



Long-term variability of nutrients, major elements and trace metals above the Mediterranean



Theodosi C.¹, Aubert D.², Becagli S.³, Desboeufs K.⁴, Dulac F.⁵, Francesc P.⁶, Herut B.⁷, Kocak M.⁸, Remoundaki E.⁹, Mihalopoulos N.^{1, 10 *}

(1) Dep. of Chemistry, University of Crete, Heraklion, Greece, (2) CEFREM, University of Perpignan Via Domitia-CNRS, Perpignan, France, (3) Dep. of Chemistry, University of Florence, Sesto Fiorentino, Italy, (4) IPSL-LISA, UPEC-CNRS, Créteil, France, (5) IPSL-LSCE, CEA-CNRS-UVSQ, Gif-sur-Yvette, France, (6) Institut de Ciències del Mar, CMIMA (CSIC), Barcelona, Spain, (7) IOLR, National Institute of Oceanography, Haifa, Israel, (8) Institute of Marine Sciences, Middle East Technical University, Erdemli-Mersin, Turkey, (9) Laboratory of Environmental Science and Engineering, School of Mining and Metallurgical Engineering, National Technical University of Athens, (10) Institute for Environmental Research and Sustainable

Development (IERSD), NOA, Athens, Greece

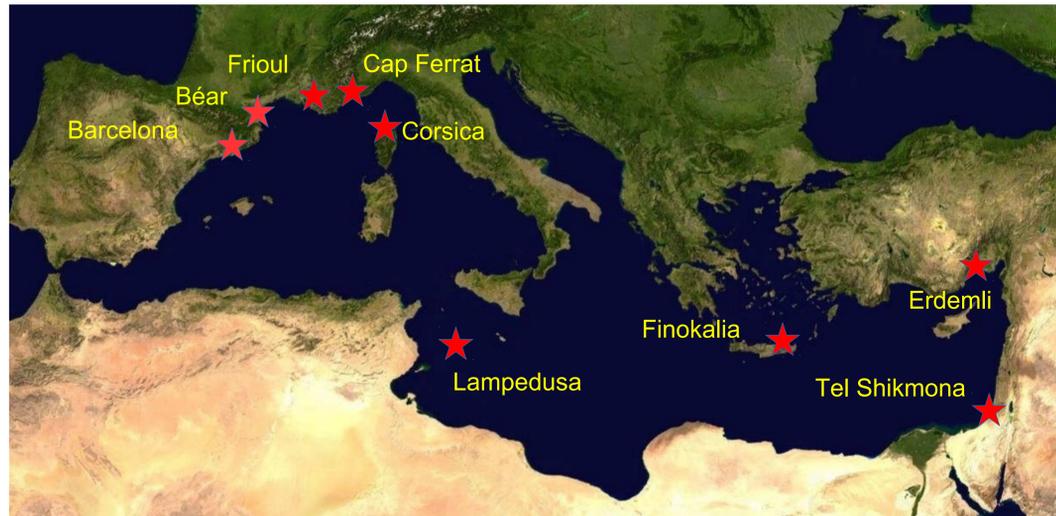
*corresponding author e-mail: mihalo@chemistry.uoc.gr

INTRODUCTION

The spatial and temporal variability of nutrients, major elements and trace metals in both western and eastern basins of the Mediterranean Sea was investigated in the framework of TRACOMED (TTransfer of Atmospheric Contaminants to the MEDiterranean Sea) under the coordination of ENVIMED program and supported by MISTRALS in both ChArMEx and MERMEX projects.

EXPERIMENTAL

Historical data sets on major elements and trace metals (Al, V, Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb) and essential nutrients (N, P) across the Mediterranean monitored over the last three decades (1985-2015) were collected and thoroughly analysed. The 9 stations studied were located in France, Greece, Italy, Israel, Spain and Turkey. We present here the most representative results over the period.



AIM OF THE STUDY

In the present study the chemical composition of both nutrients and pollutants have been studied at different geographical and temporal scales in order to evidence climatic and anthropogenic changes.

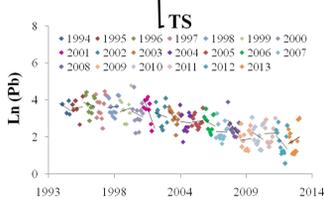
Measurement period: 1985-2015
9 stations => data representative of the open Mediterranean Sea

DECADAL TRENDS

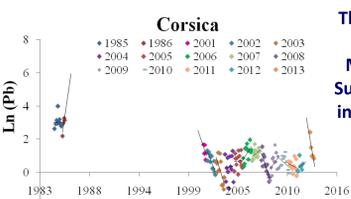
Pb, Ni, V, Al concentrations in aerosol decreased remarkably over the last 30 years

Based on emission factors, Pirrone et al. (1999) predicted for the Mediterranean during 1985-2010: Pb (-67%), Cd (-6%)
Cd aerosol concentration at FKL and CORS remained stable over the past 30yrs, whilst a significant decrease in TS is observed
Saharan dust events traced by Al decreased in the Mediterranean, as predicted by Mahowald and Luo (2003)

ng m ⁻³	Pb	Cd	Ni	V	Al
FKL (2001)	13.0	0.24	7.2	5.1	682
FKL (2014)	10.2	0.25	3.7	3.0	371
% dif	-21	4	-49	-42	-41
CORS (2001)	3.8	0.10	1.3	2.7	74
CORS (2012)	1.5	0.10	0.7	1.2	56
% dif	-60	1	-45	-55	-25
TS (1994)	36.8	0.39			1489
TS (2013)	7.9	0.17			1331
% dif	-79	-55			-11

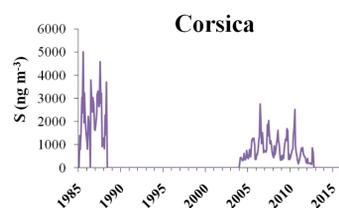


Interannual and decadal trends of Pb in Tel Shikmona and Corsica aerosols (ng m⁻³) during 1985-2013.



