**Environmental Pollution**
June 2011, Volume 159, Issue 6, Pages 1629–1634
http://dx.doi.org/10.1016/j.envpol.2011.02.046

# Impact of atmospheric deposition of anthropogenic and natural trace metals on Northwestern Mediterranean surface waters: A box model assessment

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## Abstract :

Under stratified oligotrophic conditions (May–November), the surface mixed layer of the Northwestern Mediterranean constitutes a homogeneous water volume of 10–30 m depth. In other respects, the mean residence time of Ligurian surface waters (0–200 m) is 102 days. It is therefore possible to quantify the extent to which atmospheric deposition of trace metals affects surface waters. On the basis of literature data on anthropogenic and natural trace metals, we demonstrate that the ratios between total seawater labile atmospheric deposition during 102 days ($\varphi c$) and dissolved TM concentrations in Ligurian surface waters (*c*) illustrate the impact of atmospheric deposition on surface seawater ($\varphi c/c$). High ratios indicate surface TM enrichments, while low ratios indicate surface TM depletion, due to the quasi-complete sorption and removal of TMs by plankton during spring bloom. The simple box model proposed here may be used for other marine regions where hydrodynamical and physico-chemical constraints are well defined.

## Highlights

• Tool in further understanding of trace metal cycling in the Mediterranean Sea. • Evaluation of the impact of atmospheric deposition of TMs on sea surface waters. • To be applied to interpret the impact of changes in TM emissions. • Useful for GEOTRACES, IMBER and SOLAS communities.

**Keywords :** Atmospheric deposition ; Trace metal pollution ; Box model ; Northwestern Mediterranean ; Impact evaluation ; Environmental antipollution policies

## 1. Introduction

The most efficient transport route to spread contaminants over open waters is the atmospheric pathway (e.g., Boutron et al., 1991; Jickells, 1995). This is particularly acute for the Western Mediterranean Sea, which is subject to intense particulate and dissolved atmospheric inputs, including anthropogenic inputs from Northeastern and Central Europe and pulsed Saharan dust events of natural crustal material from Northern Africa (Guieu et al., 1997; Guerzoni et al., 1999). Chester et al. (1997) have described this marine region as the superimposition of Saharan inputs on a homogeneous European background signature. As a result, trace metal (TM) concentrations in Mediterranean surface waters are higher than in the open ocean, e.g. the Atlantic Ocean (Boyle et al., 1985; Morley et al., 1997).

Owing to its reduced dimensions (surface area: 0.53 x $10^{11}$ $m^2$), and numerous and intense land-based emission sources along its densely populated shores (~ 300 inhabitant per $km^2$ in 2008), the Ligurian Sea (Northwestern Mediterranean) is particularly subject to the atmospheric input. As a matter of fact, the TM distribution patterns in the water column suggest that the atmospheric input governs local TM biogeochemical cycling (Béthoux et al., 1990; Migon et al., 2002).

In spite of more strict antipollution policies, the on-going industrialization of Europe (in particular Eastern Europe) and Southern Mediterranean countries will probably lead to increasing atmospheric TM inputs on the Ligurian Sea. On the basis of literature data, the present paper deals with the atmospheric TM enrichment of Ligurian surface waters during their transit time in the Ligurian Sea. This enrichment is subsequently compared to recent TM profiles obtained in the offshore Ligurian waters. Although many papers have already dealt with the atmospheric TM deposition on various marine areas (e.g., Jickells, 1999; Guerzoni et al., 1999; Brown et al., 2005; Measures et al., 2005; Buck et al., 2008), the present work proposes a simple box model assessing the impact of the atmospheric input of TMs on an oligitrophic stratified surface layer, using the Ligurian Sea as an example.

