



IL CONSORZIO TRA OFFERTA E RICHIESTA DI RICERCA: ANALISI E PROSPETTIVE DI MERCATO

III Convegno Nazionale CINFAI
Rovereto, 14 – 15 ottobre 2015

Nome Università

Caratterizzazione dell'aerosol atmosferico in aree a differente grado di antropizzazione

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Firenze

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Composizione UdR UniFI

Dip. Chimica

Roberto Udisti - Prof. Ass.
Rita Traversi - Ric. Conf.
Silvia Becagli - Laur. Tecn.
Mirko Severi - Assegnista
Daniele Frosini - Dottorando
Miriam Marconi - Dottoranda
Laura Caiazzo - Dottoranda
Fabio Giardi - Dottorando
Federica Bellandi - Borsista
Costanza Scopetani - Borsista

Dip. Fisica - INFN

Franco Lucarelli - Prof. Ass.
Silvia Nava - Ric. INFN
Massimo Chiari - Ric. INFN
Giulia Calzolai - Assegnista
Martina Giannoni - Borsista

6 Strutturati
4 Dottorandi
5 Assegnisti/Borsisti

Sintesi attivita' scientifiche UdR UniFI

- Caratterizzazione chimica di campioni di interesse climatico, ambientale, alimentare, tecnologico e biochimico in matrici complesse (atmosfera, acque, sedimenti, suoli, alimenti, materiali, tessuti biologici).
- Studio delle interazioni tra processi climatici e ambientali per il presente e nel passato (analisi chimica e isotopica di carote di ghiaccio e di sedimenti marini in Antartide).
- Studio dei processi di origine e trasporto di componenti chimici immessi nell'atmosfera da processi naturali o antropici nel Bacino del Mediterraneo e in aree polari (Artide e Antartide).
- Valutazioni di impatto ambientale e di qualita' dell'aria e dell'ambiente.

Strumentazione ed Attrezzature UdR UniFI



Cromatografia Ionica



ICP-AES / ICP-HR-MS
Integrated System

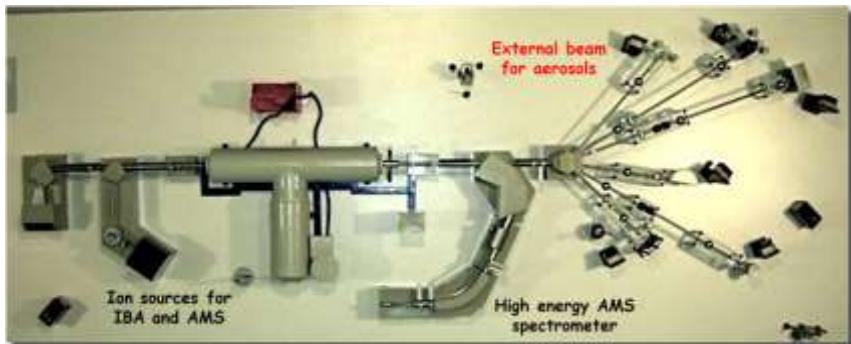


EC-OC Termo-Optical
Analyser



SEM-EDX Analysis

Strumentazione ed attrezzature UdR UniFI



INFN-3 MV Tandetron Accelerator
PIXE - Particle Ind. x-ray Emiss.
PIGE - Particle Ind. γ -ray Em.
 ^{14}C Determination



Sistemi campionamento



Gas Analysis



Classificatori di particolato

Caratterizzazione Chimica Aerosol Urbano

- Identificazione delle principali fonti emissive del particolato atmosferico (PMx);
- Determinazione nel PMx dei livelli di elementi le cui concentrazioni atmosferiche sono regolate dalle norme sulla qualita' dell'aria (IPA, Metalli pesanti)
- Valutazione degli effetti delle condizioni meteorologiche sulla concentrazione del PMx

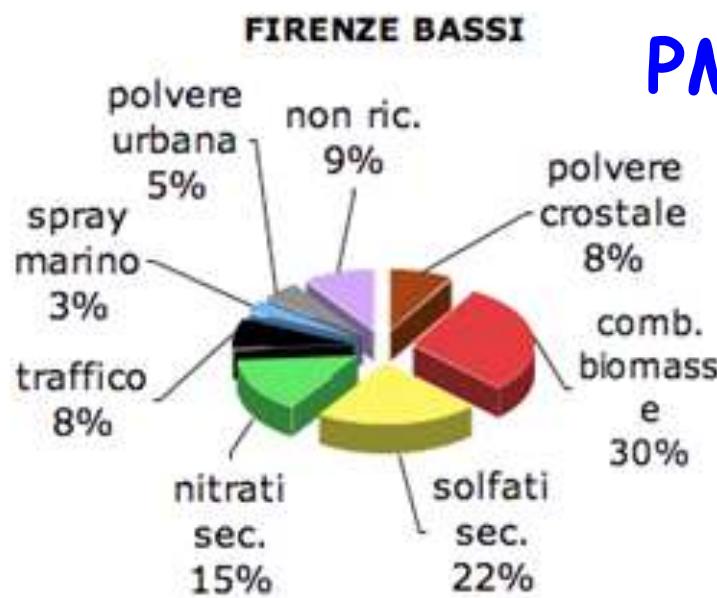
Progetto PATOS I e II



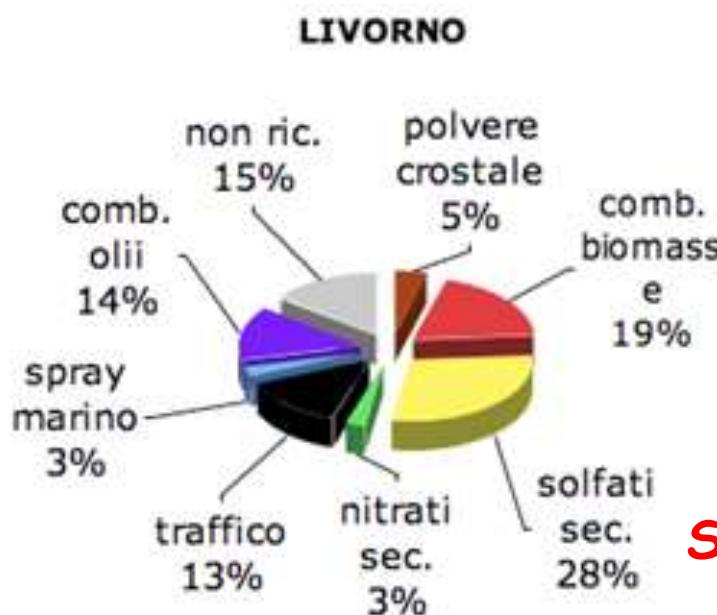
**PM10 e PM2.5 in
6 siti in Toscana,
rappresentativi di
aree di differente
tipologia
(differenti fonti
emissive e
topografia)**

