

Trace metal pollution in the Mediterranean Sea

Mediterranean Sea pollution
Trace metal
Dissolved cycles
Anthropogenic sources
Pollution en Méditerranée
Métaux traces
Cycles dissous
Apports anthropiques

Jean-Pierre BÉTHOUX, Philippe COURAU, Emmanuel NICOLAS, Diana RUIZ-PINO

Laboratoire de Physique et Chimie Marines, Université Paris-6, UA, C.N.R.S. B.P. 8, 06230 Villefranche-sur-Mer, France.

Received 25/9/89, in revised form 5/2/90, accepted 21/2/90.

ABSTRACT

In the Mediterranean Sea, the distribution of dissolved zinc, copper, lead and cadmium is primarily controlled by marine circulation, surface source dynamics and biological new production. We show that the present relatively high content of these metals in the surface layer is due to non-steady-state cycles as a result of source increases probably following increases in industrial, agricultural and urban activities around the Sea since 1960. Unlike the open ocean, for which the deep water response time to perturbations is of the order of 1000 years, the Mediterranean response to environmental disturbances is perceptible in two decades. Comparison of surface with deep concentrations permits an estimation of the growth of dissolvable anthropogenic discharges and a forecast of the biogeochemistry of this continental sea.

Oceanologica Acta, 1990, 13, 4, 481-488.

RÉSUMÉ

Pollution de la Méditerranée par les métaux traces

En Méditerranée, la circulation marine, la dynamique des apports superficiels et l'activité biologique (nouvelle production) permettent d'expliquer les concentrations dissoutes de métaux présents à l'état de traces : zinc, cuivre, plomb, et cadmium. Les fortes concentrations en métaux actuellement mesurées dans la couche de surface indiquent des cycles géochimiques non stationnaires qui résultent d'une augmentation des apports extérieurs probablement liée à la croissance des activités industrielles, agricoles et urbaines autour de cette mer depuis les années 60. Contrairement aux grands océans qui ont des temps de réponse de l'ordre du millénaire, la réponse géochimique de la Méditerranée à des perturbations de l'environnement est déjà sensible au bout d'environ deux décennies. La comparaison des concentrations de surface (directement liées aux apports extérieurs) et des concentrations profondes (qui gardent encore le souvenir d'un pseudo équilibre antérieur) permet une évaluation des apports anthropiques et de leur récente évolution, tandis qu'une prévision du devenir géochimique de la Méditerranée peut être envisagée.

Oceanologica Acta, 1990, 13, 4, 481-488.

INTRODUCTION

Over the past ten years, trace-metal concentrations have been measured in the Mediterranean Sea and around the Gibraltar Straits (Boyle *et al.*, 1985; Sherell and Boyle, 1988; Van Geen *et al.*, 1988) and particularly during the Phycemed 2 cruise (1983) in which seawater samples were taken from 11 hydrographic stations from the surface down to the bottom and analysed for mercury, cadmium, lead, chromium, vanadium, zinc and copper. The results have already been published for mercury, cadmium and lead (Copin-Montégut *et al.*, 1984, 1986) and chromium and vana-

dium (Jeandel and Minster, 1987 *a, b*). The biogeochemical cycles for Cr, V, Pb and Cd have been modelled (Ruiz-Pino *et al.*, 1990) by taking into account dissolved and particulate budgets, sedimentation and remobilization. Generally, trace-metal surface concentrations are relatively high as compared to surface concentrations in the Atlantic or Pacific Oceans, and, at depths > 300 m, concentrations appear quite homogeneous when analytical difficulties are resolved and contamination avoided. In brief, the vertical profiles of trace metals are more or less homogeneous and such distributions differ from those observed in the open ocean, the latter being similar to nutrient profiles with

a depleted surface layer and concentration increases with depth. In order to explain such a peculiarity in the Mediterranean Sea, limited recycling of nutrients (Boyle *et al.*, 1985) and surface enrichment from sources outside the Mediterranean (Sherrell and Boyle, 1988) have been invoked. In this paper, we argue that the effects of a non-steady state linked to the increase in anthropogenic discharges must be considered as well. If we neglect the reversible transfers between dissolved and particulate cycles, the six-box model (Ruiz-Pino *et al.*, 1990) facilitates the explanation of vertical profiles of dissolved concentrations of zinc, copper, lead and cadmium measured in 1983, and the determination of the whole natural and anthropogenic inputs of dissolvable trace metals. Such a marine-based estimate of surface inputs will be compared to direct terrestrial and atmospheric measurements of Zn, Cu, Pb and Cd. Neglect of particulate budgets is reasonable for cadmium and zinc which have essentially dissolved marine cycle; but for copper and lead this results in only a first approximation, which may influence the calculated inputs and transfers.

Model

The Mediterranean is schematized in a six box-model, corresponding to the surface (0-100 m) and deep layers in the Alboran Sea, the Western and Eastern Basins (Fig. 1). Horizontal and vertical water fluxes ($F_1 \dots F_{12}$) are deduced from water, salt and oxygen budgets (Béthoux, 1980, 1989, data in Fig. 1 caption). These fluxes characterize concentration basin dynamics (the loss of water by evaporation being greater than the water gain by precipitation and river discharges), with dense water formation, vertical movements and superposed flows over the Gibraltar and Sicily sills.

the Gibraltar Straits, the horizontal fluxes are confirmed by the Bryden and Stommel (1984) calculations. At the Sicily Straits, the summer flux proposed by Manzella *et al.* (1988) is in agreement with our yearly flux, but their winter flux is twice as great. The WMCE (Western Mediterranean Circulation Experiment) and POEM (Physical Oceanography of Eastern Mediterranean) cruises have not yet provided flux estimates permitting us to improve the proposed flux. At a basin scale and a yearly time scale, water and salt budgets give us the opportunity to calculate the vertical flux which particularly applies to geochemical cycles of conservative elements in homogeneous deep layers.