## 2. Materials and Methods

### 2.1. Circulation in the Ligurian Sea

The Ligurian Sea is subject to a permanent cyclonic circulation (Figure 1). The surface flux (0-200 m) of Atlantic waters ascending along the northwestern coast of Corsica is 17.3 x $10^{12}$ $m^3$ $year^{-1}$ (Béthoux, 1980). This flux encounters that coming from the Tyrrhenian Sea (20.5 x $10^{12}$ $m^3$ $year^{-1}$) via the Corsica channel. The mixing of the two fluxes generates the Ligurian current (LC) that flows in the direction NE-SW along the Riviera and exits the Ligurian Sea with a flow of 37.8 x $10^{12}$ $m^3$ $year^{-1}$.

For a 0-200 m-deep surface layer, the volume V of surface waters of the Ligurian Sea is 0.53 x $10^{11}$ m² x 200 m = 10.6 $10^{12}$ $m^3$.

Apart from vertical mixing during short episodes in winter, the residence time of surface waters in the Ligurian area ($t_R$) can be computed as:

$$t_R = V/LC \qquad (1)$$

and is equal to 0.28 year (102 days). During this relatively long period, surface waters form a distinct water volume (Béthoux, 1980). It is therefore possible to evaluate the extent to which atmospheric deposition is able to affect surface waters during their transit through the Ligurian Sea.

A frontal zone with rapid horizontal change of density separates offshore Ligurian waters from the coast (Lévy et al., 1998). Apart from exceptional hydrodynamic conditions the central Ligurian Sea is sheltered from lateral inputs (Béthoux et al., 1988). For this reason, the atmosphere is believed to be the only significant source of TMs to the open Ligurian Sea. This marine region has been used several times to study the impact of atmospheric fluxes on marine systems (e.g., DYFAMED and MEDFLUX; see special issues of *Deep-Sea Research II 49, 11 (2002) and 56, 18 (2009),* respectively).

### 2.2. Presentation of the box model

A box model was used to estimate the impact of atmospheric TM deposition on the surface ocean chemistry of the Ligurian Sea over the period during which the mixed layer (ML) is homogeneous (Lacroix and Grégoire, 2002; Pulido-Villena et al., 2008). Literature data from the Ligurian region (atmospheric TM fluxes and dissolved surface water TM concentrations) were used.

The atmospheric TM fluxes presented in Table 1 (total seawater labile fraction, i.e. the fraction likely to be dissolved into seawater) can be used to compute the surface layer enrichment during this period of 102 days for each metal. The mean increase of TM concentrations in the surface layer ($\varphi c$) may be expressed by:

$$\varphi c = [F_{TM} * t_R] / z \qquad (2)$$

where $F_{TM}$ is the seawater labile atmospheric flux of a given TM, for $t_R$ = 102 days and z is the depth of the homogeneous ML.

The z value should be considered only when the heating of surface waters leads to the formation of the thermocline, which isolates the ML from underlying waters and, therefore yields the existence of a homogeneous ML. Such conditions occur in the Northwestern Mediterranean from the end of May to November, approximately. Nutrient resources are rapidly depleted and the biological activity concurrently decreases. In such oligotrophic conditions, dissolved TM are not significantly assimilated by biota or packaged with particulate organic matter and, therefore, accumulate in the ML (Migon et al., 2002). The depth of the ML in stratified conditions varies between 10 and 30 m (Andersen and Prieur, 2000; Marty et al., 2002, 2008). The dilution of the TM atmospheric load in surface seawater should thus be considered within a maximum ML depth of 30 m. $\varphi c$ values computed using the range of atmospheric TM fluxes with z ranging between 10 and 30 m are recorded in Table 2. The impact of the atmospheric input of seawater labile TMs on the ML can then be computed as $\varphi c/c$, using the range of marine dissolved TM concentrations (c) from literature data (Table 2).

The aims of this box model could be applied to other hydrodynamic marine environments where physico-chemical constraints may be well defined (e.g., epicontinental seas, Gulf of Thailand, Gulf of St Lawrence or Gulf of Mexico, Bering Sea, China Sea, Okhotsk Sea).