PM_{2.5} Source Apportionment

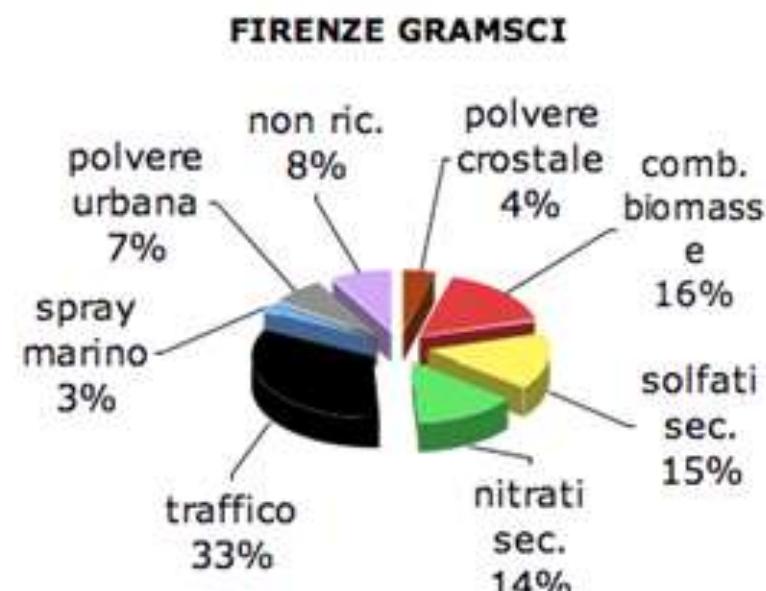
Analisi Statistica Multivariata
Positive Matrix Factorization (PMF)



Sito Urbano-Fondo

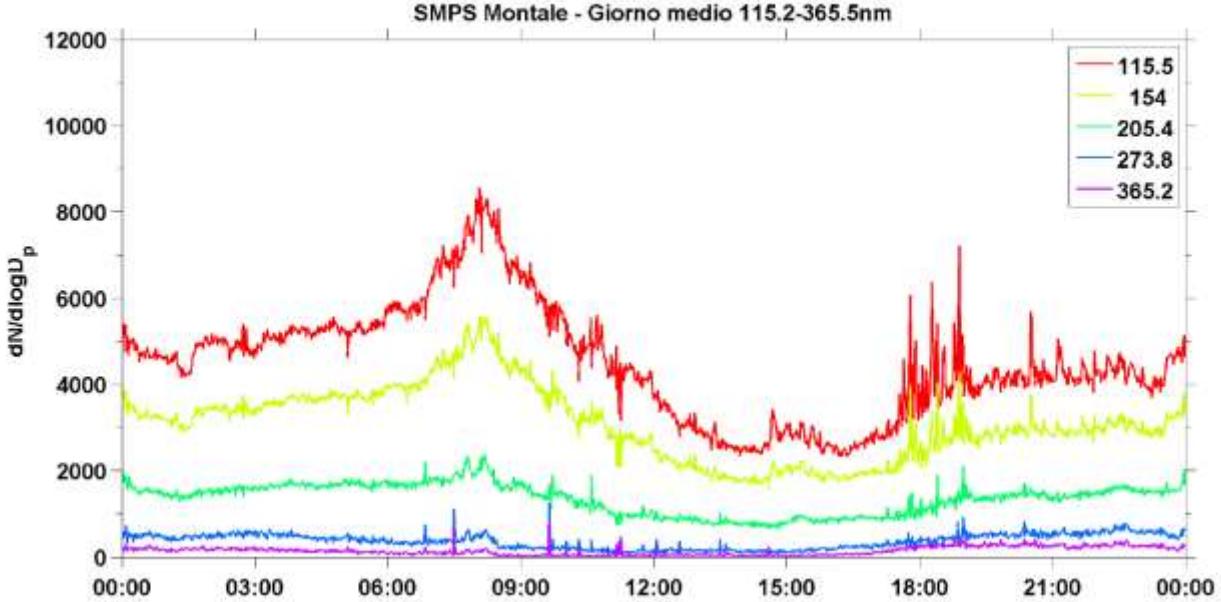


Sito Marino-Fondo



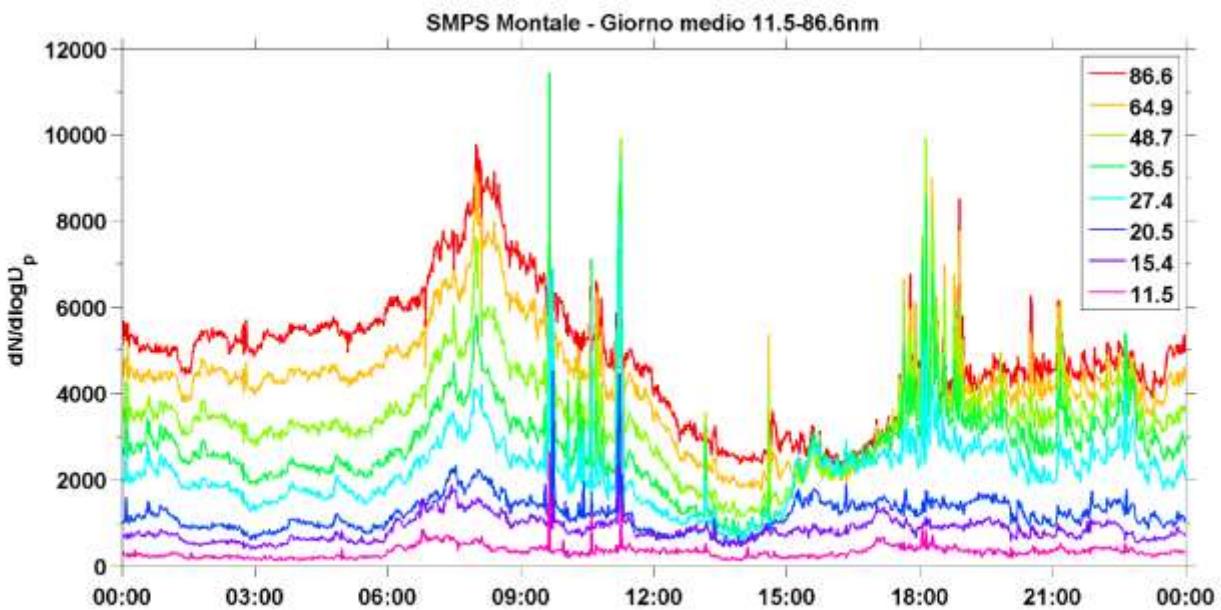
Sito Urbano-Traffico

Nano-Particelle in Sito Urbano-Periferico



Distribuzione giornaliera media della popolazione di nanoparticelle in un sito urbano periferico.

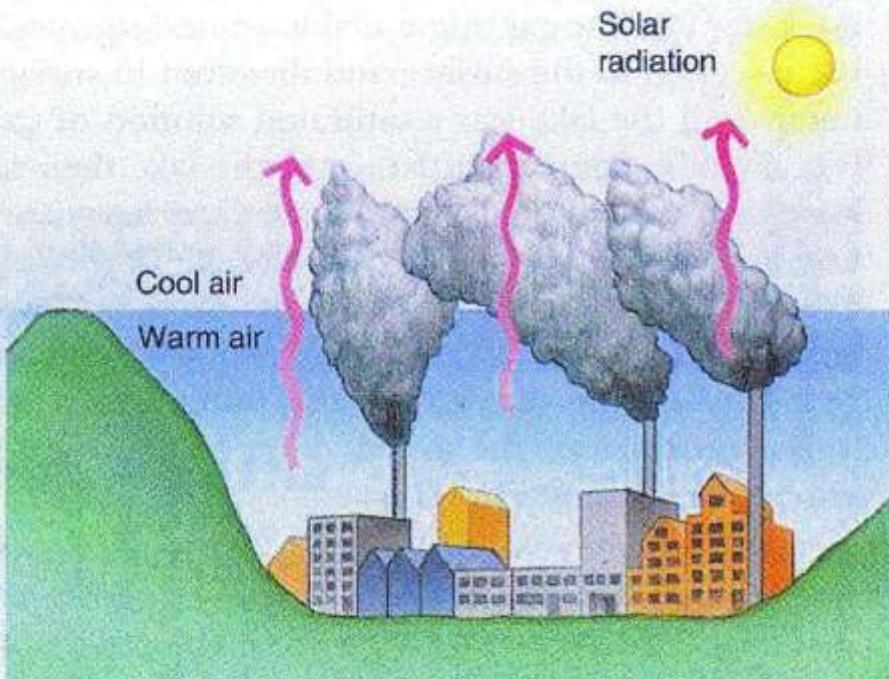
Picchi di particolato intorno alle 8:00 e dalle 18:00 alle 20:00 correlati all'andamento del traffico.



