Atmospheric input of organic matter to the surface ocean: composition, fluxes and fate in the water column

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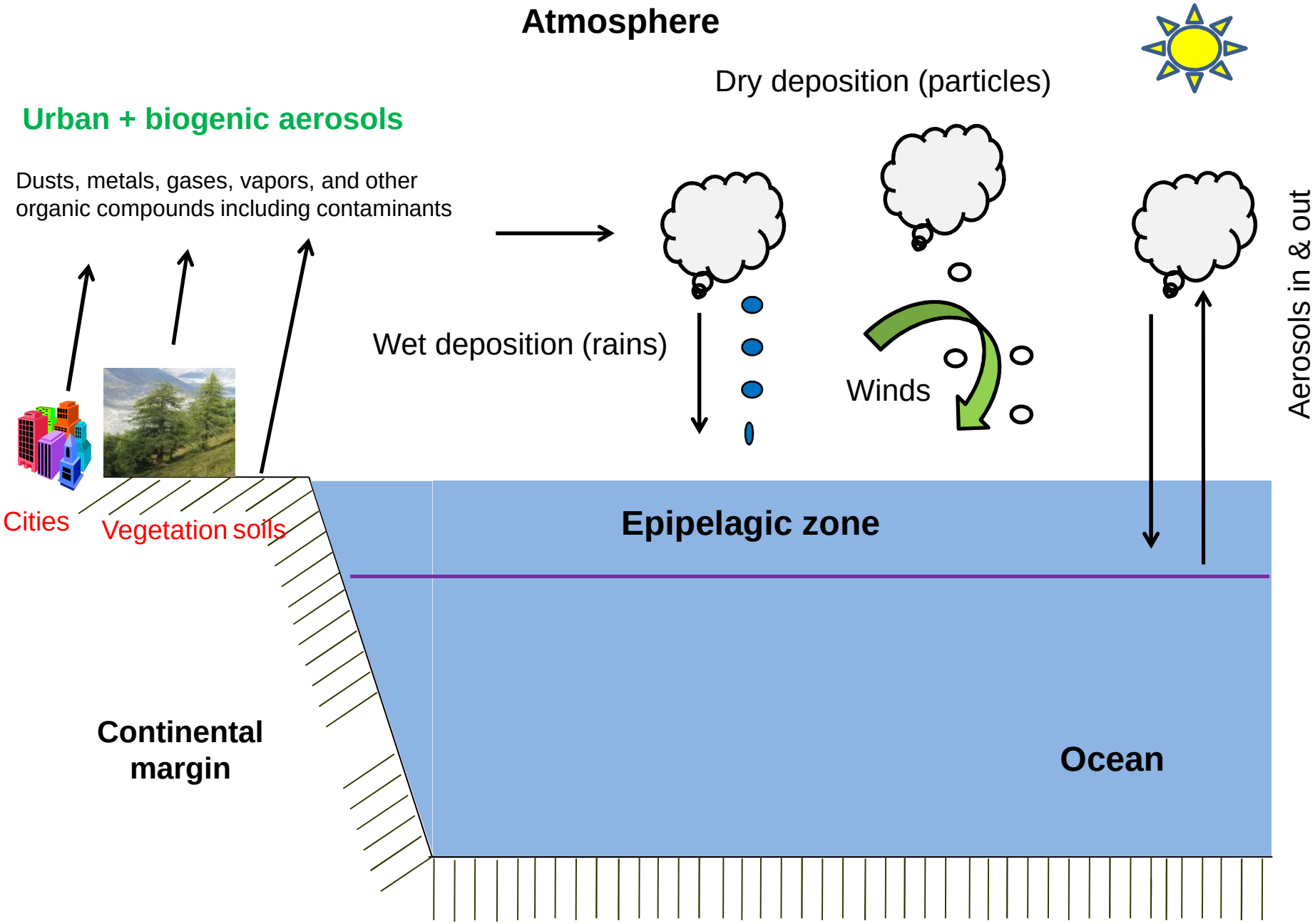
Axe DEBAT , tache 3 : Sources et dégradation de la MO dans les aérosols marins
Resp. J. Piazzola

