Reactive and total Mercury in offshore waters of the Ligurian Sea

V. MINGANTI, F. FIORENTINO, R. De PELLEGRINI and R. CAPELLI

Istituto di Analisi e Tecnologie Farmaceutiche ed Alimentari, Università di GENOVA (Italy)

Samples of seawater were collected in August 1991, during a cruise with the Decanographic Vessel N/O Minerva (CNR, Consiglio Nazionale delle Ricerche). Oceanographic Vessel N/O Sampling was carried out with acid cleaned borosilicate glass bottles at the following depths: 0.2, 5 and 10 meters. Salinity and temperature were recorded by bathysonde CTD ME (Meerestechnik-Elektronik) for all sampling sites. GPS equipment was used for vessel's positioning. Mercury determinations were done on unfiltered samples with the cold vapour technique after preconcentration over gold, with Atomic Fluorescence detection. The analytical methodology for total mercury (Hg-T) and the critical steps (sampling, storage of samples, samples pretreatement, and blank values) were described by MINGANTI *et al.* (1991). The detection limit of the method is 0.2 ng L-1. Reactive mercury (Hg-R) was determined with the same equipment directly on board the ship without any pretreatment of the samples. Accuracy and precision of analytical determinations were evaluated, and results are shown in Table 1

Table 1. Results obtained for total mercury determination on ORMS-1 Riverine Water Reference Materials for Mercury of the National Research Council of Canada. All results are in ng L-1. Confidence limits (c.l.) are calculated at p% = 95 of confidence level.

Results obtained	BottleA: Bottle B: x±c.l	5.1 6.5 5.8 ± 0.7	5.5 6.2	5.6
Certified value	x±c.l.	6.8 ± 1.3		

Sampling sites, togheter with a summary of Hg-T levels are shown in Figure 1.

Increasing levels of mercury are represented with darker shading. No correlation was found among Hg-T, Hg-R, salinity, temperature, and depth. Median, mean, standard deviation (S.D.), number of samples (n), minimum and maximum values for the parameters considered are reported in Table 2.

Table 2. Summary statistics and number of data for Hg-T and Hg-R (ng L-1), Hg-R/Hg-T ratio, salinity (‰), temperature (°C).

	Median	Mean	S.D.	n	Min	Max
Hg-T	0.7	0.8	0.5	32	0.3	2.3
Hg-R	0.3	0.3	0.2	33	0.2	0.8
Hg-R/Hg-	Г 0.4	0.5	0.2	32	0.1	1.0
Salinity	38.105	38.133	0.108	21	37.982	38.293
Temp.	24.68	24.79	0.62	21	23.50	25.67

Levels found are lower than those reported by other authors for offshore waters of the Mediterranean. FERRARA and MASERTI (1986) reported values ranging 1-6 ng L $\,$

the Mediterranean. FERKARA and MASER11 (1900) reported values ranging 1-0 ng L-1, with a mean of 4 ng L-1. Data concerning the outer part of the Estuary of River Krka (Adriatic Sea), reported by MIKAC et al. (1990), are lower, ranging 0.9-1.2 ng L-1, at 38‰ salinity. Hg-R is about 90-100% of Hg-T, higher than what found in this work. Data concerning Hg-T and Hg-R levels in offshore water of the Ligurian sea were reported by COPIN-MONTEGUT et al. (1986). No differences were reported between Hg-T and Hg-R, and mean level about 2.5 ng L-1. FILEMAN et al. (1991) in surface



FILEMAN et al. (1991) in surface water samples from the Dogger Bank and the Outer Silver Pit (North Sea), reported a Hg-T mean level (as Hg-Dissolved + Hg-Particulate) of 0.4 ng L-1, with 70%

of Hg-R. COSSA and FILEMAN (1991) in COSSA and FILEMAN (1991) in unfiltered surface waters of English Channel, reported a Hg-T concen-tration of 0.2 ng L-1 in Mid Channel, rising to 0.6 ng L-1 inshore. These values are in good agreement to the most recent measures in surface oceanic waters (Hg-T \leq 0.5 ng L⁻¹), as reported by GILL and FITZGERALD (1987) and FILEMAN and HARPER (1989).

Acknowledgements

This research was funded by the CEE under contract EV4V - 0125-I (A).

Figure 1. Sampling sites in the Ligurian Sea. Increasing levels of mercury are shown with darker shading

REFERENCES

- COPIN-MONTEGUT G., COUREAU PH and LAUMOND F., 1986.- Papers presented at the FAO/UNEP/WHO/IOC/IAEA Meeting on the Biogeochemical cycle of Mercury in the Mediterranean. Siena, Italy, 27-31 August 1984. FAO Fish. Rep., (325) suppl.: 51-57
- COSSA D. and FILEMAN C., 1991.- Mar. Pollut. Bull., 22(4): 197-200.
- FERRARA R. and MASERTI B., 1986. Mar. Pollat. Bull., 17(2): 539-534. FILEMAN C.F. and HARPER D.J., 1989.- Intern. Council Expl. Sea; Mar. Environ. Quality Com. CM, 1989-E: 14 pp. FILEMAN C.F., ALTHAUS M., LAW R.J. and HASLAM I., 1991.- Mar. Pollut. Bull.,
- 22(5): 241-244. GILL G.A. and FITZGERALD W.F., 1987.- Global Biogeochemical Cycles, 1 (3): 199-212. MIKAC N., KWOKAL Z. and BRANICA M., 1990.- Rapp. Comm. int. Mer Médit, 32, 1 :
- MINGANTI V., CAPELLI R. and De PELLEGRINI R., 1991.-Congresso Interdivisionale della Società Chimica Italiana CISCI 91, 6-11 October 1991, Chianciano Terme, Italy, Vol. II · 554-555

Rapp. Comm. int. Mer Médit. 33. (1992).