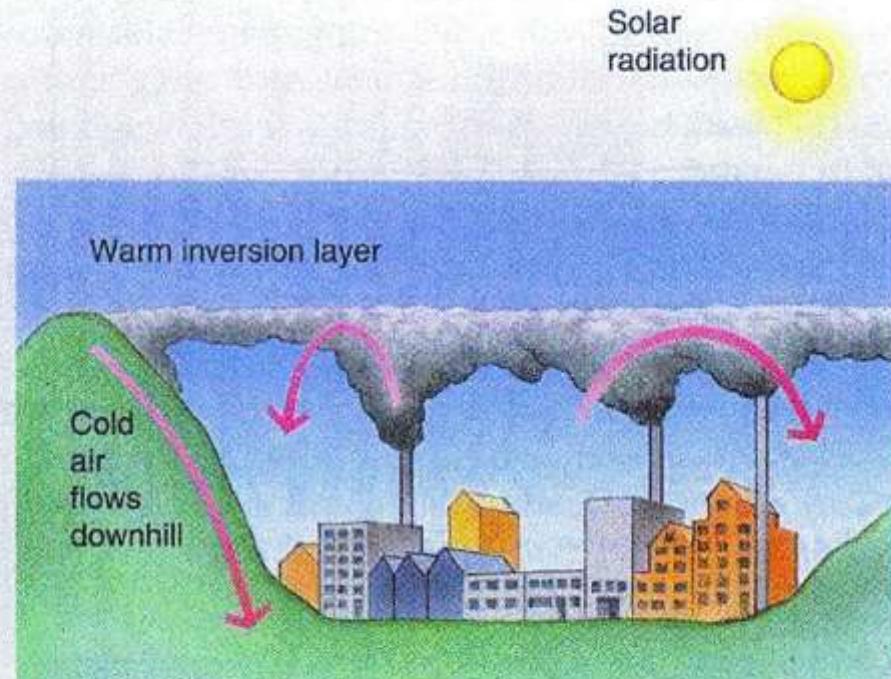
Valori notturni mediamente più elevati di quelli delle ore centrali della giornata per effetto della differente efficienza della circolazione verticale

Formazione strato di inversione termica

Circolazione verticale

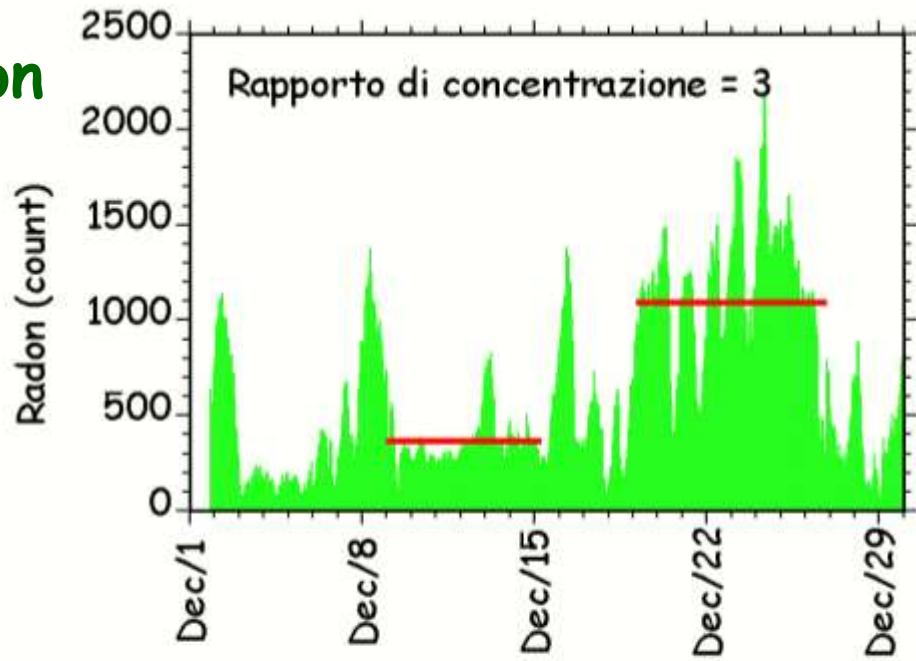


Normal pattern

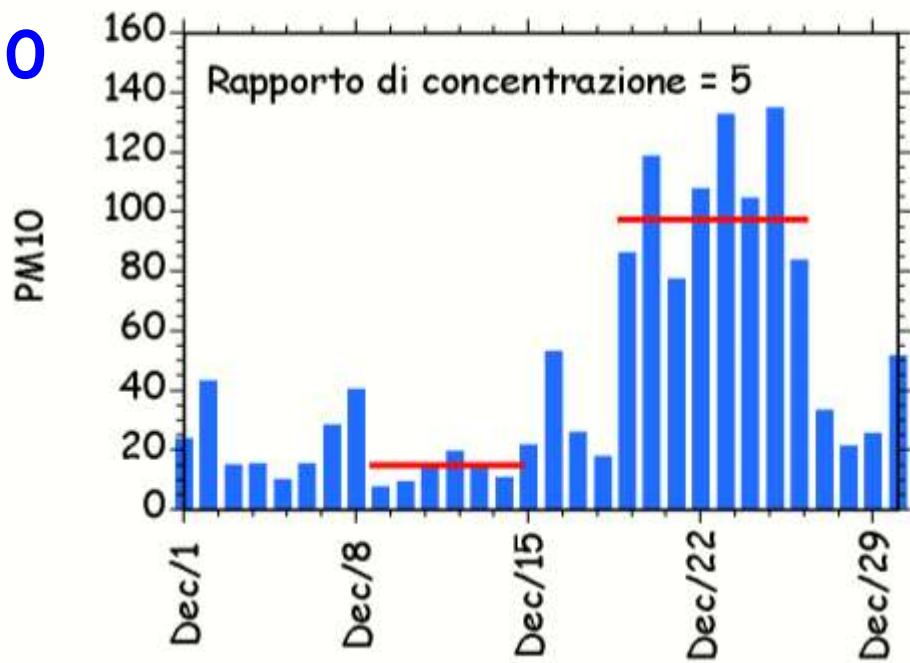


With a temperature inversion

Radon



PM10



Dicembre 05

Tutti i superamenti osservati sono attribuibili alla formazione di strati di inversione

Radon: $R = 3.0$

PM10: $R = 5.0$

Strato di inversione spiega almeno il 60% dell'aumento del PM10

(talvolta 100%)