In Figure 1, external inputs A_w (in the Western Basin) and A_e (in the Eastern Basin) concern the dissolvable part of trace metal in atmospheric and terrestrial discharges which contribute to the deep-sea cycles; they are determined from marine concentration budgets. F_w and F_e represent the flux of metals taken up by phytoplankton cells, either by absorption or by passive adsorption in the surface layers, which may subsequently redissolve or be remobilized as fine particles at greater depths due to the remineralization of organic matter exported from the euphotic layer. C_i are the concentrations in the different boxes and, as the samples were not filtered, the data provide the dissolved-plus-fine-particle metal concentrations.

In the Alboran Sea, where the residence time of water is short, atmospheric and terrestrial inputs and biological vertical transfers of trace metal are neglected as compared to horizontal and vertical advected fluxes. Concentrations vary longitudinally owing to a continuous vertical mixing (F_{11}, F_{12}) from C_1 (the Atlantic concentration) to C_2 in the surface layer, and from C_8 (the

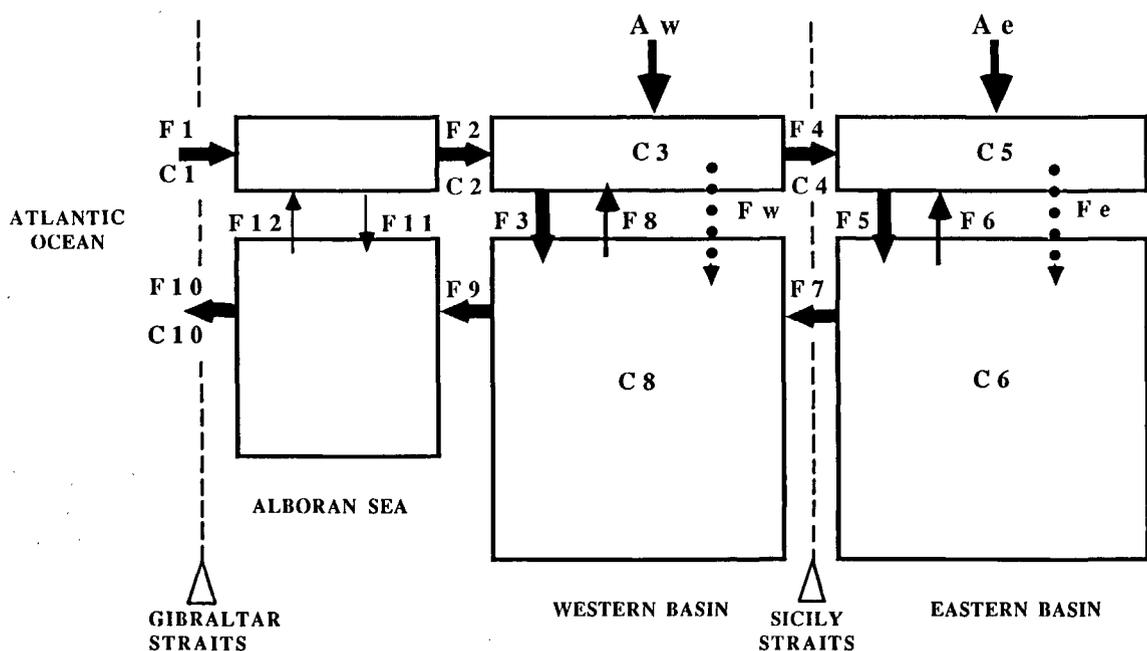


Figure 1
 Schema of water flux ($F_1 \dots F_{12}$), concentrations ($C_1 \dots C_{10}$), biological transfers (F_w and F_e) and atmospheric and terrestrial sources (A_w and A_e) in the Alboran Sea and in the Western and Eastern Basins. The water fluxes (Bethoux, 1980, 1989), in $10^{15} \text{ kg} \cdot \text{a}^{-1}$, are $F_1 = 54.38$, $F_2 = 53.19$, $F_3 = 57.45$, $F_4 = 40.9$, $F_5 = 84.1$, $F_6 = 45.0$, $F_7 = 39.1$, $F_8 = 45.86$, $F_9 = 50.69$, $F_{10} = 51.95$, $F_{11} = 14.66$, $F_{12} = 13.42$.

Représentation schématique des flux d'eau ($F_1 \dots F_{12}$), des concentrations ($C_1 \dots C_{10}$), des transferts par activité biologique (F_w et F_e) et des apports atmosphériques et telluriques (A_w et A_e) en mer d'Alboran et dans les bassins occidentaux et orientaux de la Méditerranée. Les flux d'eaux (Bethoux, 1980, 1989), exprimés en $10^{15} \text{ kg} \cdot \text{a}^{-1}$, ont les valeurs exprimées ci-contre.

western deep water) to C_{10} in the deep Mediterranean outflow. In the Western and Eastern Basins, deep concentrations C_8 and C_6 are homogeneous and the surface concentrations C_3 and C_5 are supposed homogeneous. The C_4 concentration at the Sicily Straits which results from a mixing of western water (with C_3 concentration) with Alboran Sea water (with C_2 concentration) is generally lower than C_3 (as for salinity) but is difficult to determine owing to space and time variability of the surface layer in this area.

A realistic diagram of the Mediterranean water flux (Fig. 1) makes it possible to study the evolution of trace element concentration when initial conditions, input functions and biological transfers are fixed. Previous studies with this flux diagram (Béthoux and Copin-Montégut, 1988; Ruiz-Pino *et al.*, 1990) gave some useful results: in the surface layer (0-100 m), trace element concentrations are practically balanced with the inputs and outputs on a yearly time scale; the deep-layer concentrations have response times of about two centuries and following any changes in the surface inputs, their variations are slow during the first few decades; dissolved or fine particle trace-metal incorporation into the sediment is very weak as compared to horizontal transports for cadmium, zinc and copper. As a first approximation it is also considered as negligible for lead.