Vertical Particulate Carbon fluxes in the Ligurian Sea : A time-series study

J.C. MIQUEL, S.W. FOWLER and J. LA ROSA

IAEA, Marine Environment Laboratory, MONACO (Principauté de Monaco)

In open Mediterranean waters the downward flux of particulate material may originate from either an allochtonous source (atmospheric fallout, terrigenous input) or an autochtonous source (export from the photic zone). The latter comprises particles basically originating from the primary production of particulate organic matter and the associated build up of mineral particles such as carbonates and opal. In the framework of the French JGOFS activities in the Mediterranean Sea (DYFAMED programme), a time-series study on particle matter ad these closest forms in the series of t programme), a time-series study on particle, major and trace element fluxes in the water column was initiated in the Ligurian Sea in 1986 to ascertain the role and importance of these various sources. The importance and magnitude of the atmospheric input has already been discussed by FOWLER et al. (1987) and BUAT-MENARD *et al.* (1989). In the present paper we report data on the downward carbon fluxes, primarily those associated with primary production in the upper waters.

Since 1987, we have regularly monitored particle fluxes at two offshore stations out Since 1987, we have regularly monitored particle fluxes at two offshore stations out of the influence of the Ligurian Current, one near Corsica (42°44 N and 8°32 E, 1987-1988) and the other near the French Riviera (43°25 N and 7°52 E, 1988-1990). Automated sediment traps (models Technicap PPS-3; cylindro-conical; 0.125 m² surface opening and PPS-5, conical; 1 m² surface opening) were moored at 100, 200 and 1000 m depth, and samples were sequentially collected every 9 to 15 days. The sites were visited every three months both to check the mooring line and to exchange the sample collectors. Cup collectors were filled with a 2% buffered formaldehyde solution to prevent microbekreatcophic activity and to limit the invest of loxching and to prevent microheterotrophic activity and to limit the impact of leaching and autolysis on the collected particles. Swimmers were carefully removed by sieving and hand-picking using forceps under a dissecting microscope.

The carbon fluxes, like total particulate fluxes, varied substantially over time. Important and rapid changes in fluxes were normally recorded simultaneously at the three depths surveyed indicating a rapid settling of particles through the water column. The sinking velocities were estimated to be at least 60 to 90 m per day. Carbon fluxes were the highest in late spring, and maxima were recorded in June 1987, June 1988 and May 1990 (Fig.1). Winter carbon fluxes were also important but not as high as spring fluxes. Year 1989 was particular in that the maximum amount of sedimenting carbon occurred in winter and not in spring. In general, carbon fluxes were the lowest in autumn.

Since the 200 m trap was collecting particles under the euphotic zone and the mean vertical flux of organic carbon at that depth is generally considered to be equivalent to "export production" from the overlying waters, we discuss here only the 200 m data. The average carbon flux over the entire 4-year period was 14.7 mg m⁻² d⁻¹ and ranged from a minima of 2-4 mg m⁻² d⁻¹ to a maximum of 68 mg m⁻² d⁻¹ (June 1988). The organic carbon flux was relatively high and, at 200 m, had a mean value of 11 mg m⁻² d⁻¹ (ranging from 1 to 60 mg m⁻² d⁻¹). For both total and organic carbon, the fluctuations in flux observed were considerable and varied over the year by a factor of 30 to 60. Aside from the general seasonal pattern. a pronounced variability on shorter fluctuations in flux observed were considerable and varied over the year by a factor of 30 to 60. Aside from the general seasonal pattern, a pronounced variability on shorter time scales was also observed during the continual, high resolution flux experiments. For example, short pulses of enhanced sedimentation lasting only 48 hours were recorded in spring 1990. On an annual basis, total particulate carbon export from the surface layers was 5.1 g m⁻² y⁻¹ of which 4.0 mg m⁻² d⁻¹ was organic (POC, export production) and 1.1 mg m⁻² d⁻¹ was carbonate carbon. Total particle flux followed approximately the same pattern as the carbon flux, however, the highest mass fluxes force that the in writer and in a content. occurred both in winter and in spring.

Vertical fluxes measured in the relatively unproductive Ligurian Sea (NW Mediterranean Sea) during the years 1987-1990 are of a similar magnitude as those reported for other oligotrophic oceanic waters. A seasonal signal in carbon flux is clearly observed and is related to both the seasonality of the physical environment (water column mixing in winter) and biological activity (spring phytoplankton bloom).



Fig. 1. Vertical flux of particulate carbon at 200 m depth in the Ligurian Sea, Northwestern Mediterranean, from 1987 to 1990.

REFERENCES

- BUAT-MENARD P., DAVIES J., REMOUDAKI E., MIQUEL J.C., BERGAMETTI G., LAMBERT C.E., EZAT U., QUETEL C., LA ROSA J. and FOWLER S.W., 1989 -- Nonsteady-state biological removal of atmospheric particles from Mediterranean surface waters. *Nature*, 340: 131-134. FOWLER S.W., BUAT-MENARD P., YOKOYAMA Y., BALLESTRA S., HOLM E. and
- VAN NGUYEN H., 1987.- Rapid removal of Chernobyl fallout from Mediterranean surface waters by biological activity. *Nature*, 329: 56-58.

Rapp. Comm. int. Mer Médit., 33, (1992).