## 3. Results and Discussion

### 3.1. Atmospheric deposition over the Ligurian Sea

Trace metals are transferred from the troposphere to the sea surface by dry and wet deposition. The chemical composition of atmospheric TM deposition on sea surface waters strongly depends on that of the aerosol (Chester et al., 1997, 1999). Potential spatial and temporal (e.g., seasonal) variations in the atmospheric TM input must be considered before trying to budget the TM deposition to the Ligurian Sea. Taking into account the variability of local meteorological and climatological conditions (rainfall amount, speed of prevailing winds, efficiency of the aerosol scavenging, etc.), the spatial variability of atmospheric TM deposition is relatively low: the regional atmospheric input is superimposed to a strong background aerosol originating from industrialized regions of Europe (Chester et al., 1997). For example, the lowest spatial variability in the Ligurian atmospheric aerosol (nickel (Ni) concentrations) ranges within a factor of 1.4, and the highest variability (aluminum (Al) concentrations) ranges within a factor of 3.2 (Sandroni and Migon, 1997). Atmospheric TM fluxes at coastal sites may therefore be extrapolated to the sub-basin scale, as shown by comparison with shipboard aerosol sample collection (Jickells, 1995). The shipboard collection of aerosols is difficult over long time scales and, therefore, coastal or island based measurements are generally used (e.g., Chester et al., 1999; Güllü et al., 2000; Bonnet and Guieu, 2006). However, atmospheric TM deposition exhibits a seasonal pattern. In particular, anthropogenic TM emissions from Northern or Northeastern Europe are strong in the Northwestern Mediterranean area at the end of winter (Avila and Alarcon, 1999). This is consistent with the advective transport of polluted air masses from Europe as modeled by Duncan and Bey (2004). However, the Ligurian Sea might be even more strongly affected by such anthropogenic land-based emissions at the beginning of autumn, due to the autumnal equinox that points to the moving of the polar front to the southward, yielding the arrival of air masses from Northern and/or North-Eastern industrialized regions of Europe to the Western Mediterranean (Barnaba and Gobbi, 2004).

The isolation of Mediterranean waters from Atlantic waters enhances the role of atmospheric TM inputs and, therefore, the role of local driving forces such as climate, meteorology and environment (Béthoux et al., 1999).  This strongly determines the occurrence of wet and dry atmospheric TM deposition and, therefore, the physico-chemical form (dissolved or particulate) under which atmospherically transported TMs enter the sea surface. Due to the scarcity of rain events over the whole year, the dry deposition mode is dominant in the Mediterranean Sea for the majority of TMs (Nicolas et al., 1995), except for some soluble anthropogenic TMs that are significantly transported to the Northwestern Mediterranean by Northern and Northeastern European polluted air masses during winter and autumn, i.e. the wet season. In addition, these soluble TMs are efficiently incorporated into rainwater, and therefore their cycling is strongly influenced by wet deposition. For example, the wet contribution of Cd and Zn may represent up to 50 and 48%, respectively, of the total atmospheric fluxes in Ligurian coastal areas, to be compared with the wet contribution of Co (26%) or Cu (27%) (Migon et al. 1997).

The solubilization of atmospheric particles into seawater greatly determines the involvement of TMs in marine biogeochemical cycles. Seawater solubility of TMs is believed to be related to the two following parameters:

i) The source-dependent composition of aerosol particles (anthropogenic vs. crustal). Basically, crustal TMs are associated with the high loading of coarse particles, within three-dimensional crystalline networks in which dissolution is low. On the other hand, anthropogenic TMs are associated with the low loading of small amorphous particles that are much more soluble (Chuang et al., 2005; Sedwick et al., 2007).

ii) Atmospheric solubilization processes that occur during the aerosol transport. Experimental studies (e.g., Spokes and Jickells, 1995; Hand et al., 2004) suggest that the solubility of aerosol TMs in the ocean surface may be increased by photo-reduction and pH variations. However, field evidence for the dissolution of aerosols under such conditions in the atmosphere is still lacking (Mahowald et al., 2009; Sholkovitz et al., 2009). For this reason, atmospheric fluxes of "seawater labile" TMs over the Ligurian Sea (Table 1) are estimated from a variety of literature data (averaged over 1 year, at least) that are not based only on pH-driven laboratory experiments.

