TM cycling in the Med Sea – changes since EROS 2000?

L.-E. Heimbürger[1], C. Migon[2,3], D. Cossa[4], N. Mihalopoulos[5] ,J. Sonke[1], C. Jeandel[6] and B.Thibodeau[7]

Abstract:

The Mediterranean Sea offers marine scientist an excellent playground to investigate trace metal dynamics linked to atmospheric deposition, dense water formation, riverine inputs, cascading and changes in primary production. One of the major pathways of TM inputs of natural and anthropogenic origin to the marine environment is the atmospheric pathway, which is in particular important for semi-enclosed seas as the Mediterranean. Moreover, due to its short water residence times (15 and 50 years in the western and eastern basin respectively) the Mediterranean Sea is ideal to study changes in the biogeochemical cycling of TM linked to global change and variations in the sources of emission. EROS2000 effort to represent TM distributions in the 1980s and 1990s for the North-western Mediterranean was presented in 5 workshops. Since then, analytical techniques have evolved and ultra-clean TM sampling and analysis have become routinely used and more elements including their isotopes can be addressed nowadays. In the same way as we have progressed in understanding the nutrient cycle, the technical development allows us now to study the cycling of a broad variety of TMs. GEOTRACES Mediterranean will offer scientist a unique chance to explore TM cycling in a miniature ocean, to confirm findings of the past decades and to explore any possible long-term trends with their biogeochemical implications, mainly in relation to primary production.

Trace metal cycling in the Mediterranean Sea – Changes since EROS 2000?

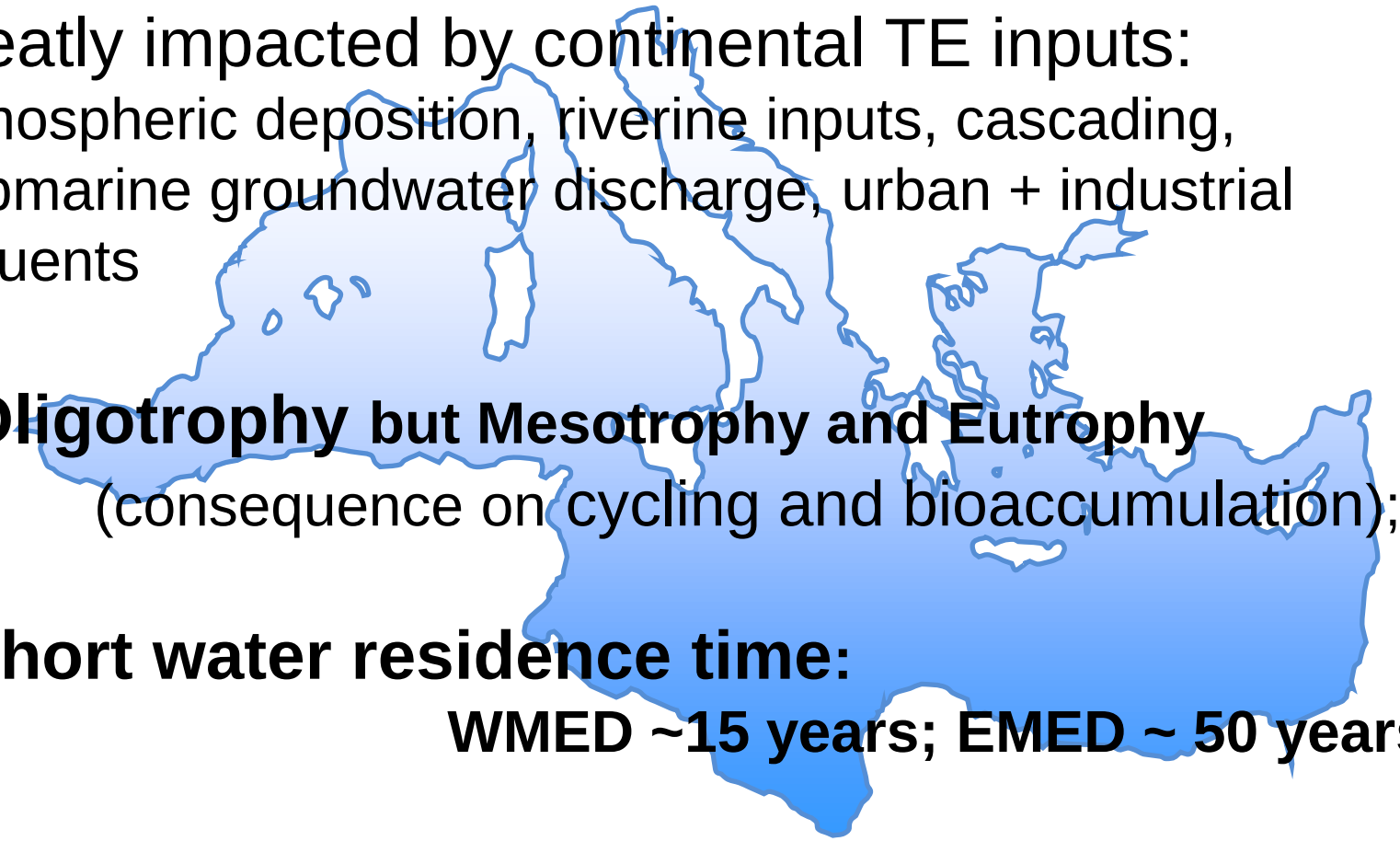
L.-E. Heimbürger[1], D. Cossa[2], C. Migon[3,4], N. Mihalopoulos[5], J.E. Sonke[1], C. Jeandel[6] and B.Thibodeau[7]

[1] LMTG-OMP, F-31400 Toulouse, France
[2] IFREMER, Centre de Méditerranée, BP 330, F-83507, La Seyne-sur-Mer, France
[3] Université Pierre et Marie Curie (UPMC), UMR 7093, Observatoire océanologique de Villefranche-sur-Mer, F-06234, Villefranche-sur-Mer, France
[4] CNRS/INSU, UMR 7093, Laboratoire d'Océanographie de Villefranche-sur-Mer, F-06234, Villefranche-sur-Mer, France
[5] Environmental Chemistry Processes Laboratory , Department of Chemistry, University of Crete, P.O. Box 2208, 71003 Heraklion, Greece
[6] LEGOS-OMP, F-31400 Toulouse, France
[7] Geochemistry and Geodynamics Research Center, GEOTOP, Université du Québec à Montréal, Montréal, Québec, H3C 3P8, Canada