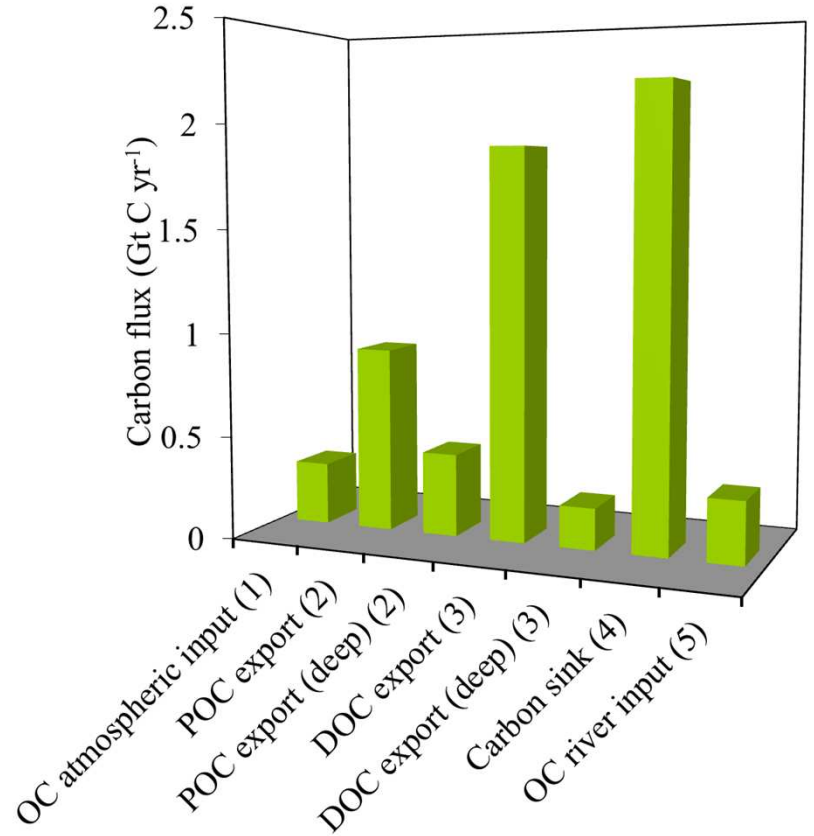
DEBAT meeting 18/11/13


Atmosphere
Dry deposition (particles)
Urban + biogenic aerosols
Dusts, metals, gases, vapors, and other
organic compounds including contaminants
Wet deposition (rains)
Winds
Aerosols in & out
Cities
Vegetation soils
Epipelagic zone
Continental
margin
Ocean

Global C-fluxes estimates

At the global scale, estimations of atmospheric input of organic carbon fall within the main C fluxes included in global biogeochemical models

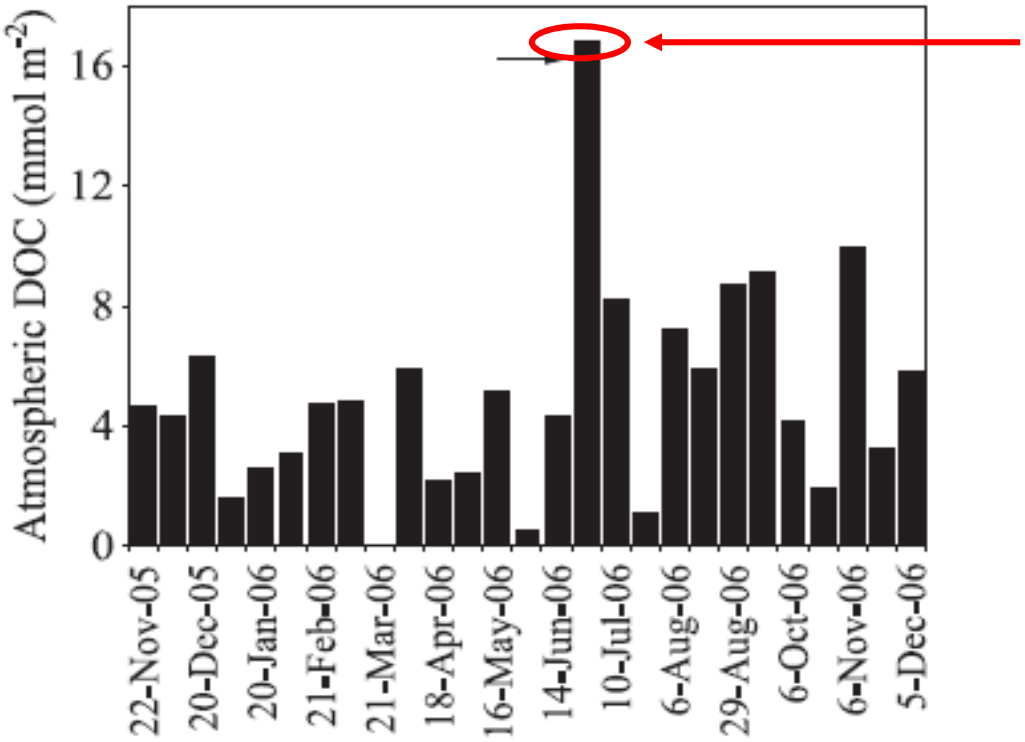
In the Mediterranean Sea, atmospheric input of organic carbon might be higher than riverine input



De Leeuw et al. (2013) In Liss and Johnson (Eds.)
« Ocean-Atmosphere interactions of particles and gases »,
Springer (in press).