### 3.2. Impact of the atmospheric input on surface water concentrations

Even if the conditions of stratification of the surface layer, which determine the confinement of atmospheric loads, are variable in space and time, the evaluations given in Table 2 permit us to roughly quantify the potential impact of atmospheric TM deposition. Such enrichments of the Ligurian surface layer represent mean situations. Higher $\varphi c$ values may probably be expected over shorter spatial and temporal scales, when strong atmospheric events occur (e.g., Saharan dust storms or intense anthropogenic episodes).

Assuming that the residence time of TMs in offshore surface waters is shorter than (or equal to) deep-water renewal time (Nicolas et al., 1998), vertical distributions of dissolved TMs in the western Mediterranean chiefly depend upon atmospheric TM fluxes. Therefore, the atmospheric TM enrichment of the ML during the stratification period in the Ligurian Sea (i.e., basically, from May to November) determines the TM concentrations above the thermocline.

Typically, when atmospheric TM deposition significantly impacts surface waters, TMs presumably exhibit surface-enriched profiles (e.g., Co, Figure 2a). On the contrary, when atmospheric TM enrichment is low, TMs may exhibit surface-depleted profiles (e.g., Ni, Figure 2b). This results from the more or less efficient removal of dissolved TMs to depth. Recent measurements of dissolved TM concentration profiles in the Ligurian Sea (Heimbürger et al., 2009) are in agreement with this statement and suggest that either surface-depleted or surface-enriched profiles (Figures 2a, b) are expected for TMs, according to the significance of their accumulation in ML, relative to the seasonal efficiency of the vertical transfer (Migon and Nicolas, 1998).

Surface-depleted profiles suggest that the deposition flux of the considered TM is insufficient to compensate for the biological removal that has occurred in spring, when primary production was high, until the beginning of the stratification period, when the ML has become nutrient-depleted. On the contrary, surface-enriched profiles suggest that biological activity (minimal during stratified, oligotrophic conditions; see, e.g., Marty and Chiaverini, 2002; Marty et al., 2002) and passive particle-surface removal are not efficient enough to remove dissolved TMs from the surface layer within the duration of Ligurian water residence time. In the latter case, the removal of dissolved TMs from ML thus depends on hydrological processes, i.e. winter vertical mixing (Migon et al., 2002).

Iron enrichments exhibit a very high variability (Table 2). Factors within the water column (e.g., pH, ligand concentration, biological uptake) may contribute to the variability of Fe enrichment. However, in the Mediterranean Sea, such marine parameters are of very little weight compared with the temporal variability of atmospheric inputs, due to changes in aerosol source (anthropogenic versus natural) and, in particular, the pulsed character of Saharan dust events. Bonnet and Guieu (2006) have shown that over 99% of the total 2004 flux of total atmospheric Fe can be attributed to a few strong pulses of Saharan dust events. As a consequence, the interannual variability of crustal inputs (and, therefore, Al and Fe inputs) is very high (Guieu et al., in press). It is believed that the wide range of $\varphi c/c$ values observed for Fe and, to a lesser extent, for Al, is due to variability in Fe and Al flux estimations. For example, the flux value proposed by Bonnet and Guieu (2006) was essentially based on a single Saharan event that brought up to 88% of total atmospherically-deposited Fe. However, if Saharan dust episodes are the most important source of atmospheric Fe, the actual flux of seawater labile Fe is significantly adjusted by the low solubility of crustal Fe. For example, seawater labile Fe fluxes given by Guieu et al. (1997)

