_2 flux to the atmosphere since the mean atmospheric pCO_2 value is 367 µatm. These results are easily predictable because coastal, 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 (Savoye et al. 2003). This heterotrophic activity, resulting in high degradation rates at the sediment surface and in the water column, produces high dissolved CO_2 concentrations (April 1999).

CO_2 fluxes to the atmosphere calculated from Equation 1 are reported in Figure 3 a, b. Carbon fluxes range from very few to 911 and 493 kg C $km^{-2}.d^{-1}$ for TRANSAT 1 and TRANSAT 2 cruises, respectively. These values are strongly dependent on the K transfer coefficient chosen (Liss and Merlivat [1986], Tan et al. [1990], or Wanninkhof and McGillis [1999]), the difference between estimations may vary by a factor of 2 or more, especially considering high wind speed.

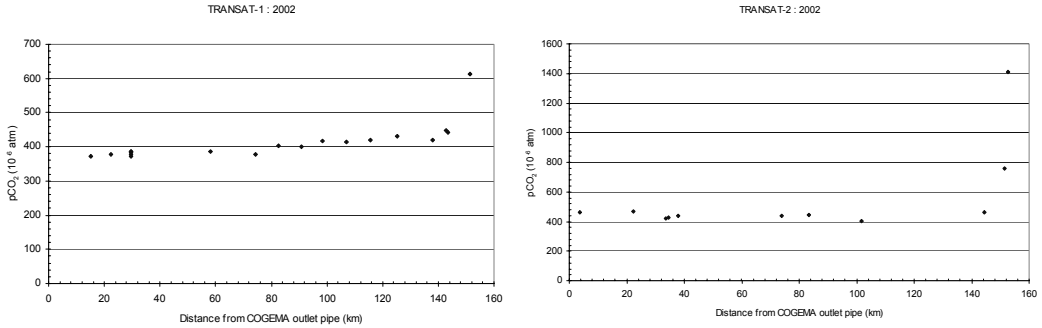

Figure 2 Variation of CO_2 partial pressure in surface seawater versus distance from pipe outlet during TRANSAT 1 and 2 cruises