Sources of aerosol-derived organic matter in the MedSea: mainly anthropogenic but Saharan influence not to be neglected

Total deposition of DOC at Cap Ferrat site (NW MedSea) during 2006 (Pulido-Villena et al. 2008)



Évènement saharien (2.5 g m^{-2}) juin 2006

Particular interest in exploring the organic fraction of atmospheric deposition during Saharan dust events

OUTLINE

1. State of the art on aerosols with focus on organic fraction

2. Project presentation (objectives, site sampling etc)

3. Suggestions / open discussion

Bulk characteristics of aerosols

Coarse particles (1,3-10 µm); OC content = 0,015-8,3 µg/m-3 ; C/N ~ 10
Fine particles (<1,3 µm); OC content = 0,109-9,5 µg/m-3; C/N ~ 11

Metals: **Ca**, Ti, V, Cr, Mn, **Fe**, Ni, Cu, Zn, Cd, Pd

Ca, Fe most abundant with higher concentrations in coarse particles. Site Eastern Med. Sea (Finokalia station). Data from Koulouri et al. (2008); Violaki 2008 (Ph.D)

P during sahara dust events

E. Med. 4-6 µmol org. P/ g & 13-20% of total P
W. Med. 7 µmol org. P/g & 38% of total P (Carbo et al., 2005)

Dissolved organic carbon in rains

~100 µMC (Eastern Med. Sea; Economou and Mihalopoulos 2002)

Organics found in aerosols

A. Dicarboxylic acids, ketoacids, aldeydes, lipids, hydrocarbons, phthalates, biogenic comp. (isoprene products, pinene etc)

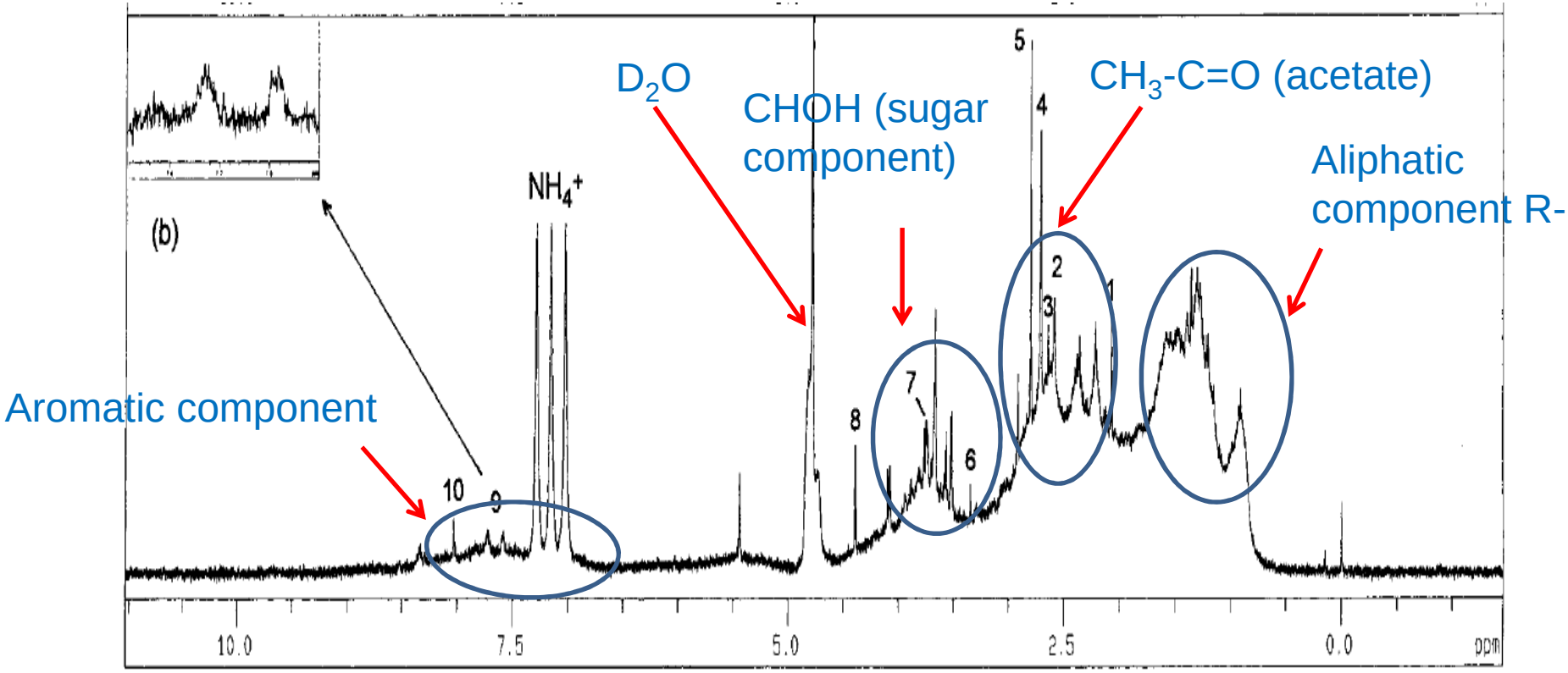
B. PAH (polyaromatic hydrocarbons), black Carbon