were computed from literature on dissolved-particulate partitioning factors, in which the dissolved fraction is believed to be overestimated (Guieu, personal communication). Despite these uncertainties, high $\varphi c/c$ values result to a large extent from strong Fe and Al atmospheric deposition, compared with seawater concentrations. This suggests an accumulation in surface waters, which yields a surface-enriched profile (Table 2). Several oceanic regions exhibit surface-depleted profiles of dissolved Fe, even when they are heavily impacted by dust events. For example, Measures et al. (2008) found increased Fe concentrations in Atlantic (62°N, 5°S) surface waters beneath Saharan dust outflows, but high dissolved Fe concentrations (>1.5 nM) in subsurface layers yielded surface-depleted profiles. However, the Ligurian Sea exhibits a different behavior: Bonnet and Guieu (2006) noticed that the atmospheric input of dissolved Fe actually accumulates in surface waters, with no significant loss from the ML, to reach its maximum around October, while subsurface concentrations were lower. As a result, Fe profiles were either rectilinear or surface-enriched. This implies that recognized Fe-depleting processes such as phytoplankton uptake/adsorption, scavenging onto sinking particles or diffusion through the thermocline are negligible during the oligotrophic period, when the ML is homogeneous. The surface accumulation of Fe occurs during a time of minimal or lower Fe uptake during the period as nutrient supply has been exhausted, i.e. the oligotrophic period.

The observed variability of atmospheric lead (Pb) fluxes mirrors the rapid decrease of Pb concentration in the Mediterranean environment since 1988 (Migon et al., 2008). Since the implementation of antipollution policies on automotive Pb in the mid-1980s, the concentration levels of Pb in the atmosphere and in Mediterranean waters have decreased sharply within a few years (Migon and Nicolas, 1998). This atmospheric decrease has markedly slowed down, at the latest, from 2003 (Migon et al., 2008), and vertical Pb distributions in the Western Mediterranean waters are expected to reflect rapidly a steady-state cycling. Therefore, it is likely that the present-day impact of atmospheric Pb inputs is lower than Pb enrichments estimated in Table 2 (surface-enriched profile). Present-day $\varphi c/c$ variability is presumably lower than that observed in Table 2 as well, because of the slight temporal shift between the references used here. For example, Guieu et al. (1997) gather results that do not correspond to the same sampling period, and the range of values given by Yoon et al. (1999) correspond to more recent data, compared with the values of Nicolas (1993).

The atmospheric fluxes for Zn used in the present box model yield high $\varphi c/c$ values, suggesting enrichments relative to the dissolved Zn concentrations in surface water. Zinc is mainly of urban origin, most of which comes from motor vehicle use, owing to tire wear (Wiesner et al., 1998), and the Ligurian Sea is subject to significant emission sources from the large urbanised area between Toulon and Genoa. In addition, significant amounts of Zn are emitted by waste incinerations (Nriagu and Pacyna, 1988), which are probably a noticeable source of Zn, particularly when waste plant residual muds are incinerated (Migon and Sandroni, 1999). However, dissolved Zn profiles measured in the Western Mediterranean show contradictory behaviors: Data from Ruiz-Pino et al. (1991) show enriched surface dissolved Zn profiles with a subsurface minimum, while data from Yoon et al. (1999) show surface depleted dissolved Zn profiles, with a subsurface maximum. Keeping in mind that contamination problems are always acute for Zn (including atmospheric measurements), the reliability of these data and their subsequent interpretation for Zn behavior in surface waters therefore remains questionable.

