What controls marine trace metal export flux?

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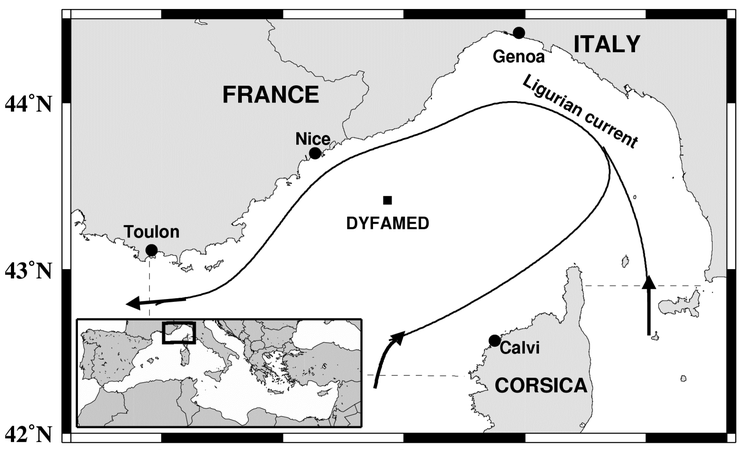
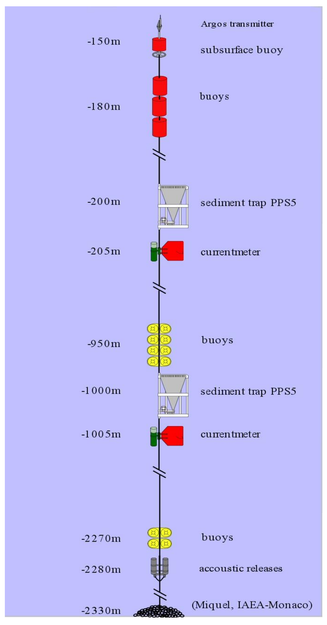
COMET : COnstructing MEditerraneen Time-series (P.I. MA Sicre and L Coppola)

The temporal evolution of the mass fluxes off the surface at DYFAMED over the past two decades reveals a strong inter-annual variability and a recurrent seasonal pattern. High fluxes occur in winter as a result of wind-driven vertical mixing; as surface waters begin to stratify in March-April, phytoplankton blooms and gives rise to a major export out of the euphotic zone. Inter-annual variability is another remarkable feature of the mass flux time-series. However, causes of this variability are not fully understood. Detailed investigation of this time-series is expected to provide a better view of the biogeochemical processes governing flux dynamics and to improve our ability to predict their effect on ecosystems and carbon sequestration. To identify the mechanisms responsible for the observed flux variability at seasonal to inter-annual time scales, knowledge on the chemical composition of sinking material is critical.

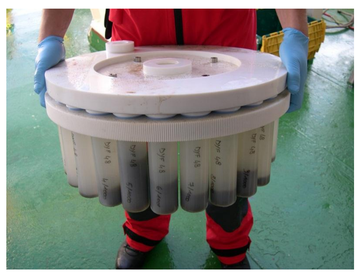


Map of the Northwestern Mediterranean Sea and the location of the time-series sampling site DYFAMED.

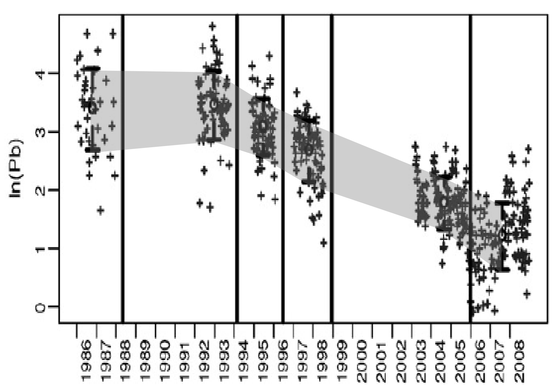


Automated time-series sediment traps were moored at the DYFAMED site since 1987.