These results permit qualitative use of the model and we shall show that present trace-metal concentrations (in 1983) do not correspond to a steady-state situation and that relatively high surface concentrations are primarily linked to a recent increase in superficial inputs. According to the diagram (Fig. 1) the mass balance equations for the eastern surface layer and western deep layer are:

$$dC_5/dt V_5 = Ae + C_4 F_4 - C_5 F_5 + C_6 F_6 - Fe \quad (1)$$

$$dC_8/dt V_8 = C_3 F_3 - C_8 F_8 + C_6 F_7 - C_8 F_9 + Fw \quad (2)$$

where V_5 and V_8 are the respective volumes and $C_i = C_i(t)$, in mol kg^{-1} ; $A_i = A_i(t)$, in mol a^{-1} ; Fw , $e = Fw, e(t)$ in mol a^{-1} .

In a steady-state regime, the dissolved concentrations are constant ($dC_i/dt = 0$) as well as the external inputs Aw , Ae , and the biological uptakes Fw and Fe . In the Eastern Basin, the mass balance and water budget give:

$$Ae + C_4 F_4 = C_6 F_7, \text{ and } F_5 = F_6 + F_7.$$

Eq. 1 may then be written as:

$$F_5 (C_6 - C_5) - Fe = 0 \quad (3)$$

Owing to water flux values Eq. 2 becomes:

$$0.7 C_6 + C_3 - 1.7 C_8 + 1.7 \times 10^{-17} Fw = 0 \quad (4)$$

If there is no biological transfer, $Fw = Fe = 0$. Eq. 3 gives $C_5 = C_6$ and a solution of Eq. 4 is $C_6 = C_3 = C_8$, *i.e.* the concentrations are homogeneous in the two basins, as is the case to a first approximation for the salinity distribution. For positive Fw and Fe values, and C_8 greater or equal to C_6 , the surface concentrations C_3 and C_5 are lower than the deep concentration

C_8 and C_6 . In a steady-state condition and independently of the flow values, the Mediterranean dynamics lead to a homogeneous vertical profile for an element without biological affinity. Conversely, for an element which reacts in the biological cycle, the Fw and Fe biological vertical transfers induce a more or less depleted surface layer.

Biological vertical transfers Fw and Fe .

In the Mediterranean Sea, phosphorus is a limiting nutrient and, whatever the increase in discharges, owing to biological activity, the surface layer remains depleted in this element. During the PHYCEMED cruise, the deep layer phosphorus concentrations were equal to 177 and $388 \times 10^{-9} \text{ mol kg}^{-1}$ in the Eastern and Western Basin respectively. With the hypothesis of a complete depletion (*i.e.* the surface phosphorus concentrations $C_4 = C_5 = 0$), measured deep concentrations in Eq. 3 and 4 give maximum vertical transfers of phosphorus by biological activity:

$$Fe = 14.9 \times 10^9 \text{ mol P a}^{-1},$$

$$Fw = 31.5 \times 10^9 \text{ mol P a}^{-1}.$$

With a C/P molar ratio of 105 in plankton (Redfield *et al.*, 1963), phosphorus transfers can be expressed as carbon transfers or new production (Dugdale and Goering, 1967). New production is the primary production based on new sources of nutrients, and also represents the flux of organic matter which descends from the surface and is remineralized in deeper layers. The preceding Fe and Fw , expressed as new production, are equal to 11 and $47 \times 10^{-3} \text{ kg C m}^{-2} \text{ a}^{-1}$ in the Eastern and Western Basins respectively; they depend on deep phosphorus concentrations and on vertical and horizontal water fluxes (F_3, F_5, F_7, F_8, F_9). They may be compared to previous new production evaluations for year 1980-1985: 18 and $52 \times 10^{-3} \text{ kg C m}^{-2} \text{ a}^{-1}$ in the Eastern and Western Basins respectively (Béthoux, 1989), calculated from oxygen consumption and from deep horizontal fluxes over the sills (F_7 and F_9). In the Eastern Basin, the discrepancy between the evaluations: 11 and $18 \times 10^{-3} \text{ kg C m}^{-2} \text{ a}^{-1}$ is primarily linked to a low phosphorus concentration measured in the deep Ionian water during Phycemed.

Together with organic matter, the new production also transfers metals incorporated in the biological cycle from the surface to deeper layers. Trace-metal concentrations in the Mediterranean phytoplankton (Romeo-Hardstedt, 1982; Romeo *et al.*, 1985) give metal/carbon ratios shown in Table 1. Assuming all removal is by incorporation in phytoplankton, when applying these ratios to previous Fe and Fw phosphorus or carbon values, one can calculate the respective trace-metal biological uptakes and transfers (Tab. 1, lines 2 and 3). From Buat-Ménard *et al.* (1989), part of the downward flux of organic matter and trace metal can be related to fecal pellets and, according to Nicolas (1989, pers. comm.) and Fowler (1986), metal/phosphorus ratios are much higher in fecal pellets than in plankton. Consequently, trace metal transfers by carbon weight

Table 1

Trace-metal/carbon molar ratio in phytoplankton and biological transfers in the Eastern and Western Basins (Fe and Fw, respectively) corresponding to new production processes.

Rapport molaire métal en trace/carbone dans le phytoplancton et transferts biologiques dans le Bassin Oriental et le Bassin Occidental (Fe et Fw) associés à la nouvelle production.

	P	Zn	Cu	Pb	Cd
Phytoplankton Element/carbon molar ratio	$9.5 \cdot 10^{-3}$	$9 \cdot 10^{-5}$	$1.6 \cdot 10^{-5}$	$2.3 \cdot 10^{-6}$	$5.1 \cdot 10^{-7}$
Biol. transf. (mol a ⁻¹)					
East Basin Fe	$14.9 \cdot 10^9$	$141 \cdot 10^6$	$25 \cdot 10^6$	$3.6 \cdot 10^6$	$0.8 \cdot 10^6$
West Basin Fw	$31.5 \cdot 10^9$	$298 \cdot 10^6$	$53 \cdot 10^6$	$7.6 \cdot 10^6$	$1.7 \cdot 10^6$

unit calculated from fecal pellet fluxes would be much higher than those calculated from trace-metal concentration in phytoplankton. But as most of the dissolved trace-metal uptake is by phytoplankton which feed on the fecal pellet flux from zooplankton, the determined trace-metal uptake and transport by new production

probably constitute a good first approximation, as previously shown for cadmium by Collier and Edmond (1984).