Mediterranean Sea – Miniature Ocean model suitable for studying climate and global changes

- **Epicontinental sea with Intense human activity**

greatly impacted by continental TE inputs:
atmospheric deposition, riverine inputs, cascading, submarine groundwater discharge, urban + industrial effluents



- **Oligotrophy but Mesotrophy and Eutrophy**

(consequence on cycling and bioaccumulation);

- **Short water residence time:**

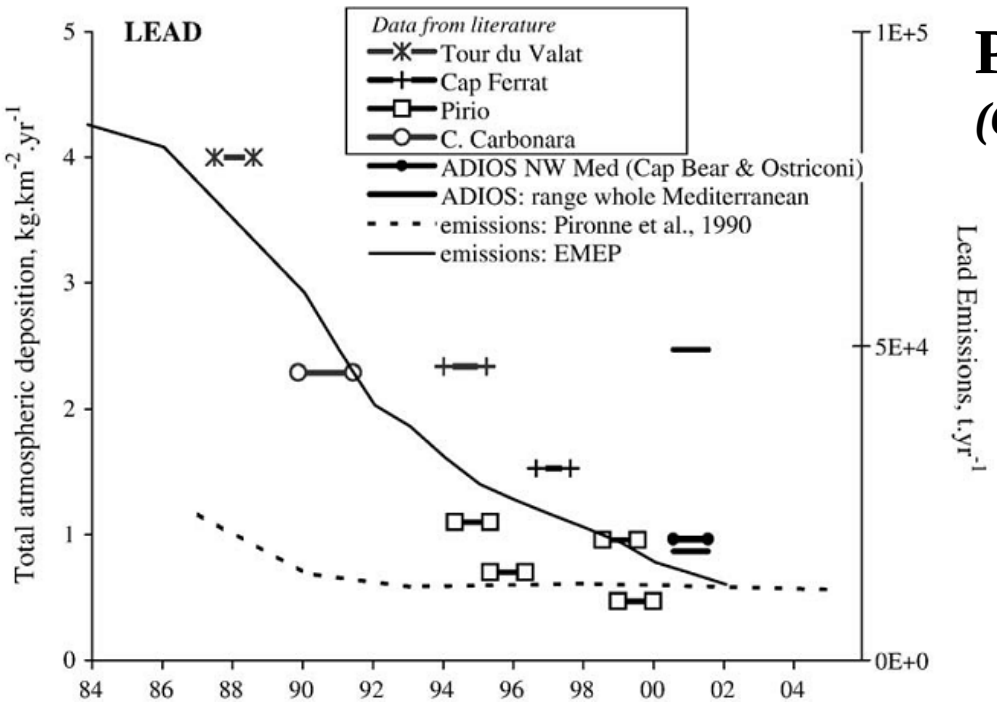
WMED ~15 years; EMED ~ 50 years,

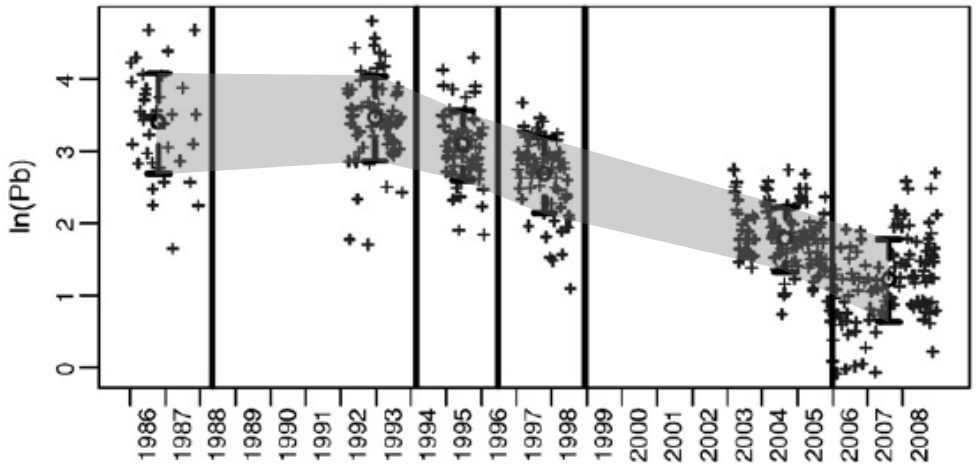
Anthropogenic TE in the Mediterranean Sea

- Human activities have increased the inputs (atmosphere & rivers) of several TE :
  - Which are they?
  - How much are the enhancements?
  - What are the temporal trends?
- Which of them present evidences for the perturbation of their natural cycle in sea water?

Examples of Pb, Cd, Cu, Zn, Hg and Sn

Lead in the Mediterranean atmosphere



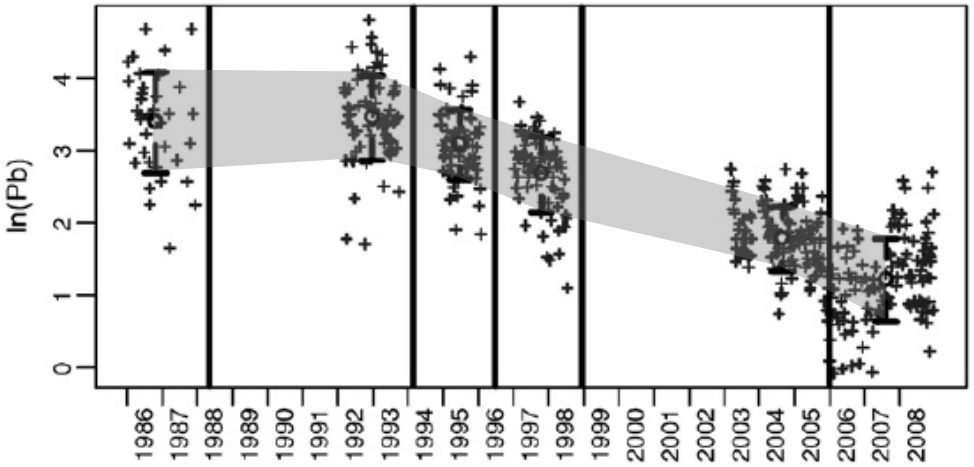


Pb total deposition (kg km^{-2} y^{-1})
(Guieu et al., 2010)