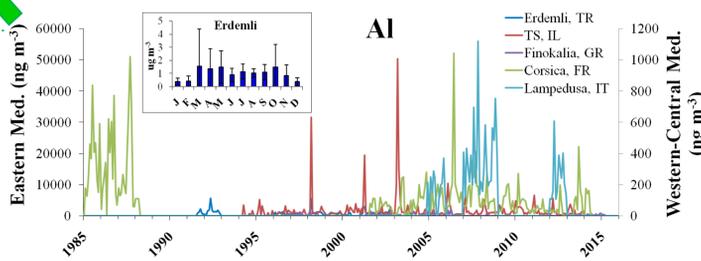
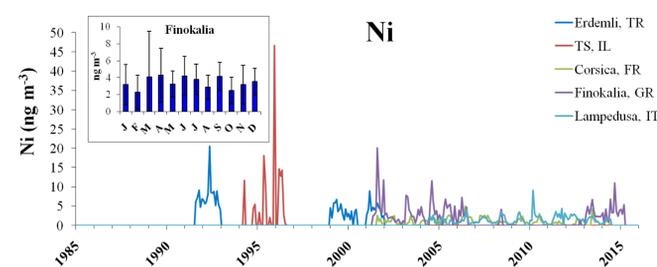
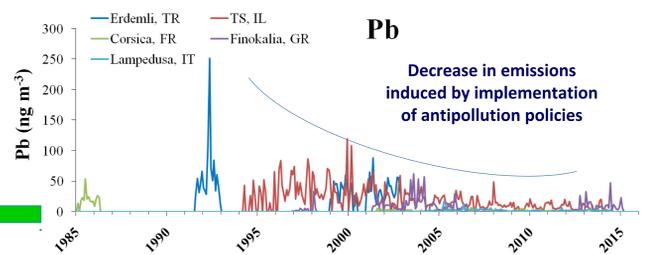
The same decrease over time is valid in the Western Mediterranean, in the case of Sulphur (S) a dominant element in the exhausts of heavy fuel oil combustion.

S concentrations remained constant from 1985-1988. A sharp decrease of 66% was observed in 2004-2012, down to 0.8 μg m⁻³.



SEASONAL VARIABILITY

Trace metals according to the nature of their emission sources present pronounced seasonal patterns.



Anthropogenic trace metals (Ni, V, Cu, Zn, Cd and Pb,) did not show a clear seasonal pattern, with relatively higher concentrations in winter, in agreement with transport of northern polluted air masses from Europe.

Comparison of aerosol concentrations regarding their origin (anthropogenic vs crustal) in the Mediterranean suggested that the Eastern basin receives higher inputs than the Western (at least 5 times for pollutants and up to 13 for Al).

POLLUTANTS

Shipping vs industrial emissions

The V/Ni ratio might give insights on the sources associated with oil combustion, discriminating between shipping and industrial emissions: industry: 2.1-3.1/shipping: 0.9-1.9 (Pandolfi et al., 2010).

Average	V/Ni	Pb/Cd
Erdemli	1.4	268
Tel-Shikmona	-	103
Finokalia	1.7	87
Lampedusa	2.3	44
Corsica	2.3	43

Anthropogenic European emissions

Remote continental aerosol

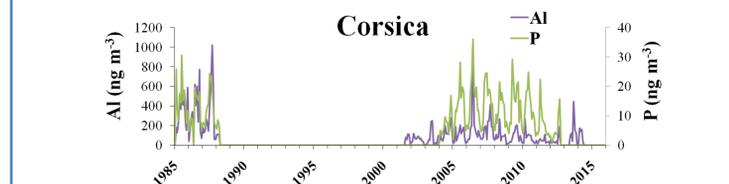
In our study, the Pb/Cd ratios are far lower than the expected value for gasoline combustion aerosols (2300). This ratio rather express a mix between several sources such as remote continental aerosol (64), anthropogenic European emissions (46), and to a lesser extent non-ferrous metal production (5-15) and marine production (26) (Dulac et al., 1987).

NUTRIENTS

IP fluxes (mmol m⁻² yr⁻²) in wet deposition samples at TS tend to decrease slightly throughout the years, with the exception of an extreme peak during 2002/2003, concomitant with precipitation, as local precipitation could strongly influence atmospheric P fluxes.

On the contrary, IN fluxes in the same area in the Eastern Mediterranean remained more or less stable over the past 2 decades.

Moreover, P in the Western Mediterranean exhibited a decrease as previously noticed in the Eastern Mediterranean.



CONCLUSIONS

- On the basis of time-series data of atmospheric aerosol acquired at 9 stations across the Mediterranean over a period of approximately thirty years for the most documented, the present work attempts to study the seasonal behavior and decadal trends of a series of pollutants and nutrients in the Mediterranean Sea.

- Despite the on-going industrialization of Europe, an actual decrease of anthropogenic pollutants in the atmosphere over the Mediterranean is observed due to the implementation of antipollution policies.
- Both pollutant and nutrient (Pb, V, Ni, S, P) concentrations decreased over the last 30yr. Only Cd levels remained relatively constant.

- Especially regarding Pb, the implementation of the antipollution policy on automotive lead in the second half of the 1980s has resulted in the rapid removal of lead in Mediterranean atmosphere by up to 70%.
- Pollutants that largely affect the Mediterranean can be classified as most likely industrial and from shipping emissions.

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