AIRUSE LIFE+: SYNERGISTIC DAILY AND HOURLY PM_x SOURCE APPORTIONMENT IN URBAN ENVIRONMENTS OF SOUTH EUROPE

Florence



Oporto



Atene



Barcellona



Milano



AIRUSE
LIFE 11 ENV/ES/000584

AIRUSE

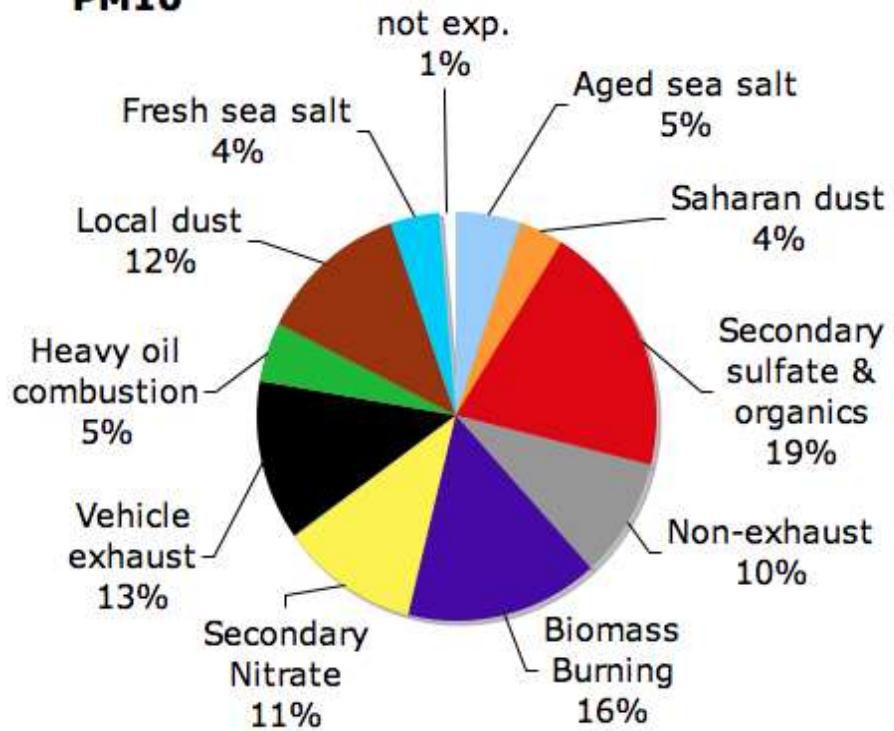


THE AIRUSE PROJECT AIMS

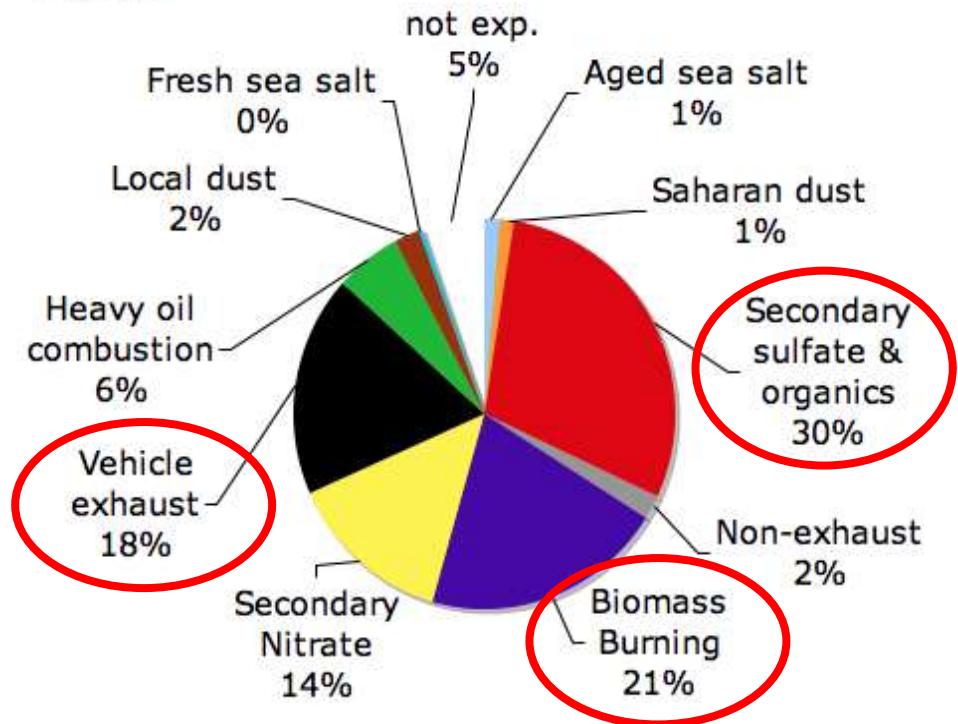
- Characterizing similarities and differences in PM₁₀ and PM_{2.5} sources and contributions across South-Europe (5 cities).
- Identification and quantification of the main sources of PM10 and PM2.5 by source apportionment models.
- Developing, testing and proposing specific and non specific measures to reduce PMx in South-Europe urban ambient air, in order to meet Air Quality standards and to approach WHO guidelines.

Florence - PMF Source Apportionment

PM10



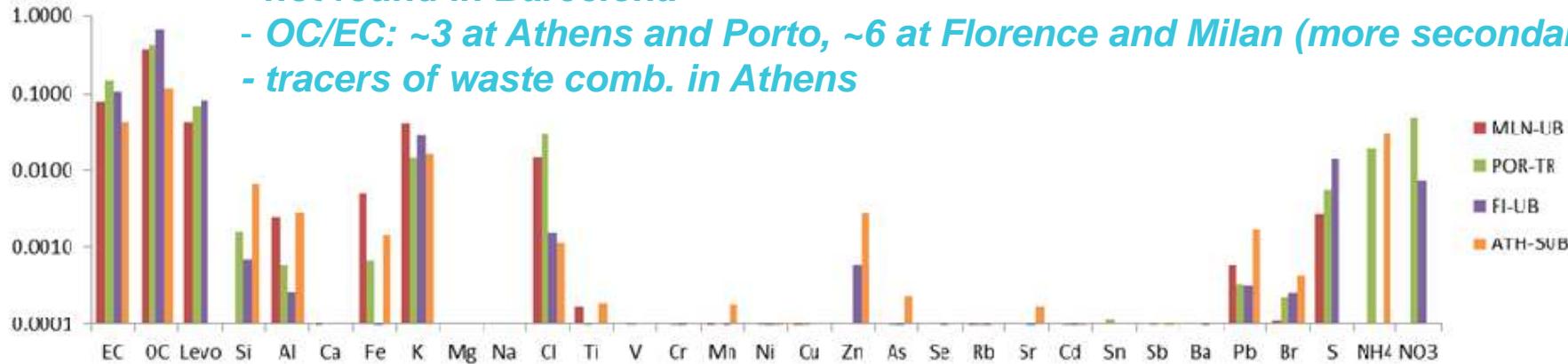
PM2.5



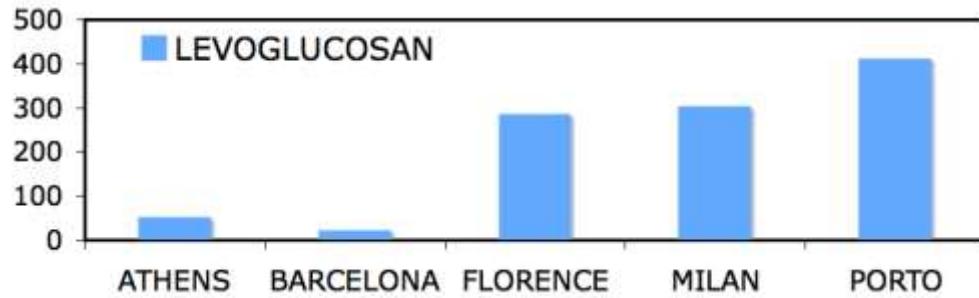


BIOMASS BURNING: comparison among different sites

- not found in Barcelona
- OC/EC: ~3 at Athens and Porto, ~6 at Florence and Milan (more secondary)
- tracers of waste comb. in Athens