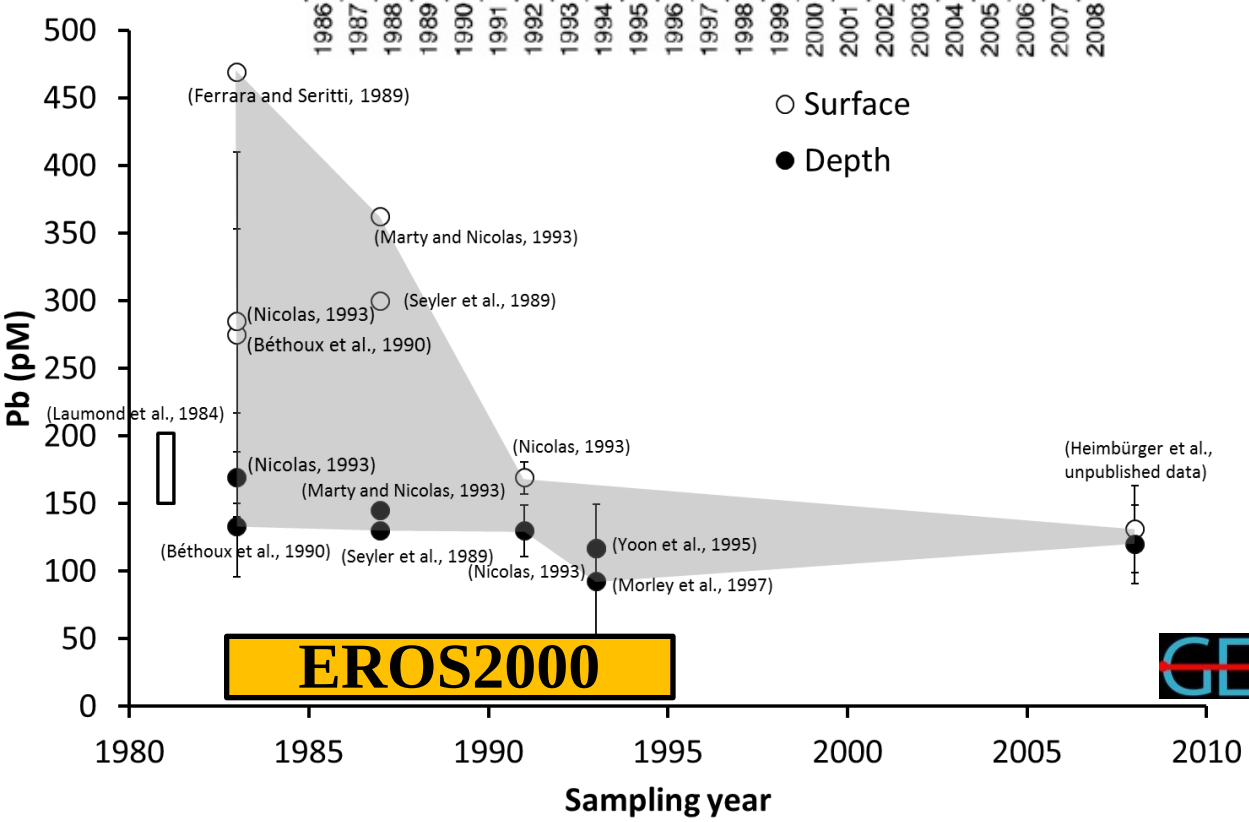
Pb aerosol conc. (ng m^{-3})
***(Heimbürger et al., 2010*)**

~90% decrease

Pb levels in the NWMED since EROS2000

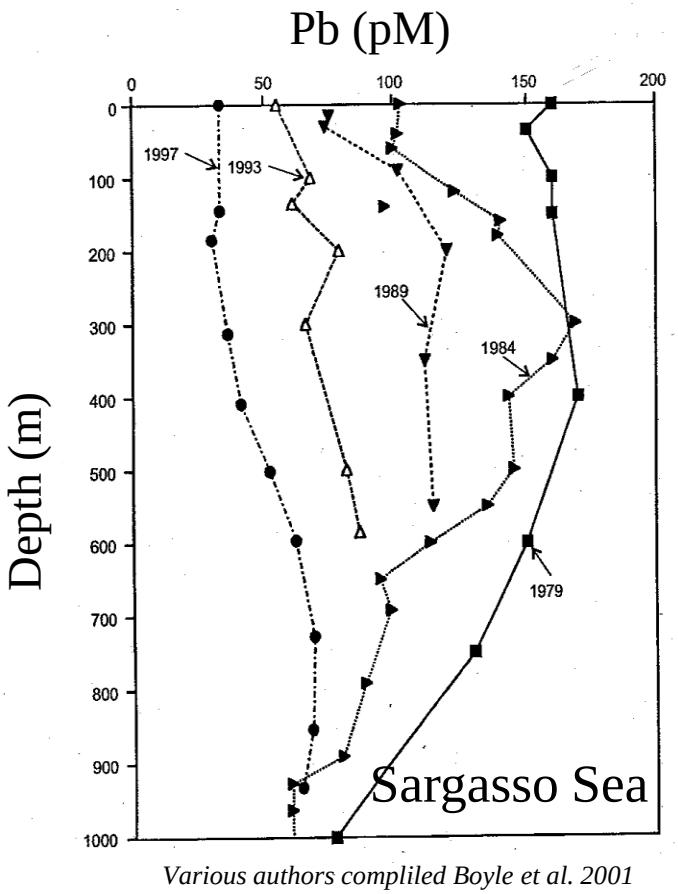


Pb aerosol
concentrations (ng m^{-3})
(Heimbürger et al., 2010)