The Phycemed 1983 Data

The Phycemed 1983 stations are located in the Atlantic and in the Western and Eastern Basins (see Fig. 2, map). Surface concentrations for P, Zn, Cu, Pb and Cd at station SRGW ($\Phi=35^{\circ}47'N$, $G=06^{\circ}27'W$), corresponding to C₁ in Figure 1 and reported in Table 2, are similar to offshore Atlantic inflow. They are much lower than the shelf Atlantic water concentrations measured in the Gulf of Cadiz: *i.e.* $40 \cdot 10^{-9}$ mol.kg⁻¹ for Zn, $10 \cdot 10^{-9}$ mol.kg⁻¹ for Cu and $260 \cdot 10^{-12}$ mol.kg⁻¹ for Cd (Van Geen *et al.*, 1988). The entrainment of an unknown quantity of Atlantic shelf water into the Mediterranean Sea complicates

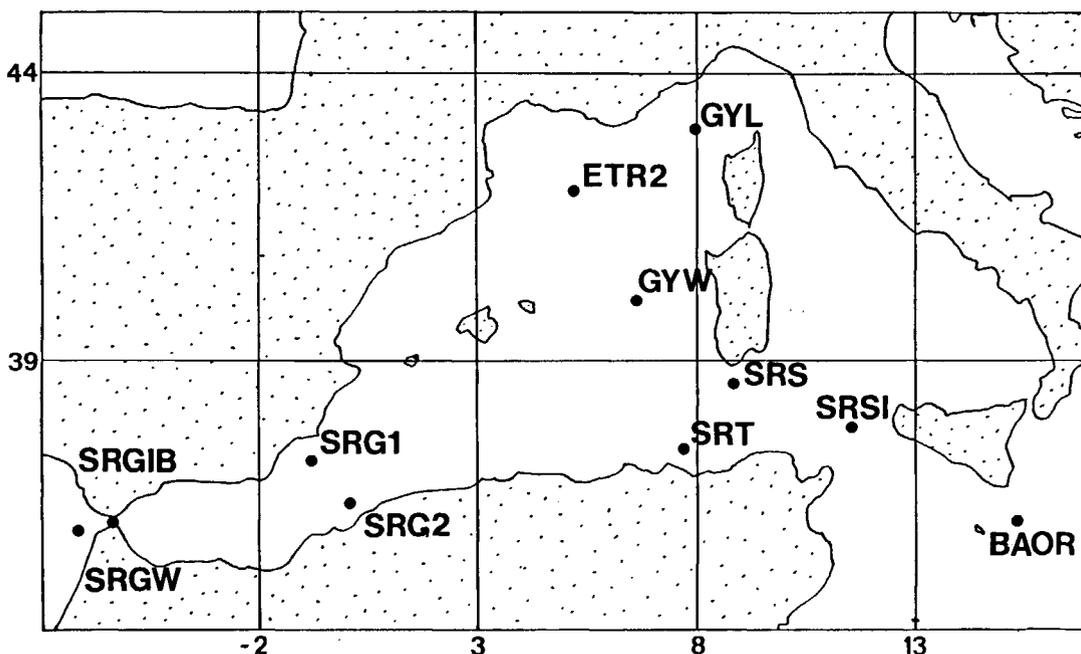


Figure 2
Map of the Phycemed 1983 cruise stations.
Carte de la campagne Phycemed 1983.

Table 2

Phosphorus, zinc, copper, lead and cadmium mean concentrations measured during Phycemed 1983 cruise in Atlantic surface inflow and in the surface and deep layers of the Western and Eastern Basins, and surface concentrations calculated with the proposed biological transfers and assuming a steady-state cycle. (a) measurements by anodic stripping voltammetry (E. Nicolas); (b) measurements by atomic absorption spectrometry (P. Courau); (c) n=sample number, SD=standard deviation; (d) totally depleted surface layer hypothesis.

Moyenne des concentrations en phosphore, zinc, cuivre, plomb et cadmium mesurées au cours de la campagne Phycemed 1983 dans le flux atlantique entrant et dans les couches superficielles et profondes du Bassin Oriental et du Bassin Occidental, et concentrations superficielles calculées en tenant compte des transferts biologiques dans l'hypothèse d'un état stationnaire des concentrations. (a) mesures par polarographie (E. Nicolas); (b) mesures par absorption atomique (P. Courau); (c) n=nombre d'échantillons, SD=écart type; (d) hypothèse d'une couche de surface sans phosphore.

	P	Zn _(a)	Cu _(a)	Pb _(a)	Pb _(b)	Cd _(a)	Cd _(b)
1983 Marine concentr. (mol kg ⁻¹)							
1 Atlantic inflow C ₁ (n)	$27 \cdot 10^{-9}$ (4)	$0.85 \cdot 10^{-9}$ (4)	$1.01 \cdot 10^{-9}$ (4)	$146 \cdot 10^{-12}$ (4)	$138 \cdot 10^{-12}$ (4)	$9 \cdot 10^{-12}$ (4)	$14 \cdot 10^{-12}$ (4)
2 Western surf. lay. C ₃ (n, SD) (c)	$67 \cdot 10^{-9}$ (27,86)	$3.55 \cdot 10^{-9}$ (31,1.38)	$2.14 \cdot 10^{-9}$ (36, 0.79)	$275 \cdot 10^{-12}$ (28,135)	$230 \cdot 10^{-12}$ (48,92)	$52 \cdot 10^{-12}$ (31,15)	$65 \cdot 10^{-12}$ (35,16)
3 Western deep layer C ₈ (n, SD)	$388 \cdot 10^{-9}$ (37,64)	$3.93 \cdot 10^{-9}$ (35,0.54)	$1.95 \cdot 10^{-9}$ (37,0.54)	$133 \cdot 10^{-12}$ (38,37)	$128 \cdot 10^{-12}$ (41,27)	$53 \cdot 10^{-12}$ (35,9)	$61 \cdot 10^{-12}$ (38,8)
4 Eastern surf. lay. C ₅ (n)	$20 \cdot 10^{-9}$ (3)	$3.30 \cdot 10^{-9}$ (4)	$1.67 \cdot 10^{-9}$ (4)	$152 \cdot 10^{-12}$ (4)	$160 \cdot 10^{-12}$ (4)	$52 \cdot 10^{-12}$ (4)	$54 \cdot 10^{-12}$ (4)
5 Eastern deep lay. C ₆ (n)	$177 \cdot 10^{-9}$ (6)	$2.01 \cdot 10^{-9}$ (6)	$1.92 \cdot 10^{-9}$ (5)	$87 \cdot 10^{-12}$ (6)	$105 \cdot 10^{-12}$ (6)	$48 \cdot 10^{-12}$ (6)	$48 \cdot 10^{-12}$ (6)
Calculated surface concentrations (mol kg ⁻¹)							
6 Eastern Basin C' 5	0 _(d)	$0.33 \cdot 10^{-9}$	$1.62 \cdot 10^{-9}$	$44 \cdot 10^{-12}$		$38 \cdot 10^{-12}$	
7 Western Basin C' 3	0 _(d)	$0.21 \cdot 10^{-9}$	$1.07 \cdot 10^{-9}$	$36 \cdot 10^{-12}$		$28 \cdot 10^{-12}$	