C. Nitrogen compounds (amino acids, urea, amines)

D. Phosphorous compounds (flame retardants, phospholipids, ATP, insecticides)

E. Sugars (alditols, anhydrosugars)

Chemical composition of aerosols by wet ^{1}H NMR



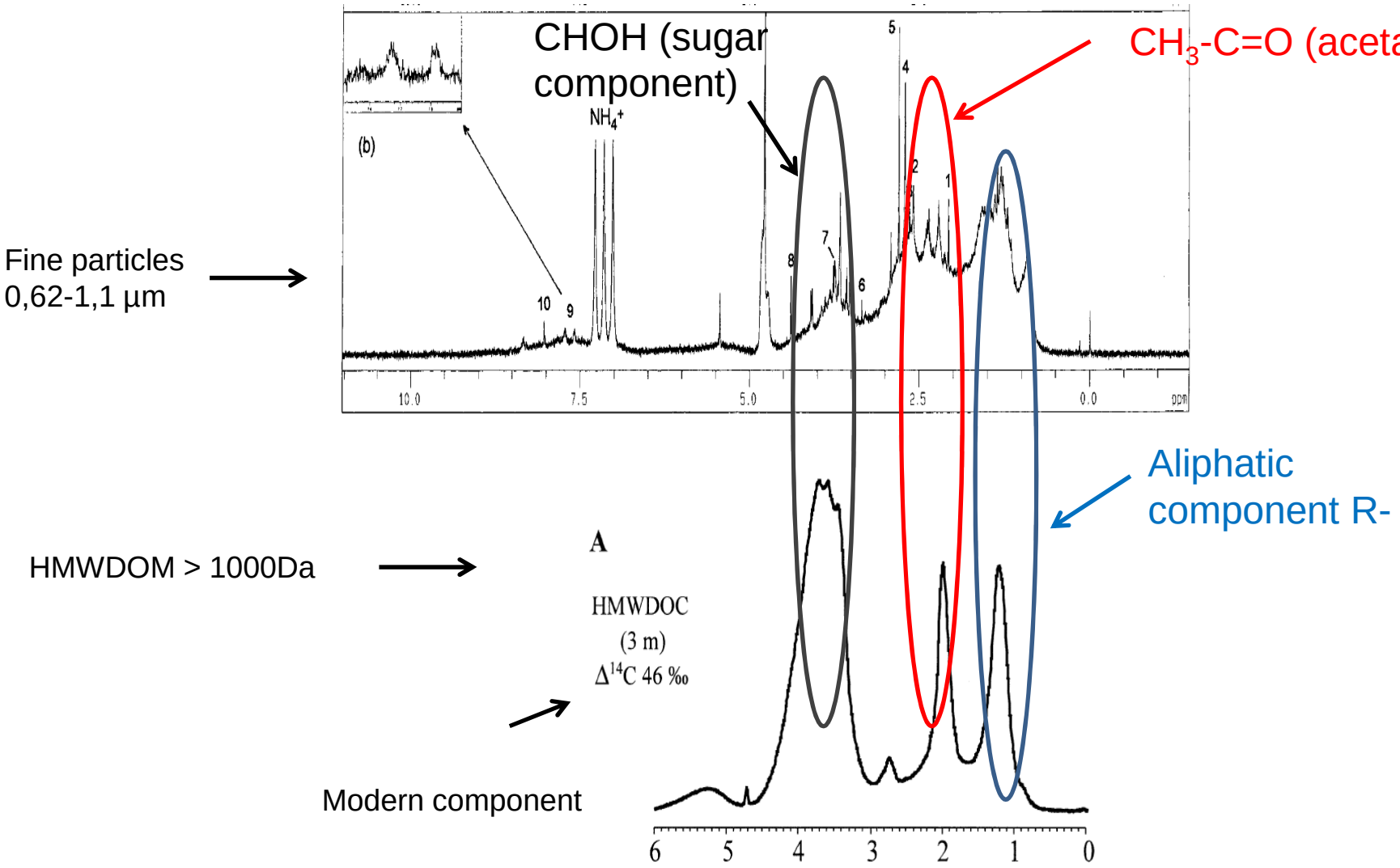
NMR spectra of fine particles 0,62-1,1 µm

(Kobe city Town ~ 1 Km of the Osaka bay)

Identified compounds : Acetic acid, mono- di- tri- methyl amines, methanol, formic acid, methanesulfonic acid Mannitol, phthalic acid, terephthalic acid, succinic acid

Suzuki et al. 2001 (Environ. Sci. Technol.)