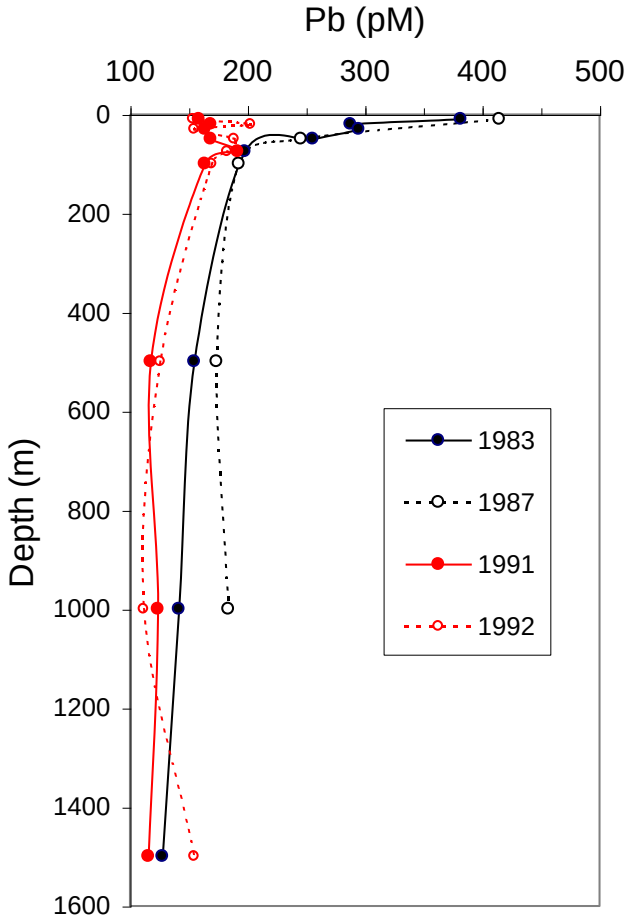


Dissolved Pb
concentrations (pM)

Pb levels in the NWMED since EROS2000



Various authors compliled Boyle et al. 2001

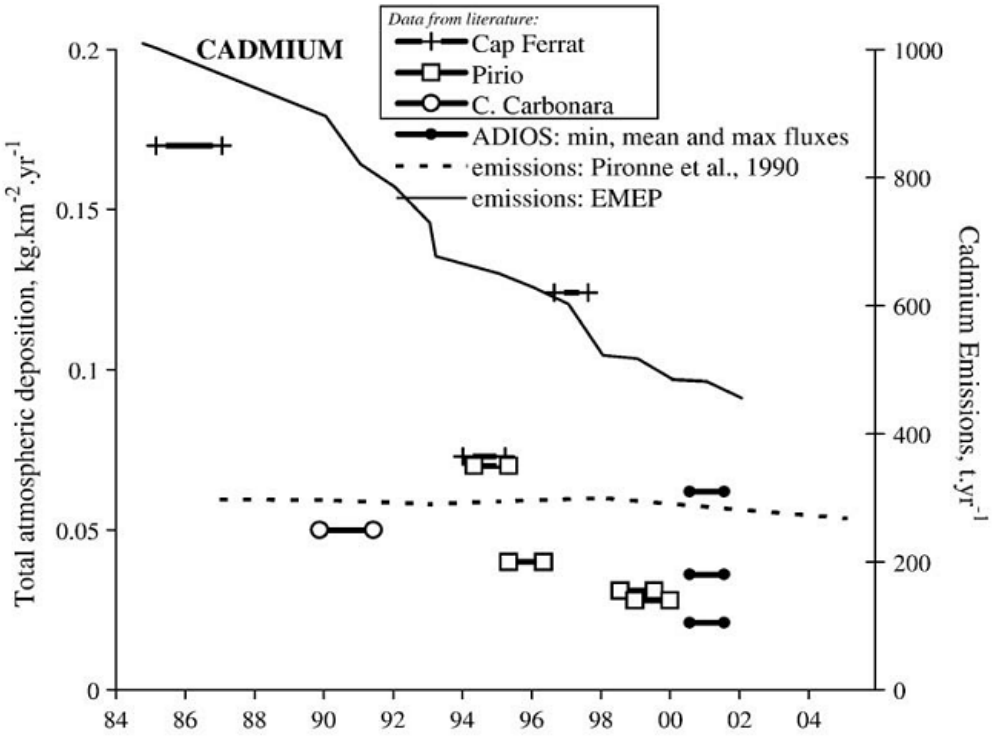


Pb concentrations in the Mediterranean as in the other part of the Ocean markedly decreased in the upper layer with slower response in the deeper waters. These decreases follow the phasing out of leaded gasoline.

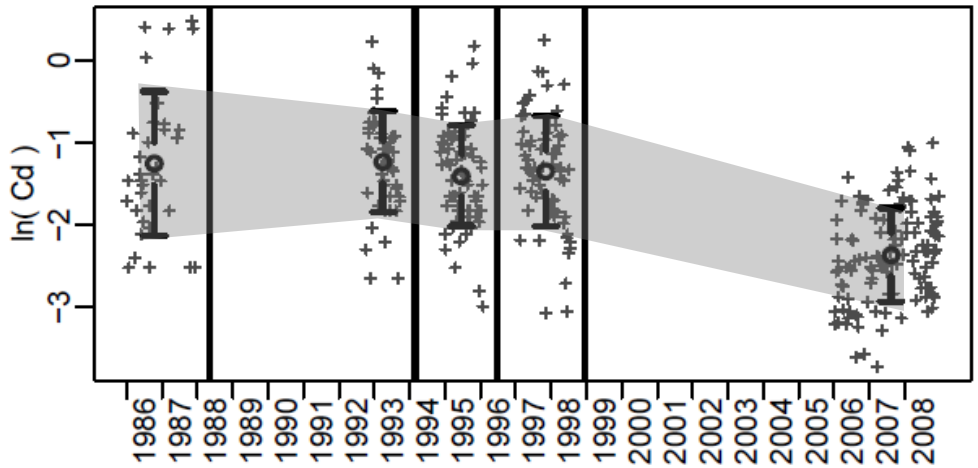
Pb key questions

- What is the current anthropogenic Pb fraction?
- Do Pb concentrations in deep waters decrease following the same trend as the surface?
- What is the Pb distribution (and sources) in the Eastern Mediterranean; is its cycling different in this ultra-oligotrophic basin?
- Have enriched Gibraltar inputs (Rio Tinto) changed?