Sediment traps Technicap PPS 5:
www.technicap.fr
- height 2.3 m
- collection area 1 m²
- 24-cup collector
- Interval ~15d



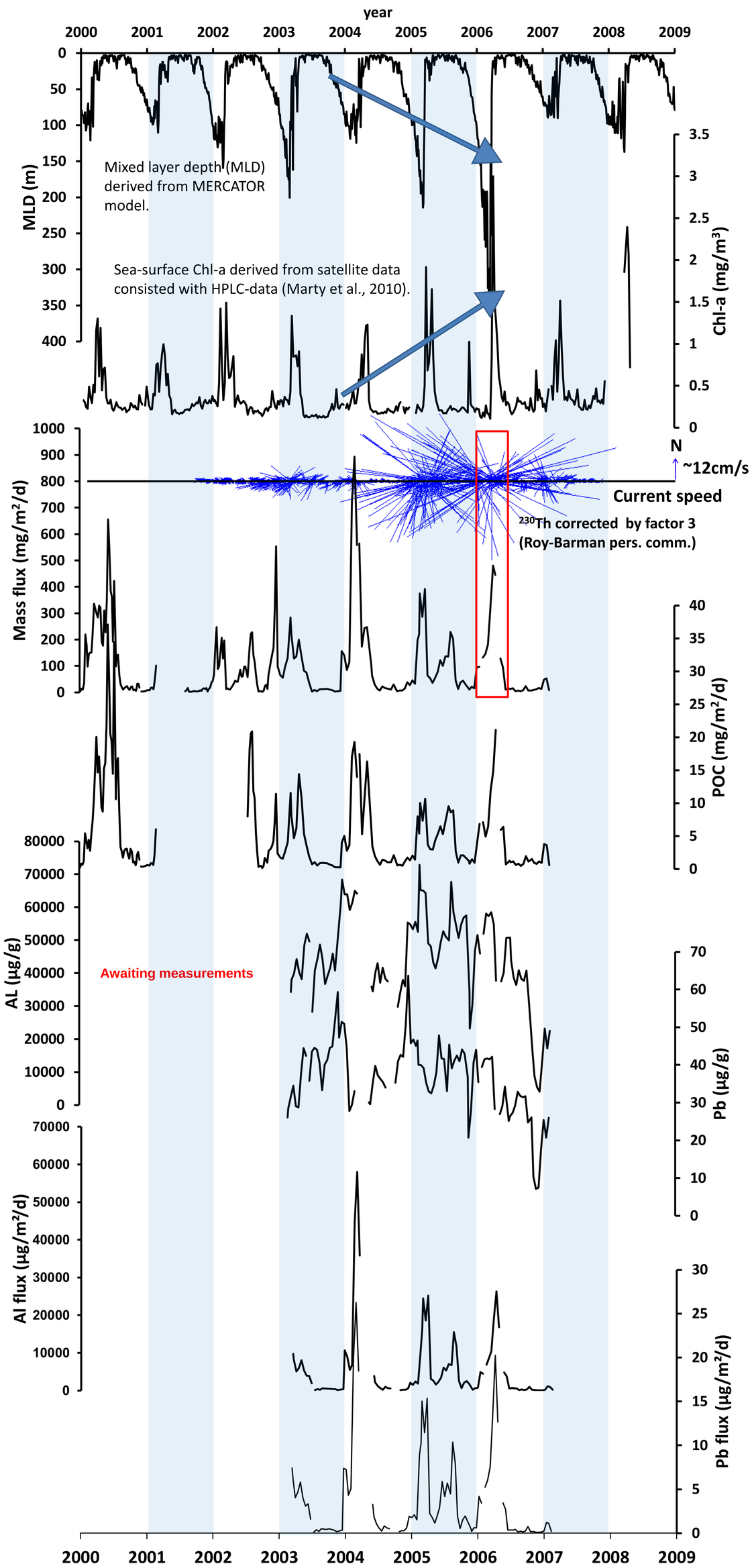
Marine response to atmospheric changes:

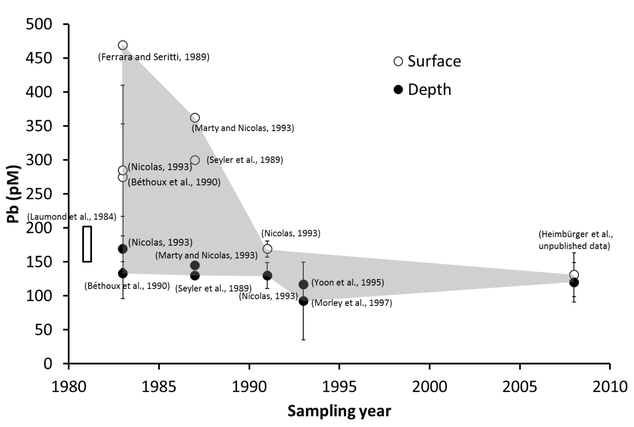


Dissolved Pb concentrations (pM) in the Northwestern Mediterranean Sea markedly decreased in the upper layer with slower response in the deeper waters (right figure).