trace-metal budgets calculated for the Mediterranean when they are mainly based on measurements around the Gibraltar Straits (Van Geen *et al.*, 1988; Sherrell and Boyle, 1988).

In the Western Basin, mean surface layer concentrations, C_3 (line 2), are derived from all the basin stations and are much higher than Atlantic inflow concentrations, C_1 , which typifies the Mediterranean surface water trace-metal peculiarities. Strictly speaking, this surface layer is not well mixed owing to geographic and depth variations in trace metal (Copin-Montégut *et al.*, 1984, 1986); the standard deviations, SD, are rather high in comparison with SD in deeper layers, and the hypothesis of a homogeneous surface layer constitutes a first approximation. For example, at the Sicily Straits, the south-east surface outflowing concentration which results more or less directly from the Atlantic inflow has a trace-metal concentration C_4 generally lower than the mean C_3 value (as seen also for salinity), while the surface concentrations along the industrialized coasts, at stations GYL, ETR or SRG are greater than at the offshore station GYW.

Concentrations in the deep layer are homogeneous (Tab. 2, line 3) attesting a well-mixed deep layer (as for T and S characteristics). The standard deviation (SD) for Cd and Zn is similar to that of phosphorus, and it is somewhat greater for Pb and Cu. We stress that for Pb and Cd comparable results have been obtained by two different analytical methods: anodic stripping voltammetry and graphite furnace atomic absorption spectrophotometry: this proves the reliability of the trace-metal analysis. The C_8 concentrations may thus be taken as constituting the 1983 data base for Zn, Cu, Pb and Cd in the Western Basin.

In the Eastern Basin, only one vertical profile was obtained during the Phycemed 2 cruise, in the Ionian Sea ($\Phi = 36^\circ 10' N$, $G = 15^\circ 30' E$). We assume as a first approximation that both surface and deep layers were well mixed, with mean concentrations equal to C_5 and C_6 respectively (Tab. 2, lines 4 and 5).

Comparison between data and model calculations

As shown in Table 2, mean surface concentrations (C_3 , C_5) are generally greater or equal to deep concentrations (C_8 , C_6) for Zn, Cu, Pb and Cd, which are generally considered as biologically active trace metals. There is thus a qualitative discrepancy between the model predictions, based on the steady-state hypothesis, and the measured concentrations which argues toward a non-steady-state behaviour of elemental cycles. Effectively, after any change in Fw, Fe, Aw or Ae values, the marine scheme, described in Fig. 1, has a response time of about two centuries before reaching new constant concentration values reflecting a new steady state (Béthoux and Copin-Montégut, 1988; Ruiz-Pino *et al.*, 1990) and unexpected vertical profiles may be linked to a transitional period. Insofar as biota have not shown dramatic change, the high surface concentrations should be primarily linked to the increasing external inputs, particularly Aw and Ae, since the concentrations in the Atlantic offshore inflow

are weak. Estimates of the biological transfers of trace metal, Fw and Fe, will help us to characterize external inputs and non steady-state behaviour of the trace element. We now therefore consider quantitative predictions of the model, first dealing more with surface layer considerations, secondly with surface and deep layer budgets.

The calculated Fw and Fe values (Tab. 1), used in Eq. 3 and 4, give the surface concentrations C'_5 and C'_3 of biologically active trace metal (Tab. 2, line 6 and 7) which would correspond to a steady-state regime. When comparing C'_3 and C_8 in the Western Basin and C'_5 with C_6 in the Eastern Basin, it appears that surface concentrations ought to be mostly depleted in Zn and Pb, and, to a lesser extent, in Cd and Cu. Similar to the new biological production, the surface depletion would be more marked in the Western Basin than in the Eastern one. But serious discrepancies appear between calculated surface concentrations (C'_3 and C'_5) and the measured ones (C_3 and C_5). In the Western Basin, numerous measurements ensure good estimations of the mean C_3 and C_5 values so there is probably little error, but all the measured C_3 surface concentrations are much higher than the calculated C'_3 concentrations.

From Figure 1, $F_8 + F_9 = F_9 + F_7$, and given a steady-state hypothesis, Eq. 2 may be written:

$$C_3 = F_7/F_3 (C_8 - C_6) + C_8 - Fw/F_3$$

The C_8 and C_6 concentrations are data, the flux ratio F_7/F_3 is more or less fixed by water and salt budgets, and the C_3 calculations depend mainly on the Fw/F_3 ratio, which is the main source of uncertainty. For Zn and Cd, an overestimate of Fw (or an underestimate of F_3) by 3 and 7 respectively may to a certain extent account for the C'_3 and C_3 discrepancy. But for Pb and Cu even a nil value for Fw or an infinite value for F_3 cannot explain the C_3 measured values. Consequently, for all the trace metals, the steady-state hypothesis cannot be retained. With the assumption of a more or less constant biota in the Mediterranean Sea, the surface concentrations C_3 and C_5 which are generally greater than the deep concentrations, C_6 and C_8 , prove that external sources of trace metal must have increased in the last few decades.