$\mu\text{g}/\text{m}^3$	ATHENS		BARCELONA		FLORENCE		MILAN		PORTO	
	PM10	PM2.5	PM10	PM2.5	PM10	PM2.5	PM10	PM2.5	PM10	PM2.5
Biomass burn.	1.4	1.2	-	-	3.0	2.9	7.8	5.3	4.3	4.3



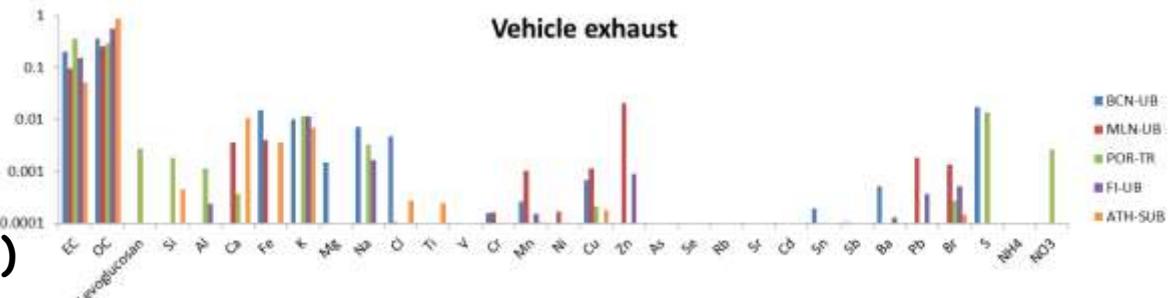
BB contributions reproduced the gradients found for Levoglucosan among the AIRUSE cities (with Levo about 4/8% of BB)



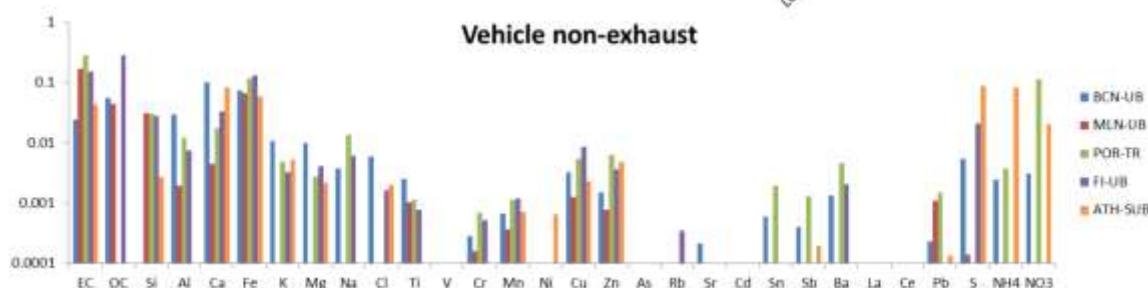
TRAFFIC: comparison among different sites

OC/EC:

- <1 at POR-TR
- 1.8-3.7 at UB sites
- 16 at ATH-SUB (low diesel)



Vehicle non-exhaust



- Fe at all sites
- Ca in BCN
- EC in POR, MLN and FI
- S in ATH

$\mu\text{g}/\text{m}^3$	ATHENS		BARCELONA		FLORENCE		MILAN		PORTO	
	PM10	PM2.5	PM10	PM2.5	PM10	PM2.5	PM10	PM2.5	PM10	PM2.5
Vehicle exhaust	2.1	1.7	3.3	3.0	2.5	2.5	2.8	1.8	8.0	8.0
Vehicle non-ex.	1.8	0.6	2.6	0.2	1.9	0.3	3.4	2.6	2.9	1.3

NASA/MODIS



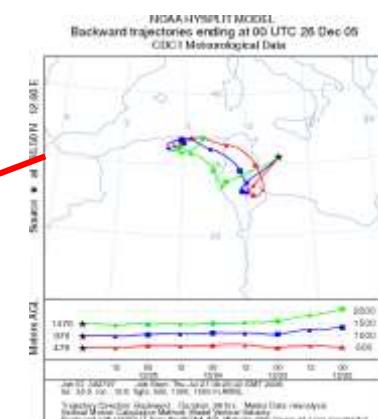
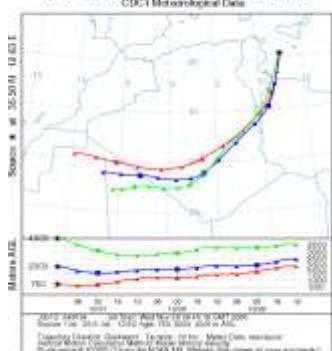
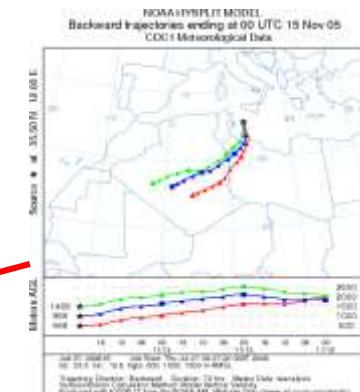
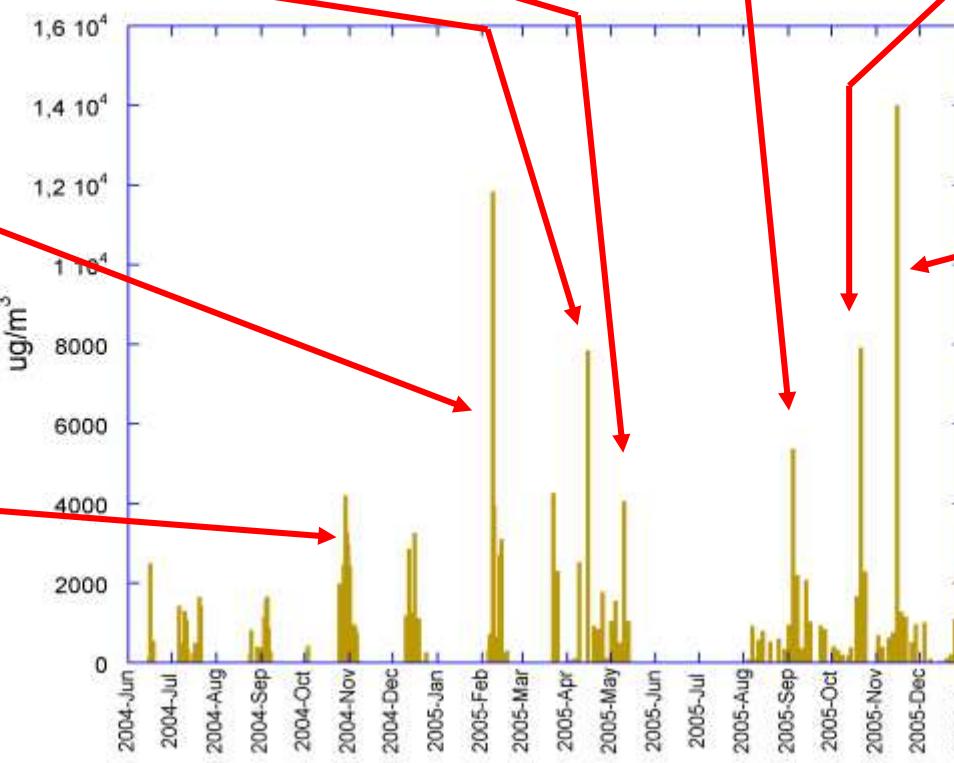
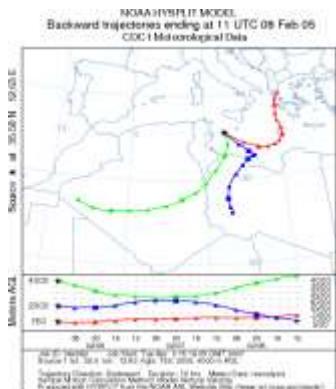
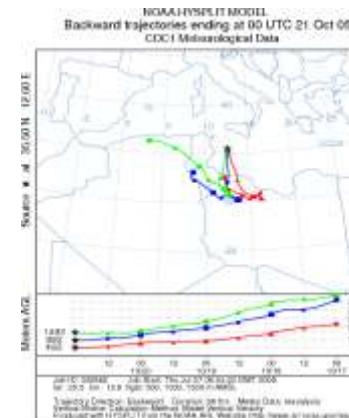
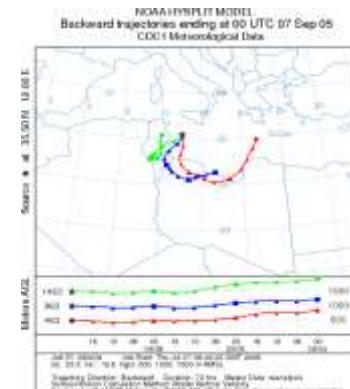
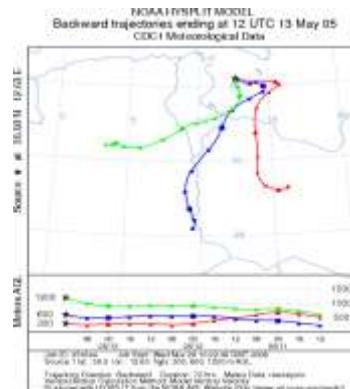
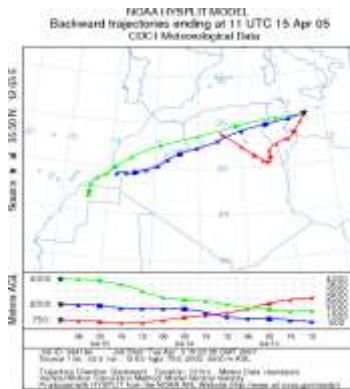
Isola di Lampedusa