Cd in the Mediterranean atmosphere



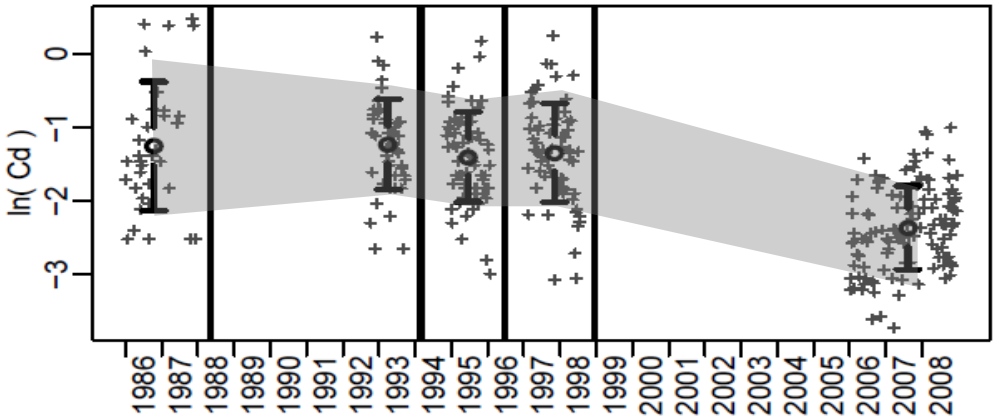
Cd total deposition
(kg km^{-2} y^{-1}) **(Guieu et al., 2010)**



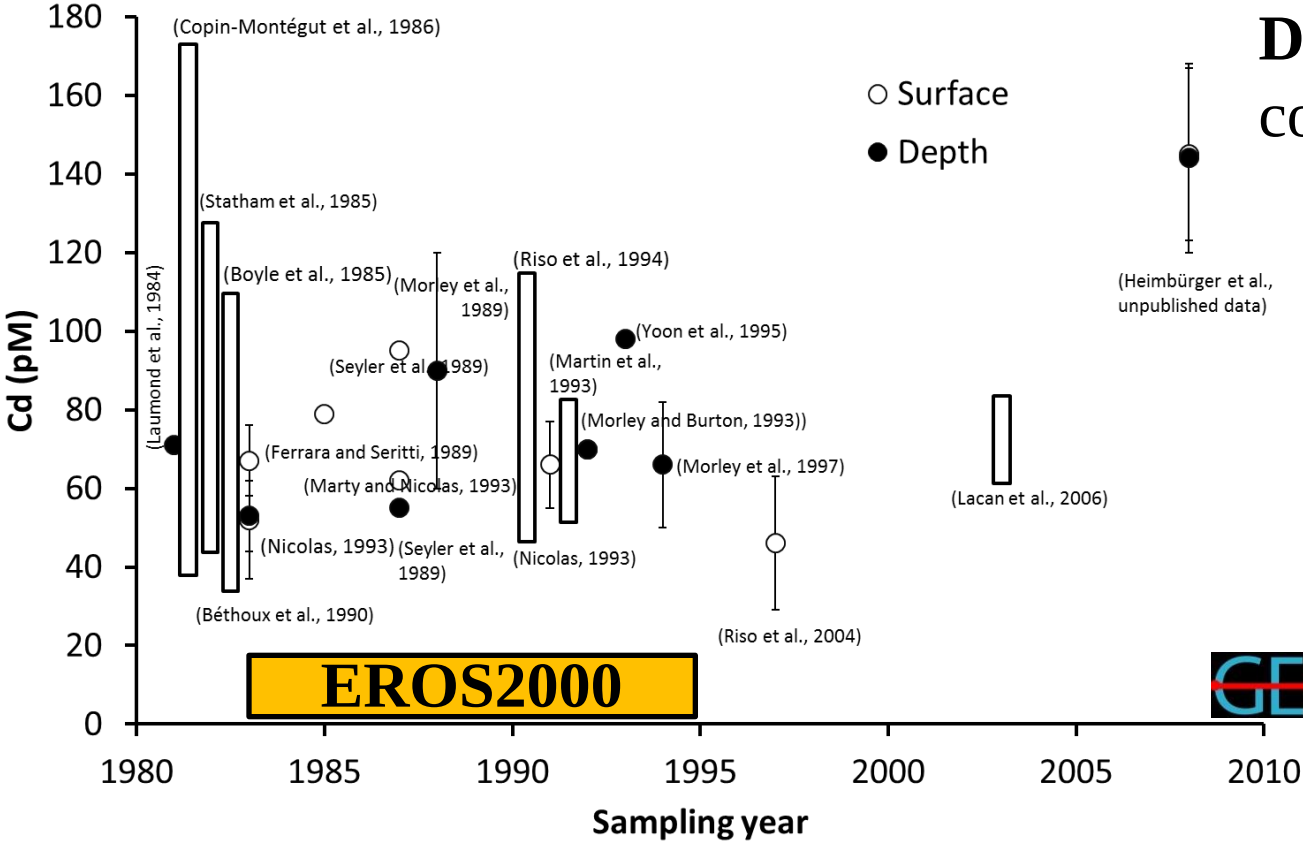
Cd aerosol
concentrations
(ng m^{-3})
(Heimbürger et al., 2010)

~66% decrease

Cd levels in the NWMED since EROS2000



Cd aerosol
~66% decrease



Dissolved Cd
concentrations (pM)