The use of transitional concentrations in a steady-state budget may thus lead to erroneous conclusions: the Eastern Basin budget, using C_3 , C_5 and C_6 concentrations measured in 1983 (Tab. 2), leads to a negative or null atmospheric and terrestrial input. Ae, and/or to a unreasonably high accumulation rate in the sediments for Zn, Pb, Cd and Cu. Similarly, the Cu, Cd and Zn concentrations calculated by Van Geen *et al.* (1988) in the Atlantic inflow (assumed strongly influenced by shelf water) are greater than the deep Mediterranean outflow concentrations. In a steady-state hypothesis, they would mean that the Mediterranean Sea is a sink for Atlantic inflowing trace metals as for atmospheric and terrestrial discharges within the basin (in so far as the latter are not denied). But, after a lowering of the calculated Zn concentration in the Atlantic inflow,

according to Sherrell and Boyle (1988) "inflow water and source within the basin itself contribute about equally to Mediterranean Zn enrichment", which rectifies the Van Geen *et al.* assertions. Nevertheless, this still constitutes an overestimate of the inflow influence since the deep outflow concentration is not at equilibrium and do not reflect the present surface inputs of trace metal.

Our conclusions are also confirmed by the surface and deep layer budgets. Surface layer volumes are about 14 times lower than deep layer volumes, and, as a first approximation, surface concentrations, which rapidly react to input variations, may be considered as in equilibrium with inputs and outputs (Ruiz-Pino *et al.*, 1990). With this hypothesis, Eq. 1 gives the external inputs to the Eastern Basin:

$$Ae + C_4 F_4 = C_5 F_5 - C_6 F_6 + Fe \quad (\text{Table 3, line 1}), \quad (5)$$

Table 3

Marine-based estimate of trace-metal flows: Eastern Basin external inputs (1) and deep output (2), Mediterranean external inputs (3) and deep output (4), Atlantic input (5) and resulting atmospheric and terrestrial inputs for the whole Mediterranean Sea (6) and for the Western Basin alone (7). Published data of terrestrial discharges (8) and atmospheric inputs (9) in the Western Basin, resulting from coastal measurements, data from: (a) Unep, 1984; (b) Arnold *et al.*, 1982; (c) Bergametti, 1987; (d) Migon, 1988; (e) and (f) Martin *et al.*, 1989, total and net input respectively; (g) Buat-Ménard, 1986; (h) Arnold, 1985; (i) Dulac, 1986.

Flux de métaux traces dans les apports de surface (1) et sorties profondes (2) au bassin Oriental, en Méditerranée (3, 4) et dans le flux atlantique entrant, ainsi que dans les retombées atmosphériques et telluriques à l'échelle de toute la Méditerranée (6) et dans le seul Bassin Occidental (7), déterminés à partir des concentrations marines. Données publiées concernant les apports telluriques (8) et les retombées atmosphériques (9) sur le Bassin Occidental résultant de mesures en des observatoires côtiers, d'après: (a) Unep, 1984; (b) Arnold *et al.*, 1982; (c) Bergametti, 1987; (d) Migon, 1988; (e) and (f) Martin *et al.*, 1989, apport total et apport net estimé; (g) Buat-Ménard, 1986; (h) Arnold, 1985; (i) Dulac, 1986.

Trace Metal Flux 10 ⁹ mol a ⁻¹	Zn	Cu	Pb	Cd
1 Eastern B. external inputs	328	79	12	3.0
2 Eastern B. deep output (C ₆ F ₇)	79	75	3.4	1.9
3 Mediterranean external inputs	650	166	29	5.3
4 Alboran Sea deep input (C ₈ F ₉)	199	99	6.7	2.7
5 Atlantic input (C ₁ F ₁)	46	55	8	0.5
6 Atm. and terr. inputs (Aw + Ae)	573	102	21	4.4
7 Western B. Aw values	(309-390)	(72-102)	(15-21)	(0-3.5)
8 Terr. input in the Western B.	141 (a)	26-78 (e) 1.6-10 (f)	10.6 (a) 7.3-23 (e) 0.7-2.4 (f)	0.43-2.8 (a) 0.13-0.7 (e) 0.25-0.4 (f)
9 Atmosph. input in the Western B.	61-137 (b) (612 (c)) 168-199 (d)	13.6 (g) 5-20 (h) 40 (e)	46 (g) 25.96 (h) 13-78 (a) 16 (i) 126 (c) 22-52 (d)	1.04 (g) 0.4-1.6 (h) 3.6 (i) 1.4-1.6 (d) 1.8-3.2 (e)
10 Variation range (ter. + at. inputs)	(202-753)	(66-118)	: (14-119)	: (0.5-6.4)

which are compared to outputs from the basin: C₆ F₇ (line 2). Instead of an equality between lines 1 and 2, which would correspond to a steady state, the Zn and Pb surface inputs are four times greater than the deep outputs. From Figure 1, the external inputs to the Mediterranean Sea, line 3, are:

$$(6) \quad Aw + Ae + C_2 F_2 = C_5 F_5 - C_6 F_6 + Fe + C_3 F_3 - C_8 F_8 + Fw$$

The corresponding Alboran deep inputs, C₈ F₉, are listed on line 4. As previously found in the Eastern Basin, the surface inputs to the Mediterranean Sea, when determined from marine trace-metal flux, are three to four times greater than the deep output for Zn and Pb, and about twice for Cd and Cu. Maximum values for biological transfers (maximum new production values) and the hypothesis of an entire remineralization for biogenic particles may have somewhat enlarged the Pb and Zn imbalances.