The case of mercury deserves special consideration, since the atmosphere is known as the main transport medium of this element to the open sea, and phytoplankton uptake and abiotic sorption are not the main, and in no case the only removal process of this TM from surface seawater in many biogeochemical conditions (see the review by Fitzgerald et al., 2007). Indeed, it is well established that elemental Hg evolves in the atmosphere as a result of the photochemical and microbiological reduction of $Hg^{II}$ present in marine surface waters (e.g., Mason et al., 2001). This peculiarity of the Hg cycle applied to our model would lead to the risk of obtaining $\varphi c/c$ ratios inconsistent with the Hg profiles observed in the water column (Cossa and Coquery, 2005; Cossa et al., 2009), a surface-depleted profile possibly reflecting not only the efficiency of biological or chemical scavenging processes, but also removal by Hg escaping from the sea surface into the air. However, the surface-enriched profiles actually observed suggest that Hg deposition in the Ligurian Sea is significant enough to overcome its evasion. Indeed, the high $\varphi c/c$ ratios for Hg (Table 2) testify to the intensity of Hg deposition in the Ligurian Sea. The western Mediterranean basin is affected by Hg-enriched air masses from regions of North Europe, mainly as a result of coal combustion, caustic soda production, power plants and waste incineration (Pirrone et al., 2003; Pacyna et al., 2006), and by aeolian dust with low Hg content (Baturin et al., 1995). It is thought, from modeling, that scavenging by water droplets is an efficient removal pathway for atmospheric Hg after its (re)oxidation by halogen radicals within the marine boundary layer (Pirrone et al., 2003). However, according to the same authors, dry deposition (including gas transfer) may dominate on the Mediterranean Sea surface. Anyhow, in both wet and dry deposition, Hg is present mainly as divalent Hg, which suggests that its solubilization in surface water is facilitated.

Copper (Cu), with a moderate $\varphi c/c$ ratio (up to 40.8), marks the boundary between surface-depleted and surface-enriched TM distribution profiles. Once $\varphi c/c$ ratios are computed, dissolved TM profiles are examined. One can then estimate the interval within which these profiles shift from the depleted state to the enriched state. The threshold between one state and another is within this interval. It is then possible to know approximately where the edge is. Seawater labile Cu inputs to the Ligurian Sea are probably very close to the quantities that appear to be removed from surface waters by plankton activity. Thus, a minor change in $\varphi c$ or $c$ might yield a change of the profile character (surface-depleted or surface-enriched). Whereas $\varphi c$, defined by the variation of the atmospheric Cu flux, remained stable over the past 2 decades (Heimbuerger et al., 2010), a change of $c$ could occur by increased biological activity, because Cu would be removed more efficiently from the surface. Indeed, surface depleted Cu profiles have been observed during spring bloom conditions (Heimbürger et al., 2009). Therefore, a change of biological productivity, e.g., as a response to climate change, is likely to impact the biogeochemical cycling of Cu in the Ligurian Sea.

In the Mediterranean Sea, oligotrophy is characterized by low concentrations of macro-nutrients. In such conditions, primary production is mainly controlled by phosphorus availability (Marty et al., 2002), and despite the accumulation of biologically utilized TMs such as Fe in the ML (Bonnet and Guieu, 2006), no observable plankton growth is triggered, and the maximum of phytoplankton biomass is always observed under the ML (Marty and Chiaverini, 2002). The ratio between the magnitude of seawater labile TM atmospheric fluxes and the removal potential of biological activity may thus be a key parameter to control the shape of the dissolved TM vertical profiles, i.e. surface-depleted or surface-enriched. For example, it is hypothesized that, in oligotrophic conditions, the removal potential of biological activity is insufficient to remove dissolved Cu accumulated in surface waters, while dissolved Cu exhibits a surface-depleted profile during the period of high biological productivity, i.e. spring bloom.

It is noteworthy that the two types of TM behavior observed in the Ligurian Sea (surface-enriched or surface-depleted) mirror a Mediterranean specificity: owing to the magnitude of atmospheric deposition over Mediterranean waters, the TM surface enrichment may exceed the ability of plankton to assimilate these TMs and, therefore, to transfer them to deep waters. On the other hand, TMs actively assimilated by phytoplankton are generally depleted in open ocean surface waters, either as a result of their quasi-complete assimilation by phytoplankton, or because they are packaged onto biological sinking material (Morel, 2008).

Ligurian waters are transported westwards with the LC and are further enriched on their pathway to be ultimately exported to the Atlantic Ocean. East of Gibraltar, the relative proportion of the Mediterranean outflow water (MOW) can be calculated on the basis of a conservative mixing with adjacent North Atlantic waters. During the mixing, Cu and Ni behave conservatively, while Cd is ~ 80% conservative (Cotté-Krief et al., 2002). Since the Ligurian Sea is separated from the Alboran Sea where the MOW characteristics are formed by various hydrological features (cascading, fronts, etc.), and since, on the way to the Gibraltar strait, dense water formation (cascading) brings surface waters from the shelf with continental influence (Gulf of Lions) to depths (Riso et al., 2004), the influence of TM-enriched Ligurian waters seems very difficult to trace in the Atlantic Ocean.