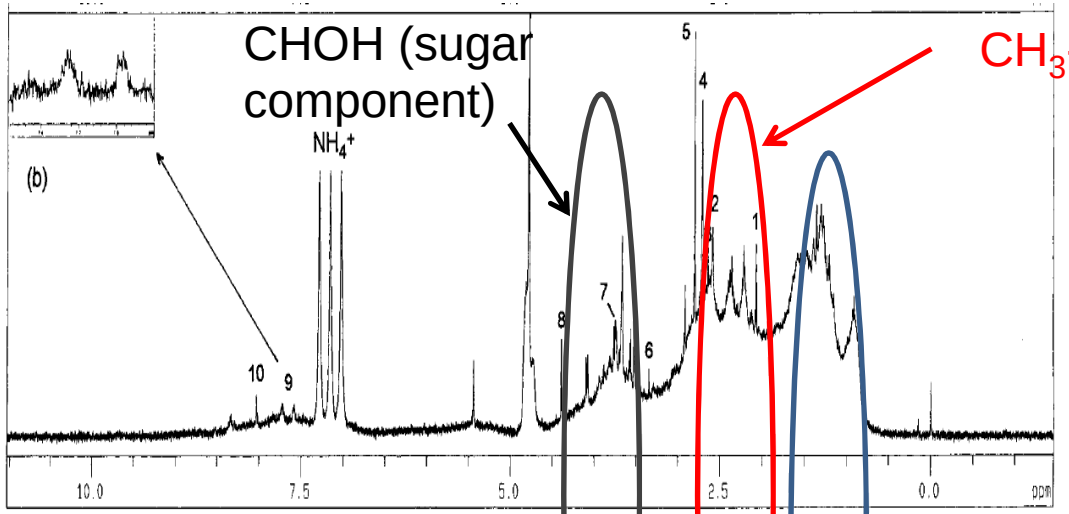
Comparison of aerosols and HMWDOM by ^{1}H NMR



HMWDOM = High molecular weight dissolved organic matter

Repeta and Aluwihare (2006)

Comparison of aerosols and HMWDOM by ^{1}H NMR

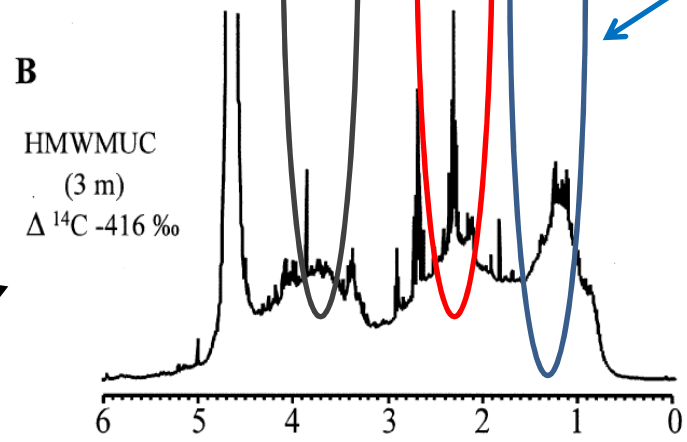


CH_3-C=O (acetate)