Estimated trace-metal inputs in the western basin

Insofar as surface concentrations in the Sicily Straits (C₄) and in the eastern Alboran Sea (C₂) are known, atmospheric and terrestrial inputs of dissolvable trace-metal (Aw and Ae) may be calculated from Eq. 5 and 6. Unfortunately, in these areas, mixing of various surface waters prevent any direct evaluation of concentration from the limited data set of the Phycemend cruise. The surface inflow towards the Eastern Basin results from some enriched western water (with C₃ concentration) and some Alboran Sea water (with relatively low C₂ concentration). Eq. 5 can give two extreme Ae values as C₄ may vary between C₃ and C₂ values. The C₂ mean concentrations are calculated from water and mass budgets in the Alboran Sea, where owing to water flux values (Fig. 1) and assuming a conservative mixing:

$$C_2 = 0.1967 C_8 + 0.8024 C_1 \quad (7)$$

The C₁ concentrations (Tab. 2, line 1), taken in an offshore Atlantic station, are probably lower than concentrations in the coastal enriched waters which may also contribute to the Atlantic inflow. Consequently, the calculated C₂ concentrations: 1.45 and 1.2 × 10⁻⁹ mol kg⁻¹ for Zn and Cu respectively, and 140 and 18 × 10⁻¹² mol kg⁻¹ for Pb and Cd respectively, probably are minimum estimations. On line 5 (Tab. 3) are reported the Atlantic input C₁ F₁, and on line 6 the atmospheric and terrestrial inputs Aw and Ae resulting from Eq. 6. For Zn and Cd, the Atlantic inputs (C₁ F₁) constitute small fractions of the total inputs to the Mediterranean Sea (C₁ F₁ + Aw + Ae), respectively 7 and 10% while for Cu and Pb the fractions are relatively high: 35 and 28% respectively.

Two extreme Aw values were proposed on line 7 for comparison with direct atmospheric and terrestrial input measurements which are mainly focused in the Western Basin. The maximum Aw value is calculated from the sum (Aw + Ae) with a Ae minimum value (*i.e.* for C₄ = C₃) and the minimum Aw value results from putting C₄ = C₂. Deep concentrations (C₆ and

C_8) are somewhat underestimated (non-steady-state regime) as is probably the C_2 concentration, while F_w and Fe are maximum values. Consequently, the sums $A_w + Fe$ calculated from Eq. 6 probably constitute maximum estimates and, *a fortiori*, the maximum A_w constitute upper limits of marine-based estimates.

Various estimations of terrestrial and atmospheric inputs in the Western Basin are reported on lines 8 and 9. The variation range of the total input, summarized on line 10, reflects the spatio-temporal variabilities of inputs over the Western Basin and the difficulties of extrapolations of local observations to the whole basin estimation. These trace-metal surface inputs mostly originate in anthropogenic activities around the Mediterranean Sea.

For cadmium and zinc, which have essentially dissolved cycles, the marine-based maximum A_w estimates are comparable to the mean of direct evaluations, and particularly agree with Martin *et al.* (1989) results for Cd and with UNEP (1984) data and Migon (1988) results for Zn. The marine-based estimates of copper inputs to the Western Basin agree with total atmospheric and terrestrial inputs from Martin *et al.* (1989), but are much higher than their "net input" estimates and than the evaluations from Arnold (1985) and Buat-Ménard (1986). These results may be linked to a great remobilization of terrestrial particulate input and/or to underestimated copper inputs to the sea. The marine-based estimates of lead inputs (which concern the dissolvable part of discharges) are directly comparable to the lower limit of total input estimates. The marine cycle of dissolved Pb is mainly linked to atmospheric inputs, which are mostly dissolvable (Migon, 1988), while the terrestrial discharges are mostly refractory (Martin *et al.*, 1989).

In spite of the quite different methods used, a rather good coherence appears between estimates of the whole Western Basin surface inputs. This agreement confirms that Zn and Cd marine concentrations in the Mediterranean Sea result mainly from pollution within the basin, which widely exceed the offshore Atlantic input. For Pb and Cu, sedimentation and remobilization processes, together with a rather large Atlantic input somewhat reduce the pollution fraction which nevertheless remains preponderant.

CONCLUSION

In 1983, metal concentrations in the Mediterranean deep layers mainly kept the characteristics of a former quasi-steady state, while surface layers exhibited transi-

tional concentrations linked to increased external inputs. These inputs are probably derived from increase in industrial, agricultural and urban activities in the surrounding countries, since the early sixties. With a scenario of continuous growth of these activities, the calculated rates of increase in dissolvable surface inputs are about 6% a year for Zn and Pb, and about 2% a year for Cd and Cu between 1960 and 1983. When the initial conditions are fixed (*i.e.* surface and deep concentrations in year 1960), these rates of increase may constrain the input functions A_w , $e(t)$ and permit the calculation of the concentration evolution $C_i(t)$ for fixed or evolutionary biological transfers F_w , e (*i.e.* Ruiz-Pino *et al.*, 1990, for lead and vanadium). The increase in surface inputs may reflect the major role of Zn in human activities and of Pb used as an anti-knock compound in petrol. They may be compared with phosphorus discharge increases which amount to 2-3% a year when calculated from the evolution of deep phosphorus concentrations from 1960 to 1983 (Béthoux and Copin-Montégut, 1988). According to UNEP (1988) enquiries in the Mediterranean region, the 1960-1983 period shows respective yearly increases: 1.6% in inhabitants, 4.7% for the mean gross national product, 6% for the energy consumption and 7.5% for the number of cars. These data summarize the increasing anthropogenic activities which cause atmospheric and terrestrial pollution. The surface trace-metal and deep phosphorus enrichments constitute a first perceptible response of deep sea biogeochemistry to recent anthropogenic effects and, in the near future, a new impact on intermediate and deep Atlantic waters. The Mediterranean Sea may constitute a case study of environmental evolution, for instance, the new European settlement concerning lead-free petrol will reduce the anthropogenic discharges to the sea, the Pb surface concentration and, some decades later, the deep concentration. Marine concentrations allow a basin-scale estimation of the dissolvable atmospheric and terrestrial inputs, and a possible monitoring of environmental pollution.