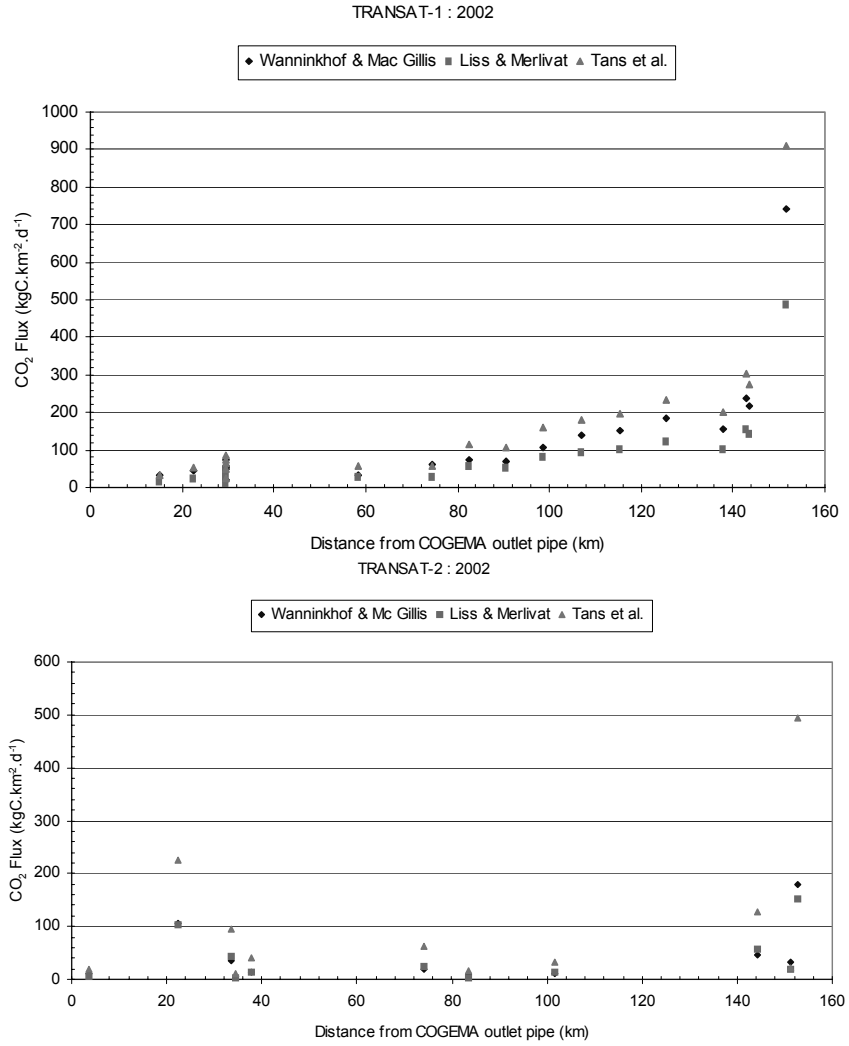

Figure 3 Variations of CO_2 fluxes versus distance from pipe outlet during TRANSAT 1 (above) and 2 (below) cruises

^{14}C Flux

Preliminary experiments performed during the TE-SEA cruise are reported in Table 1 and Figure 4. The ^{14}C activities of ΣCO_2 in seawater vary between 342.2 Bq.kg^{-1} at station 11 in the northwest part of the studied area to 580.8 Bq.kg^{-1} C near the mouth of the pipe. The values (except station 11) range between 479.6 to 580.8 Bq.kg^{-1} C, decreasing from south to north and recording clearly the plume and the dilution of waste. These values are about twice the reference values in 2000 (248 Bq.kg^{-1} C) for modern surface waters measured in Brittany, off Brest. ^{14}C values in air samples are more homogenous, varying between 257.6 to 292.2 Bq.kg^{-1} C. However, these values are higher than the atmospheric reference (248 Bq.kg^{-1} C).

Table 1 Location of sampling, distance from the pipe outlet, ^{14}C activity in seawater and air during the TE-SEA cruise. Shaded rows are under plume influence (see Fontugne et al., these proceedings).

Station TE-SEA	Latitude (N) (°)	Longitude (W) (°)	Distance (km)	^{14}C in water (Bq/kg C)	^{14}C in air (Bq/kg C)
1	49.70	2.00	5.2	480.7	268.5
2	49.68	1.97	2.2	506.0	279.1
3	49.65	1.96	1.5	527.0	257.6
4	49.63	1.92	4.4	562.3	269.8
5	49.66	1.94	1.2	520.3	259.4
6	49.71	2.00	5.9	479.6	428.9
7	49.66	1.97	0.9	539.7	468.7
8	49.66	1.94	1.4	559.6	435.1
9	49.63	1.91	5.1	557.8	908.1
10	49.64	1.96	2.5	506.2	426.0
11	49.74	2.11	14.0	342.2	271.2
12	49.66	1.96	0.0	580.8	292.2