Fine particles
0,62-1,1 µm

Aliphatic component R-

HMWDOM > 1000Da

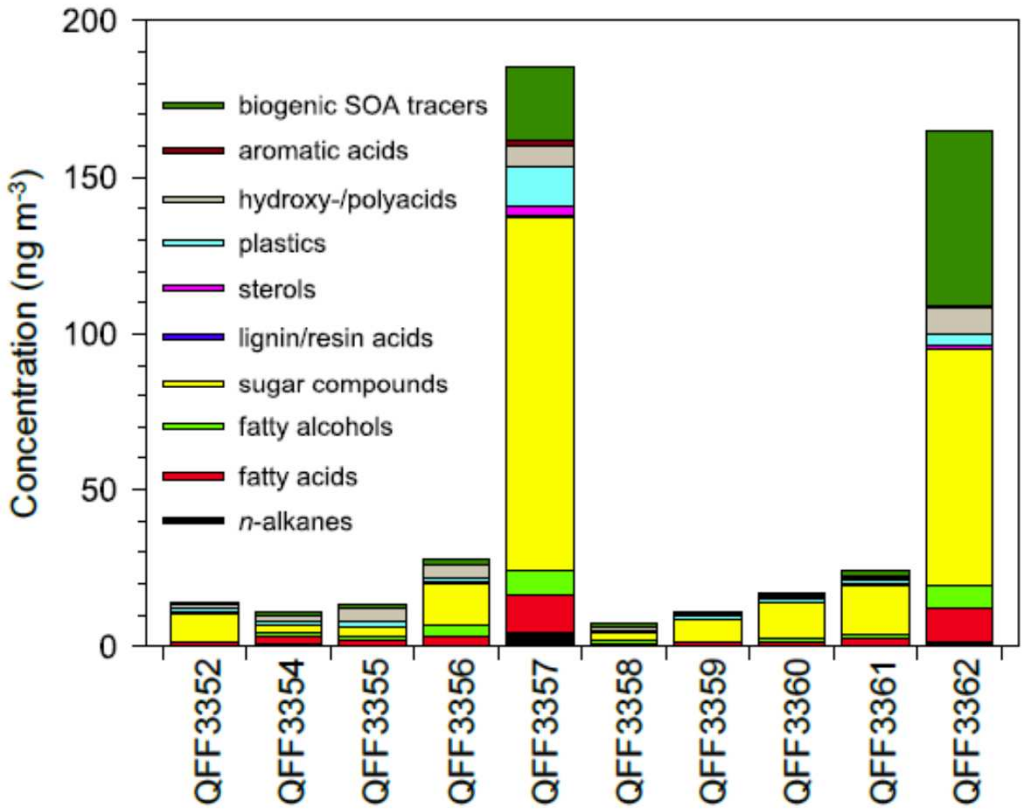


old component of the HMWDOM
In the surface (age = 4320 y)

Repeta and Aluwihare (2006)

HMWDOM = High molecular weight dissolved organic matter

Chemical composition of aerosols by wet chemistry (GC-MS)



Beaufort Sea, Arctic Ocean

Fu et al. 2012 *Biogeosciences*

Sugars= Anhydrosugars, Mannitol, arabitol, fructose, sucrose, glucose

Lipids = n-alkanes, fatty acids, fatty alcohols, sterols

Biogenic SOA tracers = monomethylated tetrols, isoprene products

→ Lots of sugars

What we know about the isotopic composition of aerosols

Very very few studies

Sahara dust :

OC content 1,2% dry weight

Bulk Organic carbon: $\Delta^{14}C = 1260 \pm 40$ y ; $\delta^{13}C = -18.9$ ‰

Black carbon: $\Delta^{14}C = 2070 \pm 40$ y; $\delta^{13}C = -15.1$ ‰

→ C4 vegetation accumulated in soils over the late Holocene

Marine $\delta^{13}C$ -21 – -23 ‰

Terrestrial $\delta^{13}C$

C3 plants -27 ‰

C4 plants -15 ‰

n-alkanes (C_{23-33}), n-alkanols (C_{22-32}), n-alkanoic acids (C_{22-32}) ; with $\delta^{13}C$ values ranging from -22.6 ‰ to -30 ‰

Eglinton et al., 2002 *G3*

→ **Mixture of C3 , C4 vegetation**

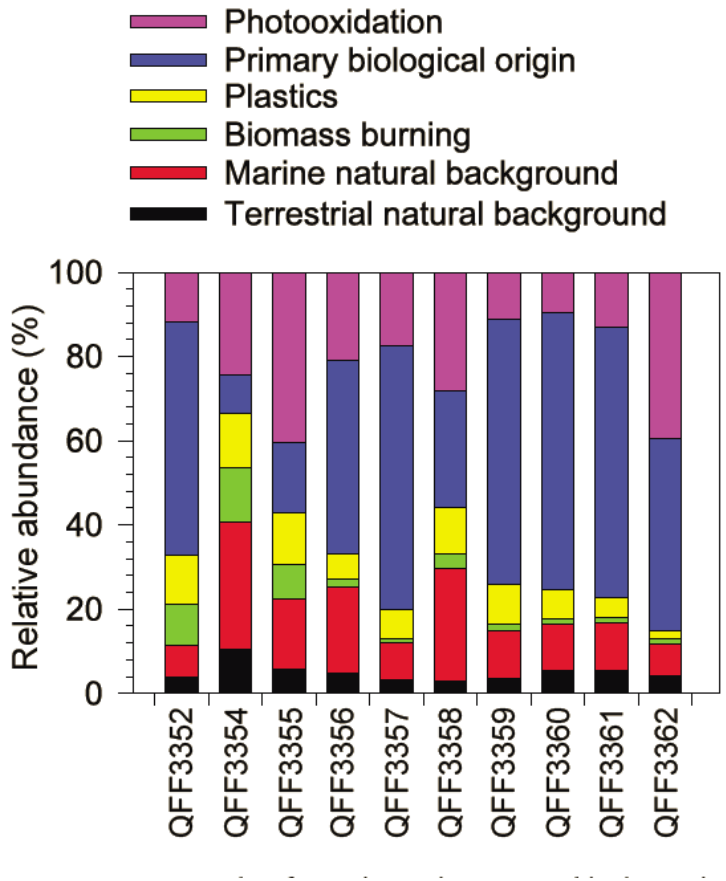
Urban aerosols:

Odd n-alkanes (C_{25-33})
Even n-alkanes (C_{26-32})
n-alkanes (C_{21-24})

$\delta^{13}C$ = - 27 to - 30 ‰

Yamamoto and Kawamura, 2010
(Geochemical Journal)