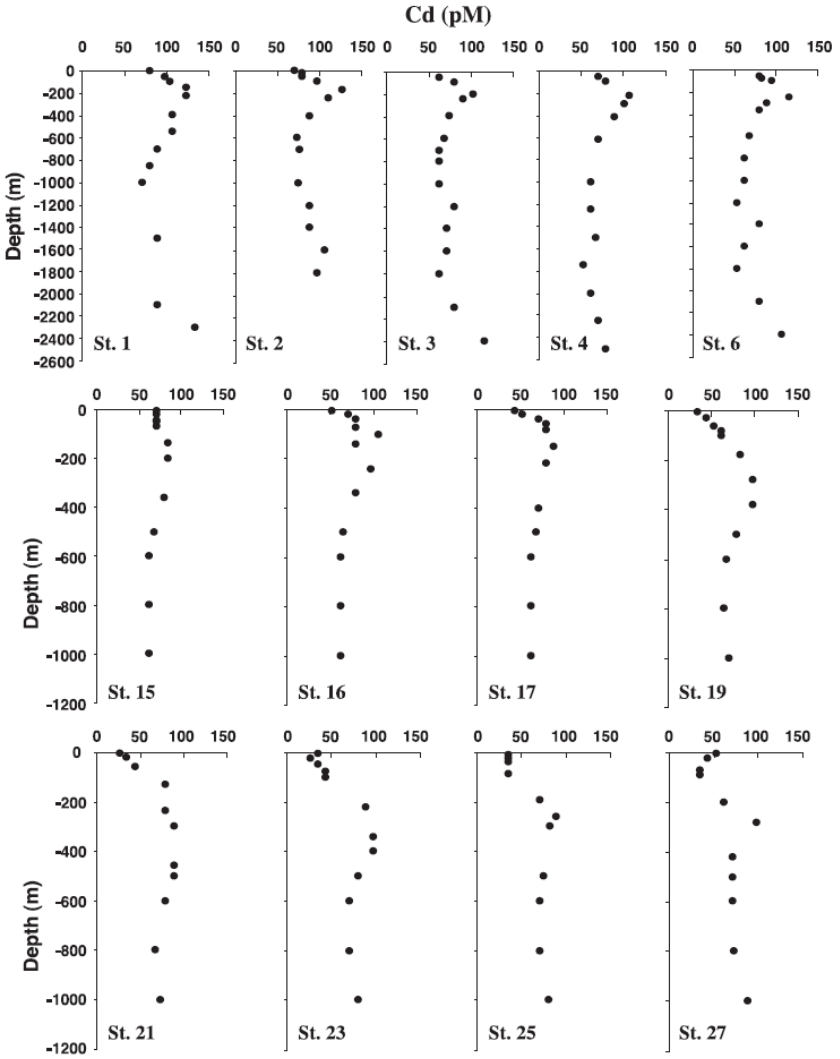
Atmospheric Cd decreased over the past 20 years (Heimbürger et al. 2010), but no oceanic response visible. On the contrary Cd levels seem to rise or at least remain steady.

GEOTRACES

Cd in the Western Mediterranean

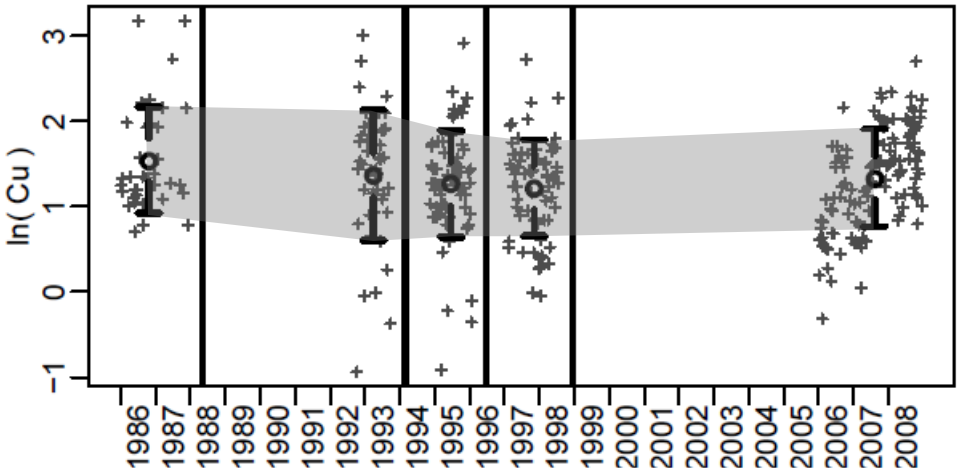
A subsurface Cd-rich layer, related to the presence of Winter Intermediate Water (WIW), was a prominent feature in the Alboran Sea. The WIW is formed in the northwestern coastal sector of the western Mediterranean Sea, and the high Cd concentrations in this water mass are therefore likely to be of coastal origin.

This example rises the influence of coastal waters and embayments.



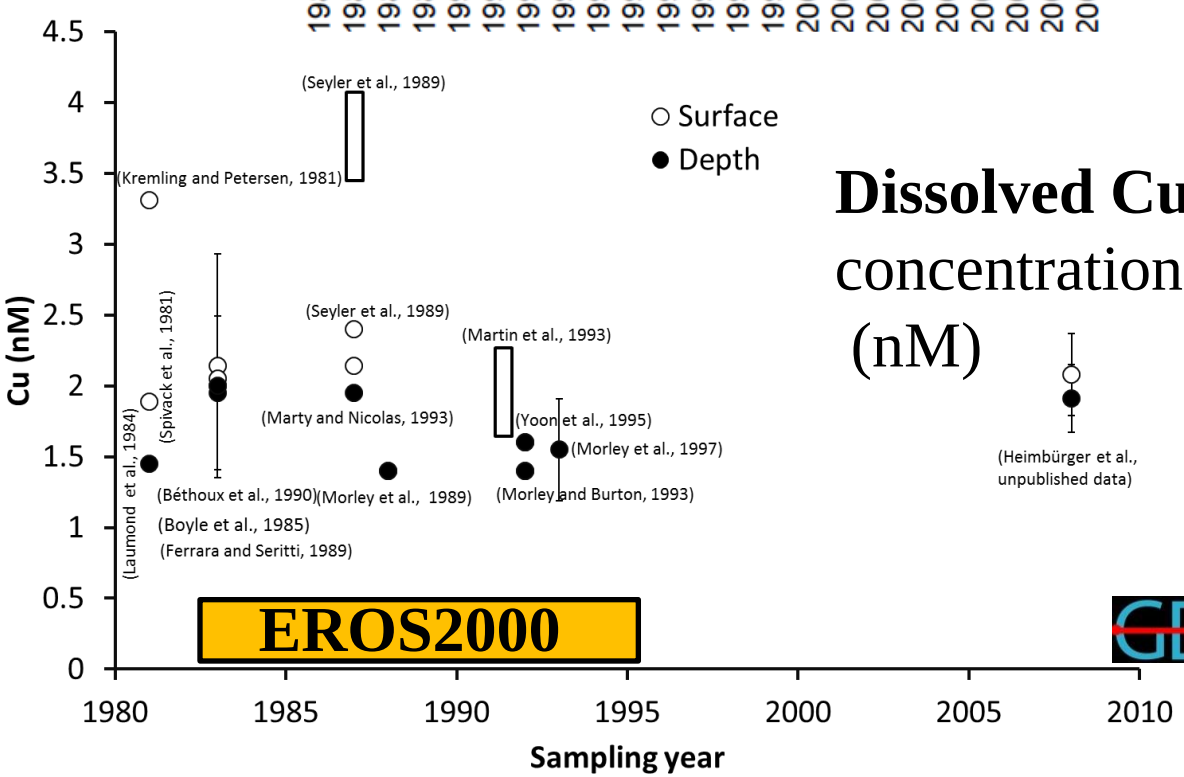
Riso et al., 2005

Cu levels in the NWMED since EROS-2000



Cu aerosol
concentrations (ng m^{-3})
(Heimbürger et al., 2010)