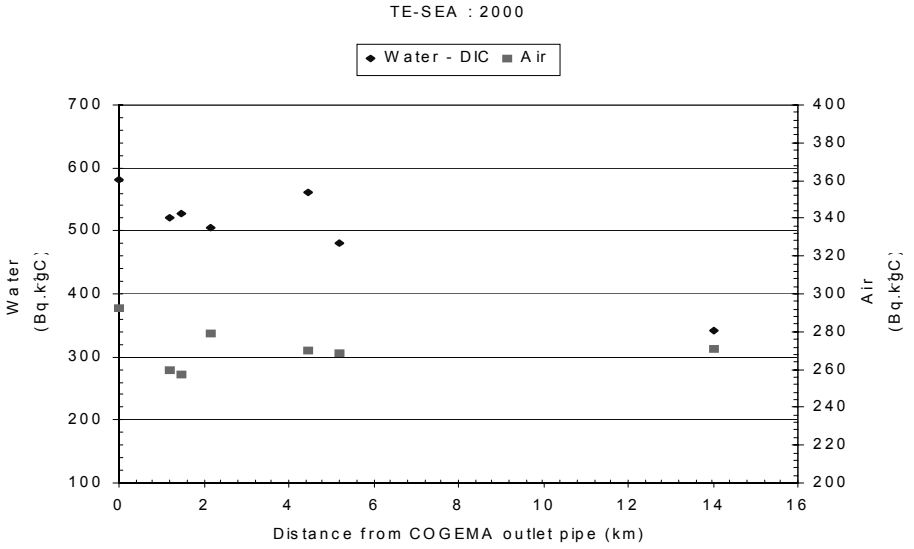

Figure 4 Variations of ^{14}C activities (Bq.kg^{-1} C) in surface seawater and air versus distance from the pipe outlet during the TE-SEA cruise

Table 2 Location of sampling, distance from the pipe outlet, ^{14}C activity in seawater and air, wind speed at 10 m, temperature, salinity, and CO_2 partial pressure in surface seawater during TRANSAT cruises.

Station	Latitude (N)	Longitude	Distance	[^{14}C] water	u10	Temperature	Salinity	pCO_2	[^{14}C] air
TRANSAT 1	(°)	(°)	(km)	(Bq/kg C)	(m/s)	(°C)	(pm)	(µatm)	(Bq/kg C)
1	49.73	1.88W	15.0	587.8	12.0	9.7	33.91	373.4	238.8
2	49.70	1.73W	22.4	—	11.0	9.8	33.86	378.6	—
3	49.67	1.63W	29.4	410.2	12.0	9.5	33.49	377.1	239.4
4	49.67	1.62W	29.6	—	11.0	9.5	33.61	386.3	—
5	49.67	1.62W	29.6	—	10.0	9.6	33.55	384.1	—
6	49.67	1.62W	29.6	—	10.0	9.6	33.42	386	—
8	49.67	1.62W	29.6	—	10.0	9.6	33.63	373.5	—
9	49.57	1.24W	58.3	378.4	8.0	8.7	33.01	387.5	237.1
10	49.51	1.03W	74.4	379.5	12.0	9.2	33.43	378.5	239.3
11	49.48	0.93W	82.5	—	9.0	8.8	33.05	402.8	—
12	49.46	0.82W	90.7	353.3	9.0	8.7	32.88	400.7	236.4
13	49.44	0.71W	98.5	—	9.0	8.6	32.41	416.8	—
14	49.43	0.60W	107.2	331.0	10.0	8.5	32.35	415.3	236.2
15	49.42	0.48W	115.5	—	10.0	8.5	32.31	419.9	—
16	49.40	0.35W	125.4	324.8	10.0	8.5	32.17	430.3	241.3
17	49.40	0.17W	137.9	—	10.0	8.5	32.37	421	—
18	49.39	0.09W	143.6	—	10.0	8.4	31.26	441.2	242.7
19	49.44	0.09W	142.8	—	10.0	8.4	31.65	448.6	—
20	49.47	0.04E	151.5	286.3	10.0	8.1	25.63	613.6	236.2
TRANSAT 2									
1	49.70	1.73W	22.40	342.5	7.3	17.9	34.78	465.7	226.4
5	49.42	2.25W	33.7	270.7	6.2	18.0	35.10	422.7	222.2
7	49.64	2.44W	34.4	—	3.4	16.7	35.10	424.0	—
9	49.69	1.96W	3.6	706.7	3.4	17.8	34.89	462.9	346.4
10	50.00	1.94W	37.7	281.6	4.1	17.1	35.06	438.0	240.9
13	50.00	1.01W	83.4	—	3.4	17.7	34.90	442.5	—
17	50.00	0.35E	175.4	343.6	1.8	18.6	34.56	452.0	262.6
18	49.47	0.04E	151.3	258.3	3.1	19.6	29.01	759.0	243.5
19	49.45	0.05E	152.7	—	5.9	19.5	22.40	1407.6	—
34	49.38	0.09W	144.4	—	5.5	19.4	31.66	464.3	—
36	49.46	0.66W	101.7	—	4.8	19.6	33.30	402.0	—
37	49.51	1.04W	74.0	351.5	4.6	18.7	34.35	441.0	262.2

During the TRANSAT cruises, ^{14}C activities in the surface seawater vary between 258.3 to 706.7 Bq.kg^{-1} C (Table 2). The highest value corresponds to a station within the plume of the liquid waste near the pipe outlet (Figures 5 a,b). All these values are higher than the reference value of 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 which induce a greater mixing of the atmosphere. During the TRANSAT 2 summer cruise, ^{14}C activities in the air present a positive correlation with ^{14}C in surface water, confirming transfer from the sea.