Acknowledgements

We thank Dr. R. Delmas and Dr P. Tréguer for providing phosphorus data from Phycemed 2 cruise. For the revision of the manuscript, the authors owe much to Dr P. Buat-Ménard and to the anonymous referees.

REFERENCES

- Arnold M. (1985). Géochimie et transports des aérosols métalliques au dessus de la Méditerranée Occidentale. *Thèse Doctorat. Université Paris-VII*, 226, pp.
- Arnold M., A. Seghaier, D. Martin, P. Buat-Ménard, R. Chesselet (1982). Géochimie de l'aérosol marin au-dessus de la Méditerranée occidentale, *VI^e Journées Etud. Pollutions*, Cannes, CIESM, 27-37.
- Bergametti G. (1987). Apports de matière par voie atmosphérique à la Méditerranée: aspects géochimiques et météorologiques. *Thèse Doctorat Université Paris-VII*. 296 pp.
- Béthoux J.-P. (1980). Mean water fluxes across sections in the Mediterranean Sea, evaluated on the basis of water and salt budgets and of observed salinities. *Oceanol. Acta*, 3, 79-80.
- Béthoux J.-P. (1989). Oxygen consumption, new production, vertical advection and environmental evolution in the Mediterranean Sea, *Deep-Sea Res.*, 5, 769-781.
- Béthoux J.-P., G. Copin-Montégut (1988). Phosphorus and nitrogen in the Mediterranean Sea, specificities and forecasting, *Oceanol. Acta*, 9, 75-78.

- Boyle E. A., S. D. Chapnick, X. X. Bai, A. Spivack (1985). Trace metal enrichments in the Mediterranean Sea. *Earth planet. Sci. Lett.*, **74**, 405-419.
- Bryden H. L., H. M. Stommel (1984). Limiting processes that determine basic features of the circulation in the Mediterranean Sea. *Oceanol. Acta.*, **7**, 289-296.
- Buat-Ménard P. (1986). Air to sea transfer of anthropogenic trace metal. In: *The role of air-sea exchange in geochemical cycling*. P. Buat-Ménard Ed., D. Reidel Publishing Compagny, 477-496.
- Buat-Ménard P., J. Davies, E. Remoudaki, J.-C. Miquel, G. Bergametti, C. E. Lambert, U. Ezat, C. Quétel, J. La Rosa, S. W. Fowler (1989). Non-steady-state biological removal of atmospheric particles from the Mediterranean surface waters. *Nature*, **340**, 131-134.
- Collier R., J. Edmond (1984). The trace element geochemistry of marine biogenic particulate matter, *Prog. Oceanogr.*, **13**, 113-199.
- Copin-Montégut G., P. Courau, F. Laumond (1984). Occurrence of mercury in the atmosphere and waters of the Mediterranean, *FAO Fish. Rep.*, **325**, 51-57.
- Copin-Montégut G., P. Courau, E. Nicolas (1986). Distribution and transfer of trace elements in the Western Mediterranean, *Mar. Chem.*, **18**, 189-195.
- Dulac F. (1986). Dynamique du transport et des retombées d'aérosols métalliques en Méditerranée occidentale, *Thèse Doctorat Université Paris-VII*, 241 pp.
- Dugdale R. C., J. J. Goering (1967). Uptake of new and regenerated forms of nitrogen in primary productivity, *Limnol. Oceanogr.*, **12**, 196-206.
- Fowler S. W. (1986). Trace metal monitoring of pelagic organisms from the open Mediterranean Sea. *Environm. Monitoring and Assessment*, **7**, 58-78.
- Jeandel C., J.-F. Minster (1987a). Chromium behaviour in the oceans: global versus regional processes, *Global Biogeochem. Cycles*, **2**, 131-154.
- Jeandel C., J.-F. Minster (1987b). Vanadium behaviour in the global ocean and in the Mediterranean Sea, *Mar. Chem.*, **21**, 51-74.
- Manzella G. M. R., G. P. Gasparini, M. Astraldi (1988). Water exchange between the eastern and western Mediterranean through the Strait of Sicily. *Deep-Sea Res.*, **6**, 1023-1035.
- Martin J. M., F. Elbaz-Poulichet, C. Guieu, M. D. Loye-Pilot, G. Han (1989). River versus atmospheric input of material to the Mediterranean Sea: an overview. *Mar. Chem.*, **28**, 159-182.
- Migon C. (1988). Étude de l'apport atmosphérique en métaux-traces et sels nutritifs en milieu côtier méditerranéen; implications biogéochimiques. *Thèse Doctorat, Université Nice*, 217 pp.
- Redfield A. C., B. H. Ketchum, A. Richards (1963). The influence of organisms on the composition of sea water. In: *The Sea*, vol. 2, M. N. Hill, Ed., Interscience, New York, 26-77.
- Roméo-Hardstedt M. (1982). Some aspects of the chemical composition of plankton from the North-Western Mediterranean Sea. *Mar. Biol.*, **70**, 229-236.
- Roméo M., M. Gnassia-Barelli, E. Nicolas (1985). Concentrations en plomb du plancton de la mer Ligure (Méditerranée Nord-Occidentale), *Chemosphere*, **14**, 1423-1431.
- Ruiz-Pino D. P., C. Jeandel, J.-P. Béthoux, J.-F. Minster (1990). Are the trace metal cycles balanced in the Mediterranean Sea? *Global and Planetary Changes*, sous-presse.
- Sherrell R. M., E. A. Boyle (1988). Zinc, chromium, vanadium and iron in the Mediterranean Sea, *Deep-Sea Res.*, **35**, 1319-1334.
- UNEP, 1984. Pollutants from land-based sources in the Mediterranean. *UNEP Regional Seas Reports and Studies*, **32**, 97 pp.
- UNEP, 1988. Le plan bleu, résumé et orientations pour l'action, *Rac/Blue Plan*. 94 pp.
- Van Geen A., P. Rosemer, E. Boyle (1988). Entrainment of trace-metal-enriched Atlantic shelf water in the inflow to the Mediterranean Sea. *Nature*, **331**, 423-426.