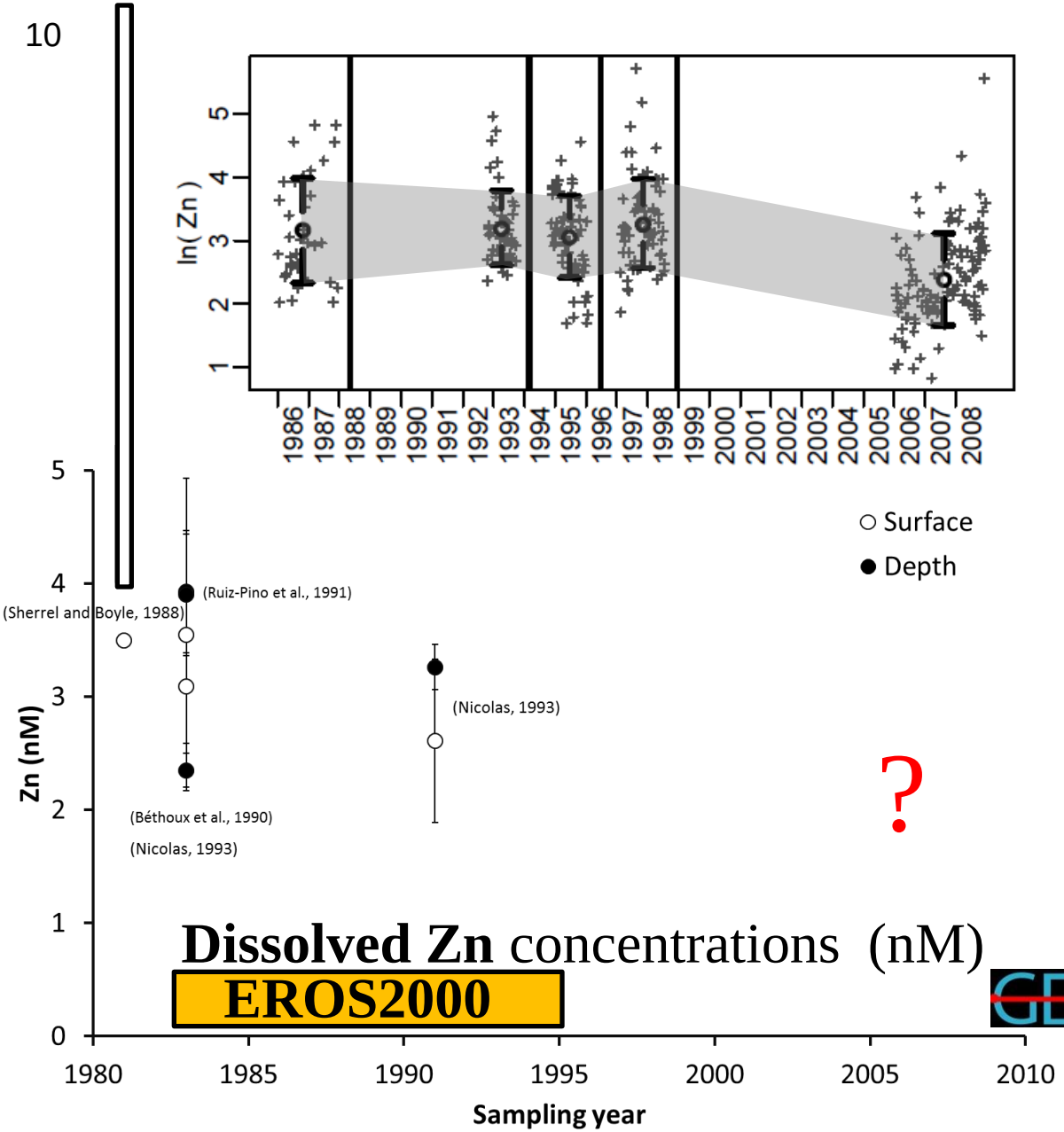
Cu levels seem to remain stable in the NWMED water as atmospheric concentration did. Close relation between Cu levels and phytoplankton presence. Few data in the eastern basin. Cu speciation needed.



Dissolved Cu
concentrations
(nM)

GEOTRACES

Zn levels in the NWMED since EROS2000



Dissolved Zn concentrations (nM)

EROS2000

Zn aerosol concentrations (ng m^{-3})
(Heimbürger et al., 2010)

~54% decrease

Zn measurements are particularly scarce, mainly due to contamination problems. Titanium rosette sampling systems are mandatory.