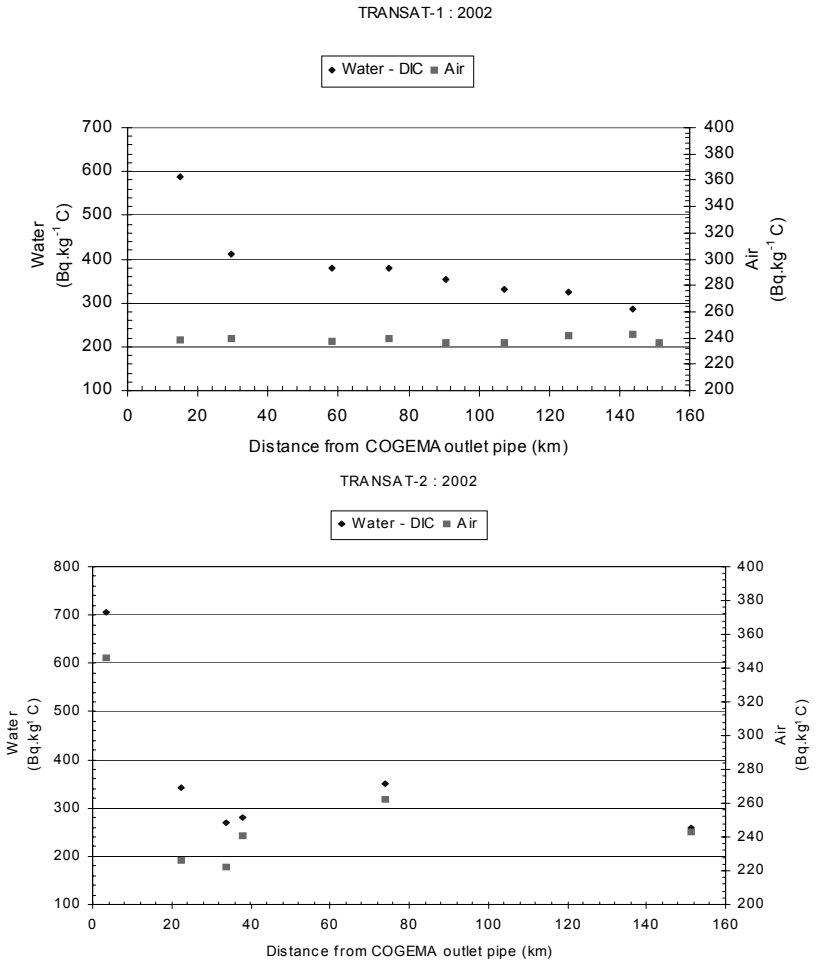

Figure 5 Variations of ^{14}C activities (Bq.kg^{-1} C) in surface seawater and air versus distance from pipe outlet during TRANSAT 1(above) and 2 (below) cruises

For each estimate of carbon dioxide flux, the ^{14}C fluxes were estimated using Equation 3. Maximum fluxes are 6.4 10^5 and 1.7 10^5 Bq.km^{-2}.d^{-1} for TRANSAT 1 and 2, respectively (Figures 6 a,b). During TRANSAT 1, the highest ^{14}C flux is encountered near the city of Cherbourg, and the lowest between Cherbourg and the Seine River estuary. The TRANSAT 2 cruise presents a maximum value near Cherbourg and a minimum value near the Seine River estuary due to lower CO_2 fluxes during these cruises (low wind speed near the Seine estuary). Following estimates derived from the Tans et al. model, the mean flux in the Bay of Seine due to the COGEMA-La Hague liquid waste 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 216 GBq 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.