Studio della
frequenza e
dell'origine degli
eventi di trasporto
delle polveri
sahariane

Relazione tra
produttivita' marina
primaria e marker
biogenici nell'aerosol
nel Mediterraneo
Meridionale

Valutazione
dell'impatto sulla
qualita' dell'aria
delle emissioni da
traffico navale nel
Canale di Sicilia

Identificazione Aree Sorgenti Saharan Dust da Back-Trajectory



Identificazione Aree Sorgenti Saharan Dust da Geochimica

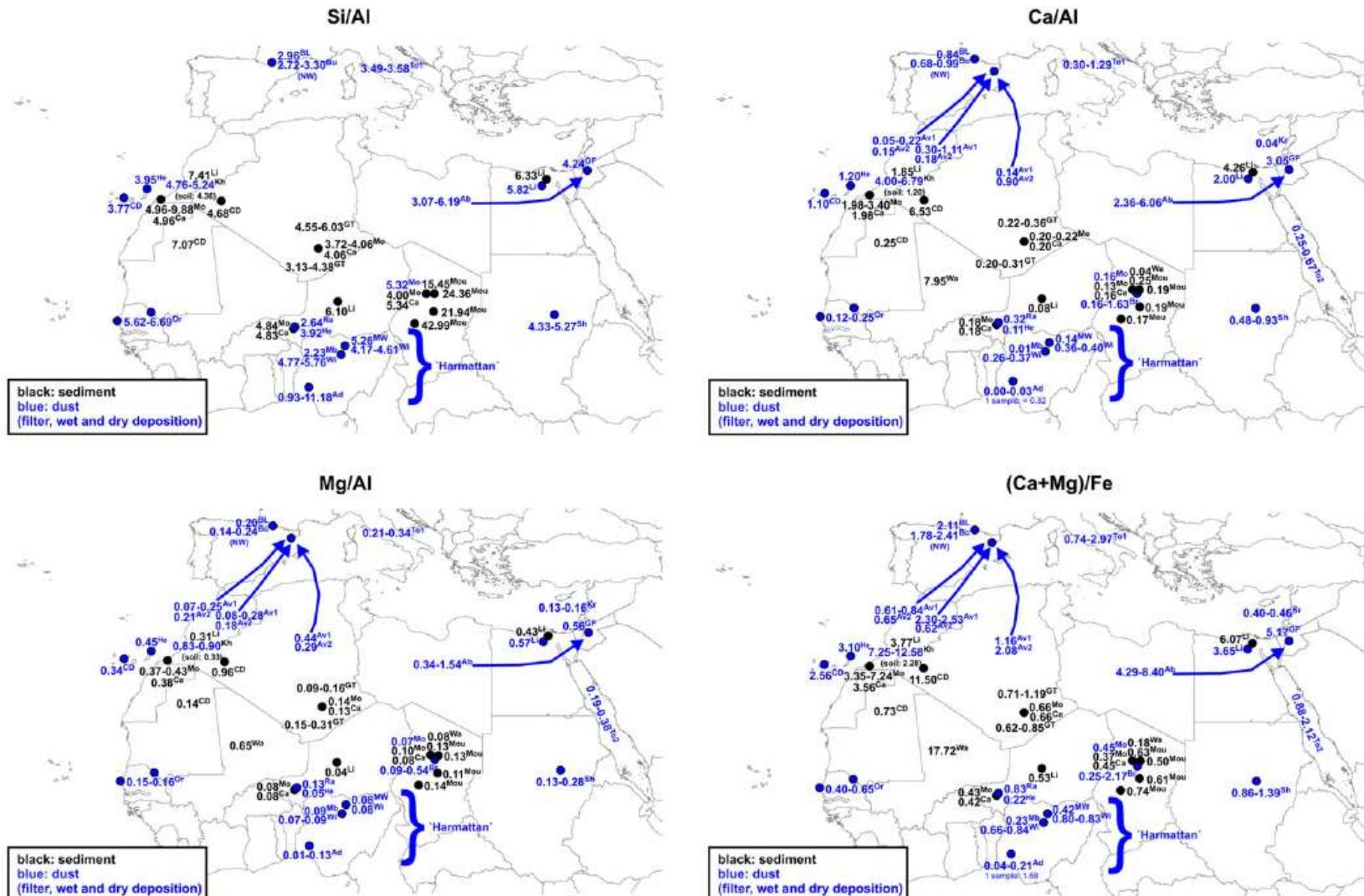
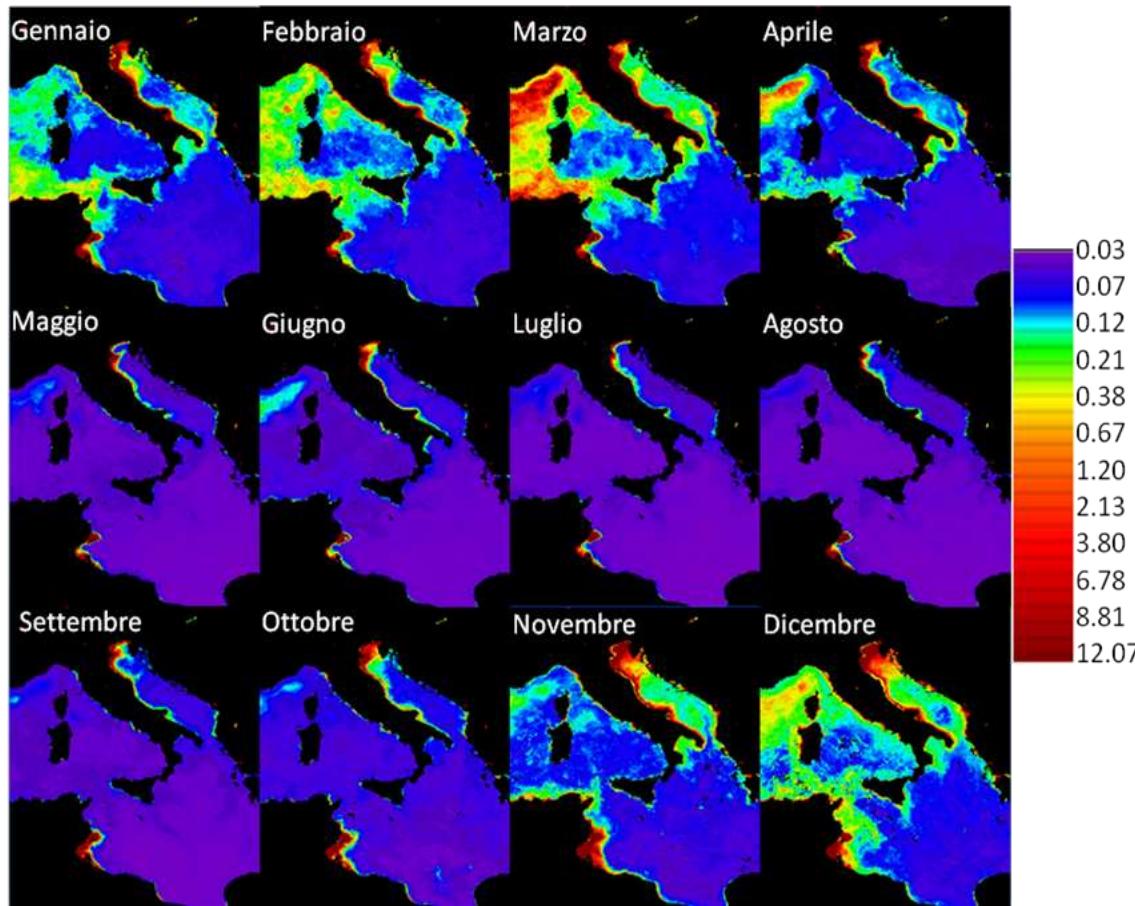