Pb aerosol concentrations (ng m^{-3}) decreased by **90%** over the past two decades as a direct response to the implementation of anti-pollution policies. Other anthropogenic TMs follow similar trends. Zn and Cd decreased by **54 and 66%**, respectively. Crustal TMs remained stable.
(Heimbürger et al., 2010)

DYFAMED sediment trap moored at 1000m-depth:





Seasonality:

January-February:
Dense water formation ➔ winter convection. Vertical mixing driven by cooling and increase of salinity of surface waters (wind forcing) carries dissolved and particulate matter, including TMs, to depth ("flush down" effect).
March to June:
Spring phytoplankton bloom drives the vertical transfer of TMs
Oligotrophic season:
Very low transfer, due to lower biological activity.

Data analysis:

Currentmeters installed beneath the sediment traps on the mooring line indicated high current speeds during 2005-06. Mass flux data has been adjusted using ^{230}Th data (Roy-Barman pers. comm.).

Export flux does not seem to be directly related to the dense water formation depth and the importance of the subsequent spring bloom.

TM concentrations:

R²	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb
Al	1										
V	0.98	1									
Cr	0.92	0.96	1								
Mn	0.81	0.85	0.87	1							
Fe	0.99	0.98	0.93	0.81	1						
Co	0.49	0.52	0.50	0.56	0.51	1					
Ni	0.83	0.85	0.92	0.79	0.86	0.47	1				
Cu	-0.24	-0.24	-0.19	-0.21	-0.20	0.00	0.05	1			
Zn	-0.11	-0.12	-0.09	-0.09	-0.07	0.05	0.06	0.30	1		
Cd	-0.24	-0.23	-0.22	-0.27	-0.19	-0.02	-0.08	0.27	0.27	1	
Pb	0.73	0.76	0.77	0.78	0.76	0.65	0.81	0.12	0.21	-0.07	1

Intercorrelation matrix of TM concentrations in sediment trap material from 2003-2007 (number of variables 11, number of observations 97). Crustal TMs (Al, V, Cr, Mn, Fe, Co, Ni) and Pb are highly correlated ($p<0.01$). Variability of TM concentrations is relatively low compared to the variability of mass flux.

TM flux:

R²	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb
Al	1										
V	1.00	1									
Cr	0.97	0.98	1								
Mn	0.97	0.98	0.99	1							
Fe	1.00	1.00	0.97	0.97	1						
Co	0.97	0.97	0.93	0.94	0.97	1					
Ni	0.96	0.97	1.00	0.99	0.95	0.91	1				
Cu	0.96	0.96	0.95	0.96	0.96	0.95	0.95	1			
Zn	0.95	0.96	0.96	0.96	0.95	0.93	0.96	0.98	1		
Cd	0.95	0.93	0.88	0.87	0.95	0.94	0.85	0.92	0.9	1	
Pb	0.98	0.99	0.99	0.99	0.98	0.96	0.99	0.98	1.0	0.91	1

Intercorrelation matrix of TM fluxes in sediment trap material from 2003-2007 (number of variables 11, number of observations 97). **All** TM fluxes are highly correlated ($p < 0.0001$). **Mass flux** and **TM flux** covary **whatever** the nature of the TM. Biogenic carbon production and winter convection control marine TM export flux.

Conclusions:

- Fluxes of a wide variety of TMs (e.g., anthropogenic such as Zn, Cd, Pb or crustal such as Al, Fe, Co, … i.e. TMs of which atmospheric deposition to the sea surface varies with different seasonal patterns) exhibit in every case the same temporal variability.

- All TMs, whether of crustal or anthropogenic origin, are strongly and significantly ($p < 0.0001$) intercorrelated, which suggests that all TMs are driven to depths at the same time and, therefore, gathered into the mass flux.

- Saharan dust episodes that were observed apart from periods of winter convection or spring bloom did not yield any significant vertical fluxes: dust particles supposedly accumulated above the thermocline. The same applies to strong anthropogenic episodes.

➔ We conclude the temporal variability of atmospherically derived TM fluxes is an effect, instead of a cause, of mass vertical transfer.
(This is not inconsistent with mineral ballasting)

As a result, mass fluxes control the temporal variability of TM removal from surface waters.

Key questions:

Can the pattern that have been observed in the atmosphere and in the water column be detected in exported material and therefore in marine sediments?
In which manner does the TM signal depend on winter convection, nutrient supply and primary production?
Will climate change (enhanced stratification) be reflected in TM export patterns?