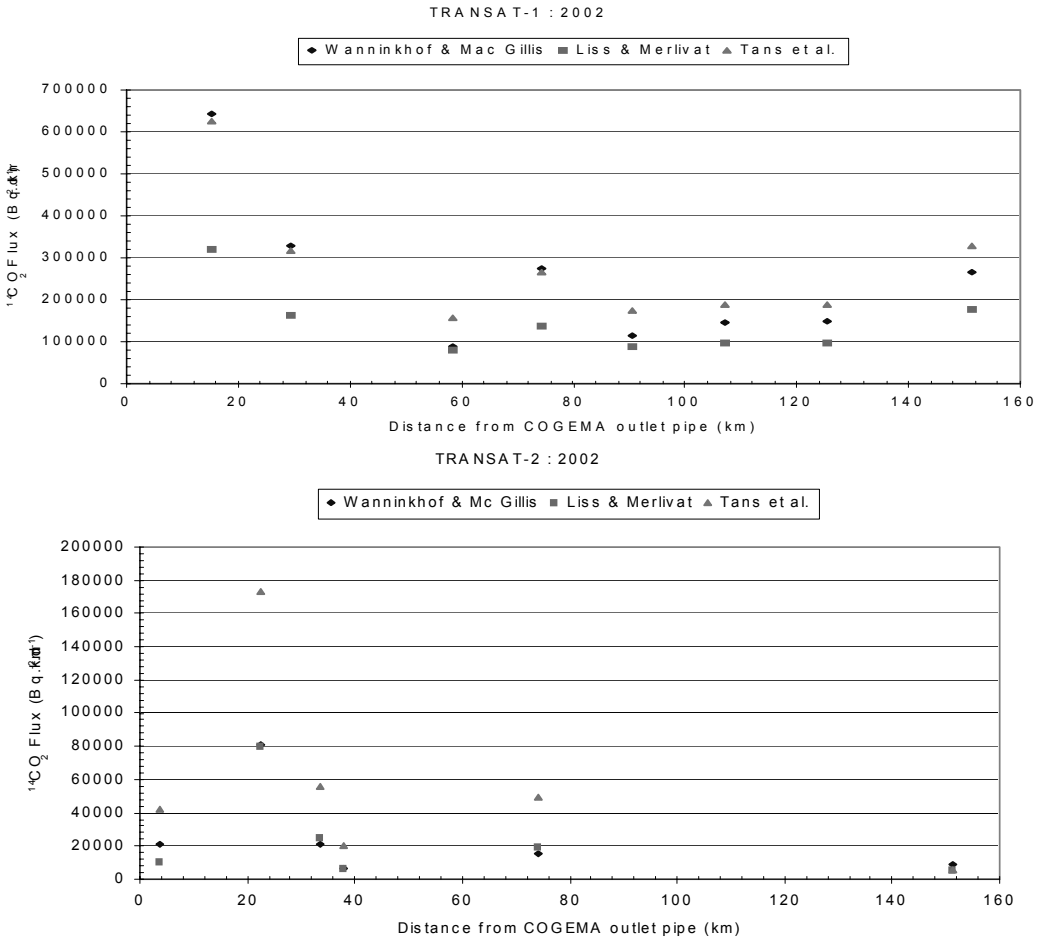

Figure 6 Variations of ^{14}C fluxes versus distance from pipe outlet during TRANSAT 1 (above) and 2 (below) cruises

CONCLUSIONS

Simultaneous measurements of CO_2 partial pressure and ^{14}C activity in air and seawater 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 proposed by different models. However, the ^{14}C releases in the 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.

ACKNOWLEDGEMENTS

Thanks are due to M Paterne for helpful discussions and M Arnold for AMS measurements and S Le Bar and M L Fitament from COGEMA for their help during the cruises. We are very grateful to Rodger Sparks for suggestions and corrections of the manuscript. We thank Mr Le Bourhis and Mr Henri captains of the crew of the R/V "Côtes de la Manche." TE-SEA and TRANSAT cruises were supported by CNRS.LSCE contribution nr 1102.

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