A number of hydrological, chemical and biological processes interact to control the biogeochemical cycling and the distributions of TMs. The literature data used in the present model integrate these processes. The type of dissolved concentration profile exhibited by a given TM is inferred from the atmospheric enrichment of the surface: On the yearly scale, the biogeochemical cycle of TMs that exhibit surface-enriched vertical profiles is dominated by removal processes mediated by hydrology: because of significant atmospheric enrichment in the ML, the removal of dissolved TMs such as Al, Co, Fe, Hg, Pb and Zn from surface waters is mainly driven by winter convection. On the other hand, dissolved TMs that exhibit surface-depleted vertical profiles (e.g., Cd, Cr and Ni) are mainly removed from surface waters by their packaging with settling biological particles. The removal of dissolved Cu may be driven either by hydrology or biology, according to the seasonal intensity of primary production.

## 4. Conclusions

The use of $\varphi c/c$ ratios allows the quantification of the impact of individual TMs on surface waters. The present observations acquired in the Ligurian Sea during a period of 102 days permitted the construction of a model that should be suitable for the whole year and for any marine region constrained by physico-chemical atmospheric forcing. While Cd, Cr and Ni do not cause any concern, other TMs, such as Hg, Pb and Zn, with elevated $\varphi c/c$ ratios, are not effectively removed from Ligurian surface waters during their passage and within their local residence time. Trace metals, which are surface-enriched (high $\varphi c/c$ ratios) might not only govern local settings at the sub-basin scale, but may be extended to the basin scale (i.e., the Western Mediterranean).

Trace metal cycling in the Mediterranean is not in a steady state, with supposedly increasing anthropogenic constraints. Future meteorological and hydrological trends with changing climate, e.g. more or less winter mixing and more or less significant subsequent spring bloom, may also drastically change the impact of atmospheric fluxes on marine TM cycling. Consequently, future studies should comprise above all else continuous monitoring of atmospheric and marine TM concentrations.

## Acknowledgements

We thank William Delor for language corrections and the anonymous reviews for their constructive comments.

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## Tables

Table 1: Mean yearly inputs of seawater labile TMs to the Ligurian Sea, expressed in µg $m^{-2}d^{-1}$.
(1) Guieu et al. (1997); (2) Values computed from total fluxes from Migon et al. (1997) and dissolved-particulate partitioning from Guieu et al. (1997); (3) Seawater labile estimations according to Sandroni and Migon (2002); (4) Bonnet and Guieu (2006); (5) and (6) mean Mediterranean values, non specific to the Ligurian Sea by Cossa and Coquery (2005) and Rajar et al. (2007) respectively.

| TM | Total seawater labile atmospheric deposition | | | |
|---|---|---|---|---|
| | *Individual studies* | | | *Summary* |
| Al | 28 ï 279[1] | | | 28 ï 279 |
| Cd | 0.12[2] | 0.16[3] | | 0.12 ï 0.16 |
| Co | 0.05 ï 0.36[1] | 0.15[2] | | 0.05 ï 0.36 |
| Cr | 0.25 ï 1.10[1] | 1.30[3] | | 0.25 - 1.30 |
| Cu | 2.19 ï 3.56[1] | 1.86 ï 2.88[2] | 3.2[3] | 1.86 ï 3.56 |
| Fe | 89 ï 384[1] | 6.4[4] | | 6.4 ï 384 |
| Hg | 0.01 ï 0.03[5] | 0.03[6] | | 0.01 ï 0.03 |
| Ni | 1.1 ï 1.4[1] | 1.63 ï 1.92[2] | 2.6[3] | 1.1 ï 2.6 |
| Pb | 2.5 ï 5.2[1] | 2.58 ï 5.07[2] | | 2.5 ï 5.2 |
| Zn | 77 - 165[2] | 107[3] | | 77 ï 165 |