GEOTRACES

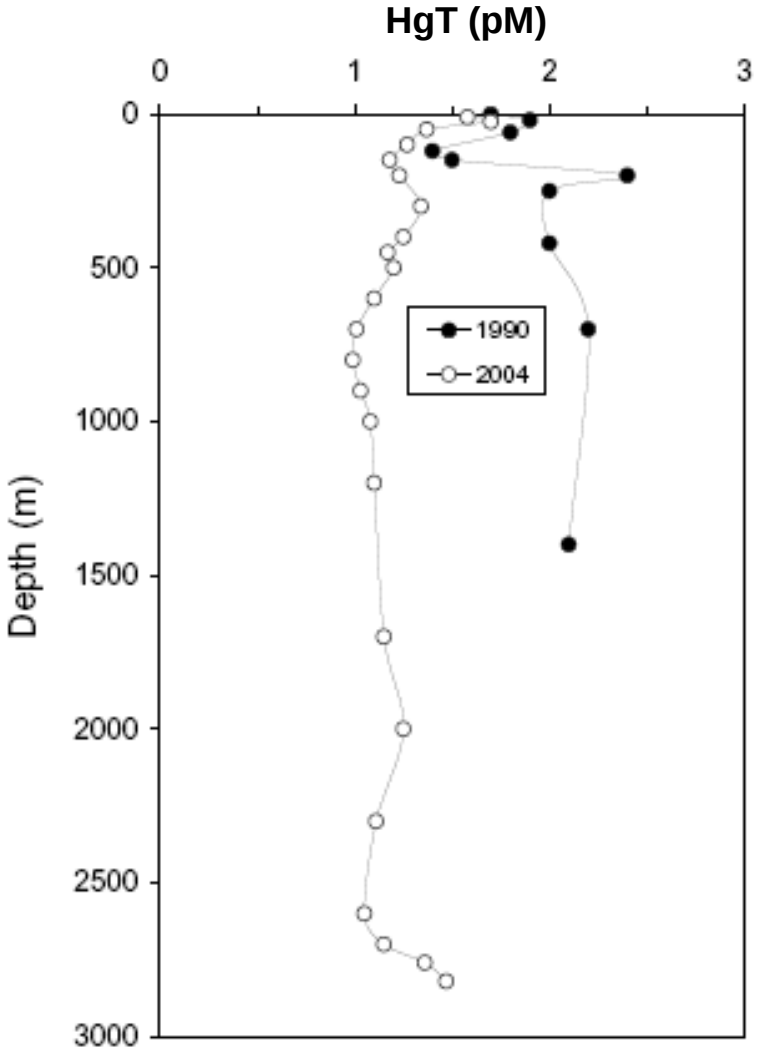
Cd, Cu & Zn key questions

- What are their distributions and sources in the Eastern Mediterranean basin?
- Have enriched Gibraltar inputs (Rio Tinto) changed?
- Is Cd recycled in the water column (Lacan et al., 2006)?
- What part of the total Cu&Zn is free ion form or organically-bound?
- How do Cu & Zn distribution profiles relate to the presence of phytoplankton? Seasonality and spatial variation?
- Are we able to measure Zn in the Med!?

Hg Northwestern Mediterranean case

Decrease in inventoried European atmospheric emissions of Hg

The [Hg] decrease observed between 1990 and 2004 in the intermediate waters of the Algerian basin may be related to the conjunction of a possible decrease of Hg deposition and the short residence time of waters in the basin

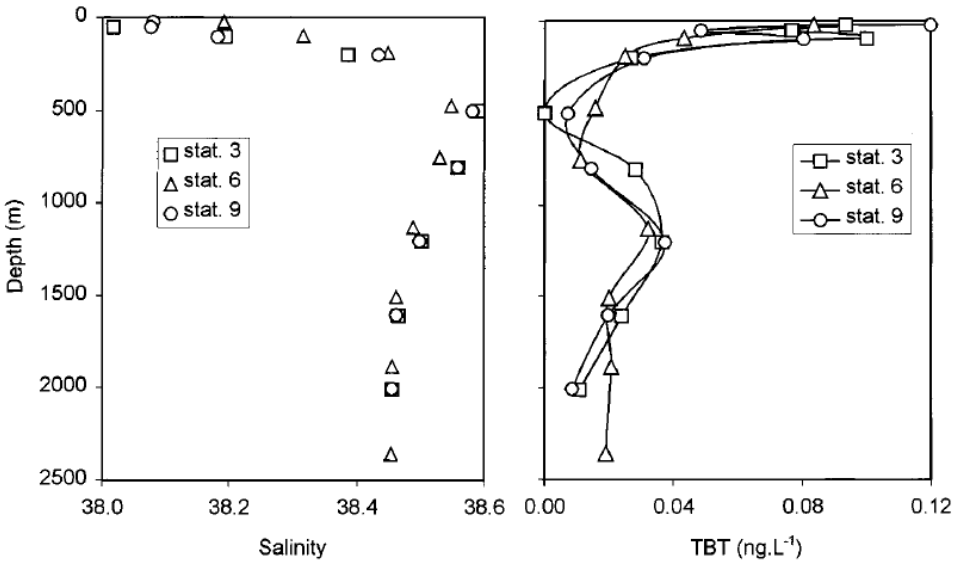


Adapted from Cossa et al. (1997) and Cossa and Coquery, (2005)

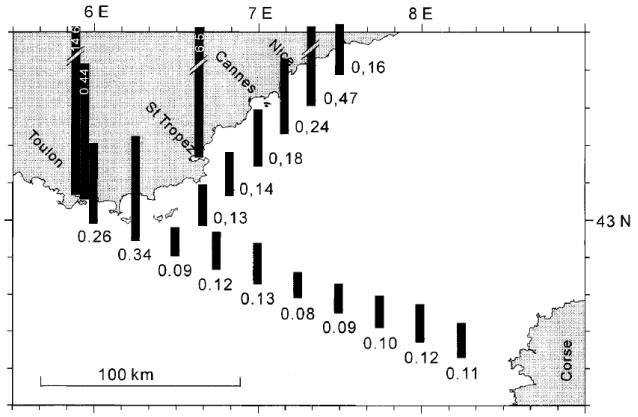
Key questions to be discussed on Wednesday

Organo-Sn in NWMed: 3 profiles only!

The presence of TBT in deep waters was attributed to the circulation of water masses during winter, while the vertical transport of particulate matter was considered to be of little importance. Contrary to results for coastal experiments, the half-life of TBT in this oligotrophic environment was estimated to be several years.



The ubiquity and persistence of TBT in these waters is a source of concern for environmentalists



Michel and Averty, 1999

Key Questions

- What is the anthropogenic fraction of TEs in the Med?
- What are the TE distribution in the Eastern Med today, where much anthropogenic changes are expected?
- Exchange at sills (Gibraltar, but also Red and Black Seas)?
- Inputs from rivers (Rhône, Po, but Nile, etc.),
- Inputs of urban effluents (exotic TE: Ag, Os / Marseilles, Napoli, Alexandria, Beyrouth, etc.), and maritime traffic
- TE deep export *via* dense water formation zones
- Impact of climate change on TE cycles (circulation, productivity, air-sea exchanges)
- TEI as tracers…….