Example of Sources in aerosols



Beaufort Sea, Arctic Ocean

Fu et al. 2012 *Biogeosciences*

Photooxidation= Biogenic SOA tracers, aromatic acids, LMW carboxylic acids

Primary biological origin = sugars, ergosterol

Biomass burning = Anhydrosugars, β–sitosterol, 4-hydroxybenzoic acid, lignin **+ Black carbon**

Marine natural background = LMW fatty acids + alcohols, cholesterol

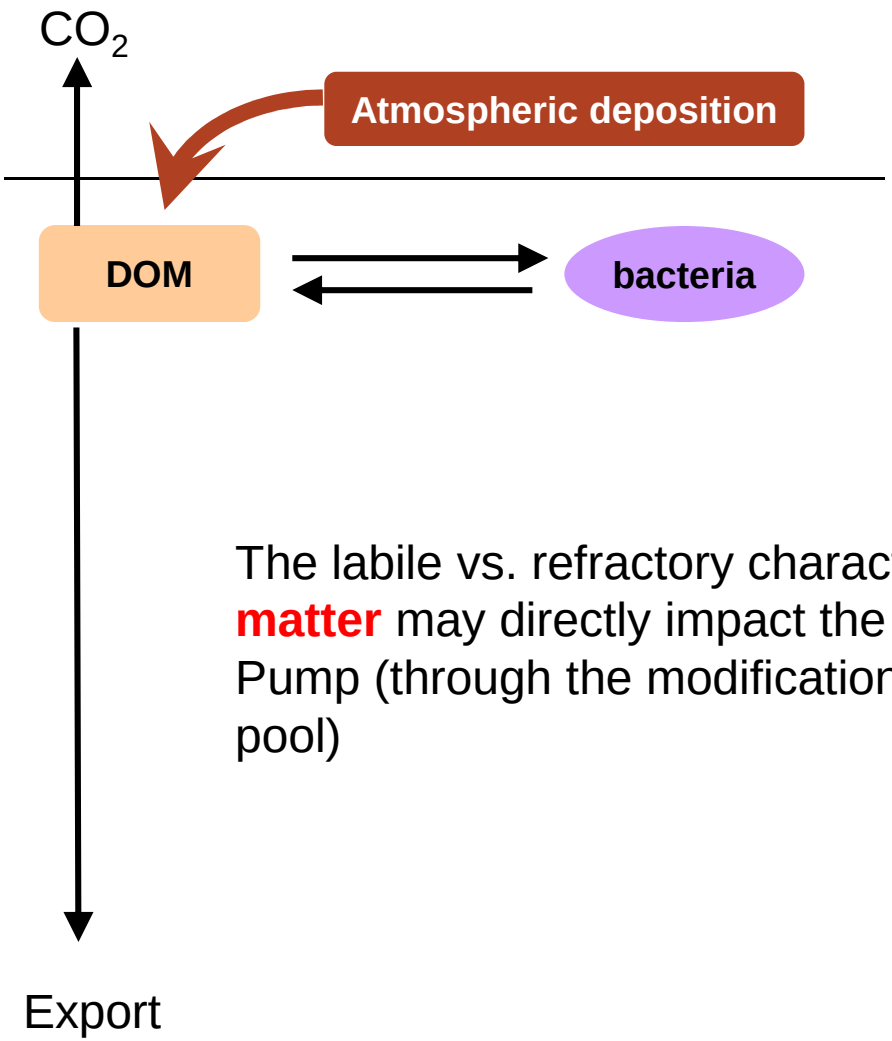
Terrestrial natural background = wax n-alkanes, HMW fatty acids + alcohols

Project research interest

First gap: lack of knowledge on the composition and degradability of atmospheric ORGANIC MATTER (OM) in surface waters

Second gap: scarcity of data on atmospheric fluxes of OM particularly under Saharan dust events

Impact of atmospheric deposition of OM on surface DOM cycling



Biological impact of atmospheric deposition traditionally focused on phytoplankton

Few studies on the response of heterotrophic bacteria (Pulido-Villena et al. 2008, Maranon et al. 2010)

The labile vs. refractory characteristics of **atmospheric organic matter** may directly impact the efficiency of the Microbial Carbon Pump (through the modification of the residence time of surface DOM pool)

Project Presentation

- Quantify and characterise atmospheric organic matter fluxes
  → Observation task

- Assess abiotic and biotic degradation upon contact with the surface waters
  → Experimentation task

- Include obtained fluxes and parameterisation of processes in atmospheric and marine biogeochemical models
  → Modelling task

Project Presentation

Objectives :

1. Understand the fate of land-derived aerosols (dusts, urban aerosols etc) in surface seawater from a chemical perspective (degradation, dissolution, contamination etc)