Fig. 2. Maps of northern Africa with elemental ratios of Si/Al, Ca/Al, Mg/Al, and (Ca+Mg)/Fe indices (bulk chemical analyses in wt.%) for dust and sediment samples; arrows show transport directions of mineral dust of selected studies. References: MW: McTainsh and Walker (1982), BL: Bücher and Lucas (1984), To1: Tomadin et al. (1984), Wi: Wilkie et al. (1984), Ad: Adedokun et al. (1989), Bu: Bücher (1989), To2: Tomadin et al. (1989), Mb: Måberg et al. (1991), Or: Orange et al. (1993), Sh: Sharif (1995), GP: Ganor and Foner (1996), GT: Guieu and Thomas (1996), He: Herrmann et al. (1996), Av1: Avila et al., 1998, Kr: Krom et al. (1999), Gu: Guieu et al. (2002a), CD: Criado and Dorta (2003), Si: Singer et al. (2003), Kh: Khirici et al. (2004), Li: Linke et al. (2006), Mo: Moreno et al. (2006), Mou: Mounkaila (2006), Av2: Avila et al. (2007), Ca: Castillo et al. (2008), Ra: Rajot et al. (2008), Ab: Abed et al. (2009), Wa: Washington et al. (2009), and Br: Bristow et al. (2010).

Relationship between aerosol markers and phytoplanktonic activity - Mediterranean Basin

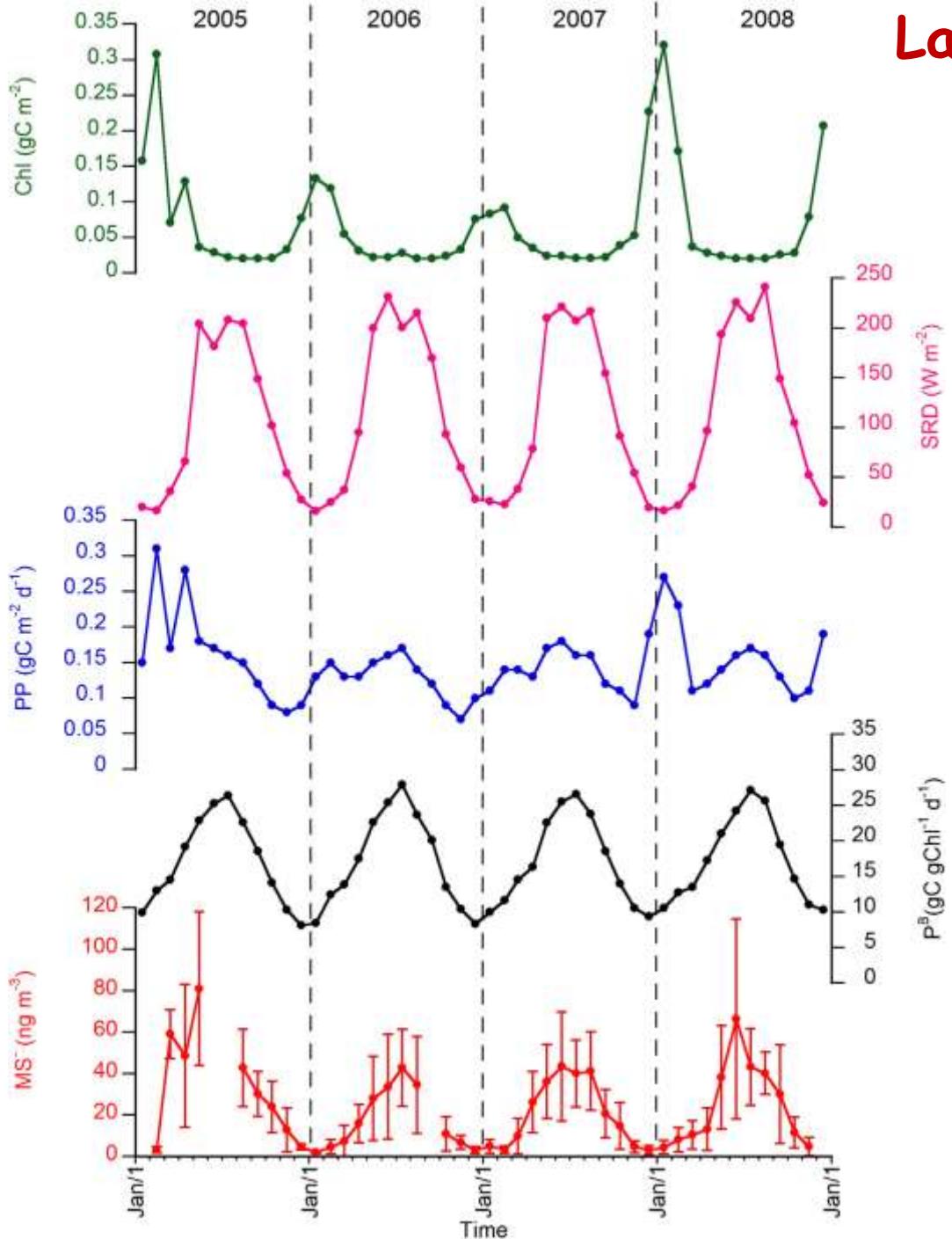


Chl-a map calculated by L-Dorma algorithm.

$$P = 12\alpha^* \varphi_{\mu\max} \int_0^L \int_0^D \int_{400}^{700} Chl_{(z)} \cdot PUR_{(z,t,\lambda)} \cdot f[x_{(z,t)}] dx dz d\lambda$$

Antoine D & Morel A, 1996,. *Global Biogeochemical Cycles* 10, 43-55.