Table 2: φc and c values (both computed using the range of literature data), both expressed in µg $m^{-3}$, from which are computed φc/c ratios.
(1) Chou and Wollast (1992); (2) Lacan et al. (2006); (3) Nicolas (1993); (4) Heimbürger et al. (2009); (5) Achterberg and van den Berg (1997); (6) Riso et al. (1994); (7) Yoon et al. (1999); (8) Bonnet and Guieu (2006); (9) Cossa and Coquery (2005).

| TM | Total seawater labile atmospheric deposition | | | | |
|---|---|---|---|---|---|
| | *This work* | *Individual studies* | | | *Summary* |
| Al | 191 | 28 ï 279[1] | | | 28 ï 279 |
| Cd | 0.17 | 0.12[2] | 0.16[3] | | 0.12 ï 0.16 |
| Co | 0.24 | 0.05 ï 0.36[1] | 0.15[2] | | 0.05 ï 0.36 |
| Cr | - | 0.25 ï 1.10[1] | 1.30[3] | | 0.25 - 1.30 |
| Cu | 3.75 | 2.19 ï 3.56[1] | 1.86 ï 2.88[2] | 3.2[3] | 1.86 ï 3.56 |
| Fe | 391 | 89 ï 384[1] | 6.4[4] | | 6.4 ï 384 |
| Hg | - | 0.01 ï 0.03[5] | 0.03[6] | | 0.01 ï 0.03 |
| Ni | 2.39 | 1.1 ï 1.4[1] | 1.63 ï 1.92[2] | 2.6[3] | 1.1 ï 2.6 |
| Pb | 2.73 | 2.5 ï 5.2[1] | 2.58 ï 5.07[2] | | 2.5 ï 5.2 |
| Zn | 95 | 77 - 165[2] | 107[3] | | 77 ï 165 |

*Refer to Figure 2 for meaning.

# Figures

Figure 1: Location (rectilinear dotted lines) and cyclonic circulation of the Ligurian Sea. Incoming and outgoing water flows are expressed in $m^3$ $yr^{-1}$. The boundaries of the Ligurian Sea area are those commonly used in literature (e.g., Béthoux, 1980; Béthoux et al., 1988).

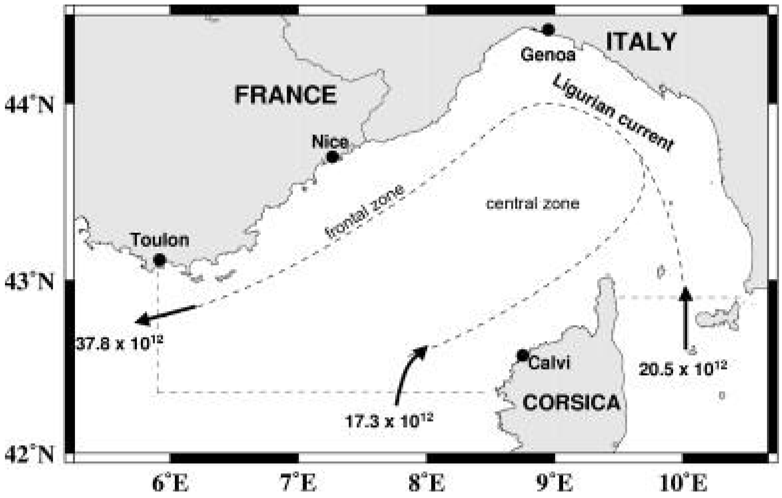

Figure 2: Dissolved Co and Ni profiles during the Ligurian stratification period (October 2007, DYFAMED site, central Ligurian Sea, 43°25′N, 7°52′E), data from Heimbürger et al. (2009). Cobalt (a) represents a typical surface-enriched profile. Nickel (b) represents a typical surface-depleted profile.