2. Follow the degradation/assimilation of specific atmospheric organic compounds/contaminants in the upper water column.

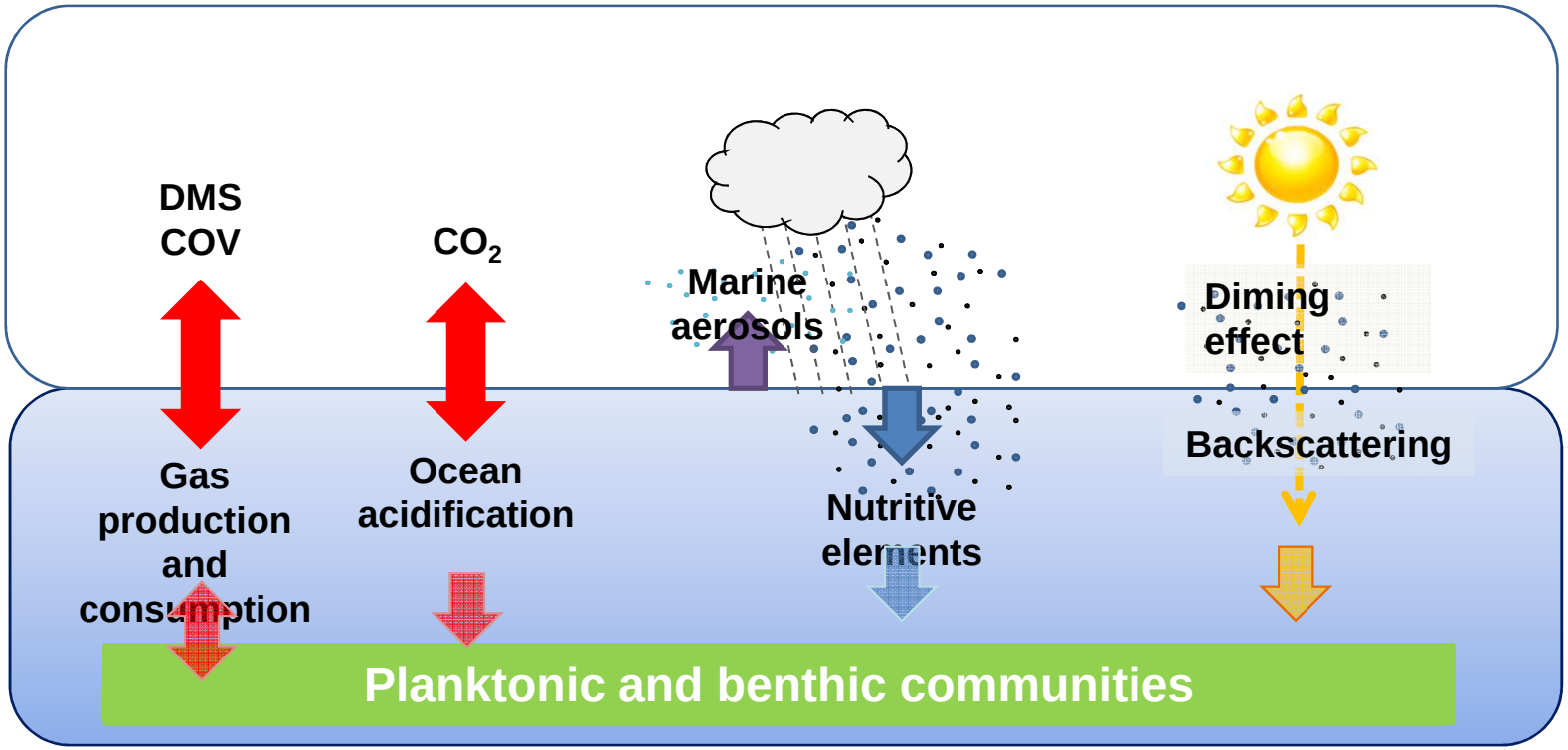
3. Provide data values (concentrations) of organics found in both atmosphere and seawater to feed biogeochemical models and **obtain fluxes for individual compounds**

Study sampling

1. Finokalia (Crete)
2. Earsa Cap (Corse)
3. Frioul (Marseille)
4. Cap Bear (Perpignan)

MERMEX-WP4: Natural and anthropogenic air-sea interactions

WP leaders: K. Desboeufs (LISA), M. Mallet (LA) and E. Pulido-Villena (MIO)



To assess the interactions between the atmosphere and the Mediterranean Sea in terms of gases, particles, nutrients and radiative exchange → Impact on ecosystem functioning

ChArMEx

Chemistry-Aerosol Mediterranean Experiment

WP5 Deposition

Atmospheric deposition of compounds of biogeochemical interest into the Mediterranean Sea

WP Leaders: Karine Desboeufs (LISA), Elvira Pulido-Vilena (MIO)

Partners : LISA ; LOV; MIO ; LPCA; GEOSYSTEMES ; LSCE ; CEREGE ; COM; LSEET; Ecole des Mines de Douai ; IRSN; LECOB

+ IDAEA (Spain), IMEDEA (Spain), ENEA (Italy)

MISTRALS