Lampedusa: MSA vs. PB



Clorofilla-a

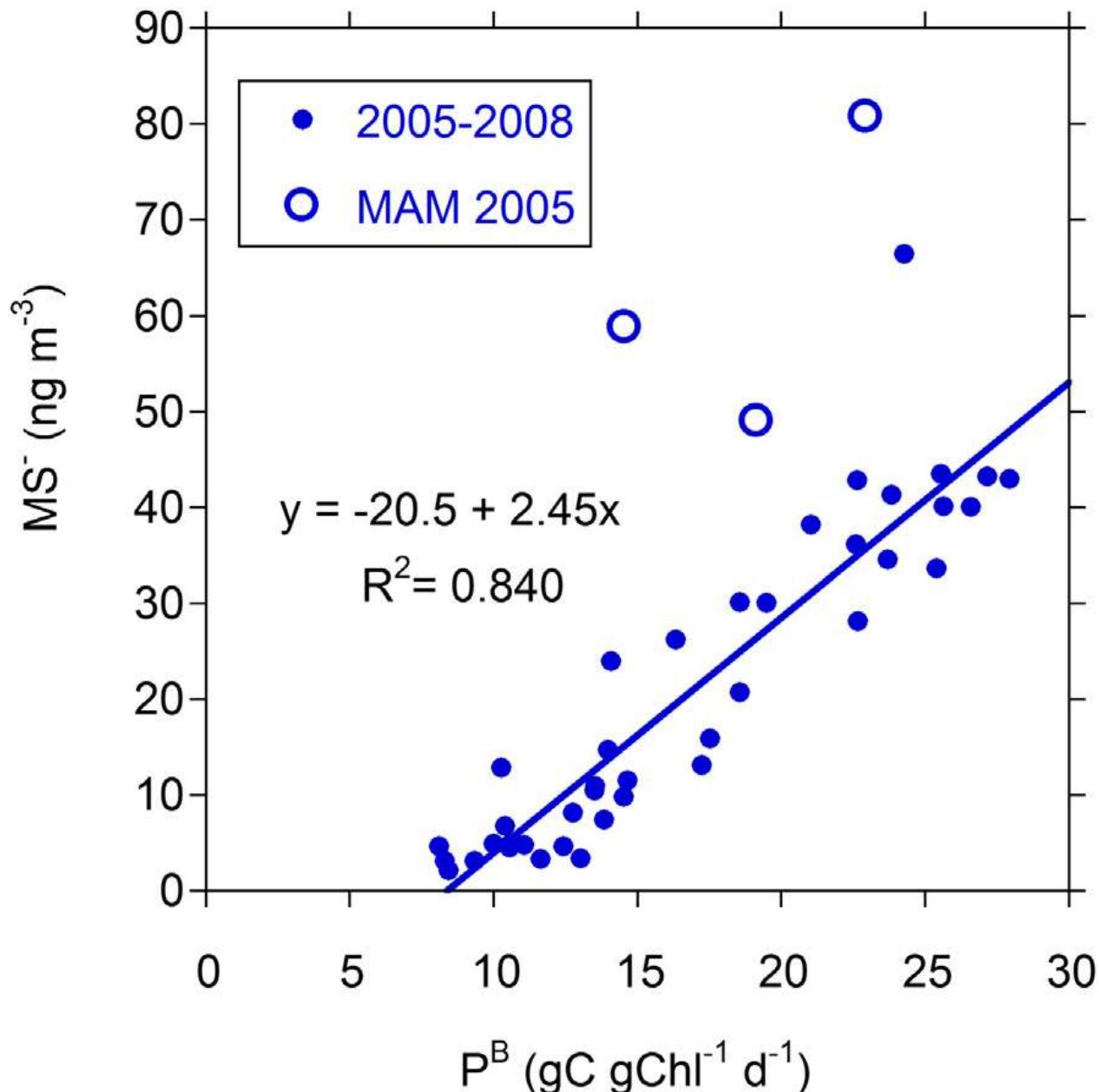
Irraggiamento Solare

Produttivita' Primaria

Indice di Produttivita'
Primaria Specifica PB

MSA
(Acido Metansolfonico)

MSA e Produttivita' Primaria a Lampedusa



Medie mensili
della conc. di
MSA
nell'aerosol a
Lampedusa in
funzione
dell'indice di
produttivita' del
fitoplancton nel
Mediterraneo
Meridionale (P^B)



LIFE Environment and Resource Efficiency - Call 2015

Assessment of the Large scale Impact of Ship Emissions on the aerosol burden over Mediterranean Sea

Acronym: **LIFE-ALISEOS**

Sector: Environment and Health

Project duration: 3 years

Code number: **LIFE15 ENV/IT/000329**

BENEFICIARIES

Coordinating beneficiary:

Università degli Studi di Firenze - Dipartimento di Chimica

Associated beneficiary:

Agencia Estatal Consejo Superior de Investigacione Scientificas (CSIC), Spagna.

ENEA - Dipartimento sostenibilità dei sistemi produttivi e territoriali.

INFN -Istituto Nazionale di Fisica Nucleare.

NOA - National Observatory of Athens, Grecia

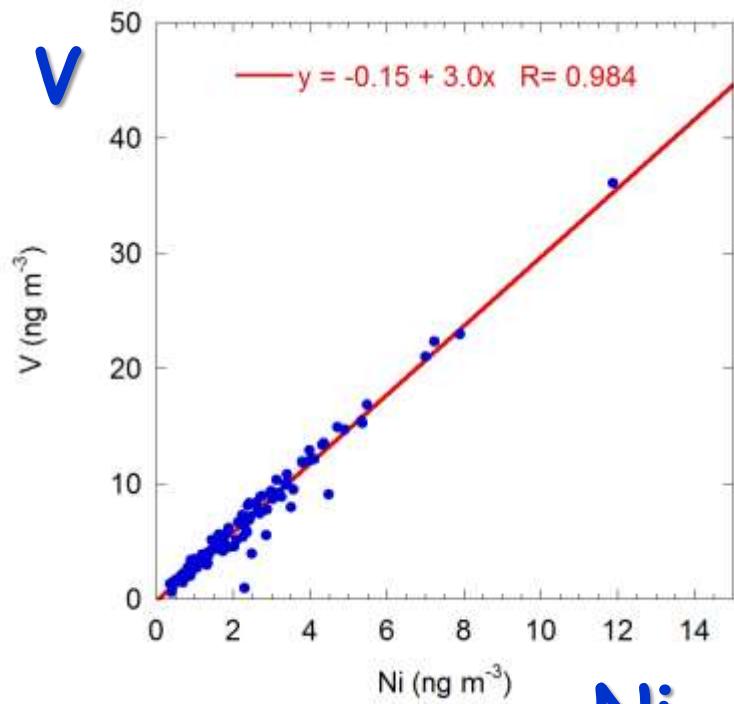
L-Universita' ta' Malta.

LIFE - ALISEOS Project Goal

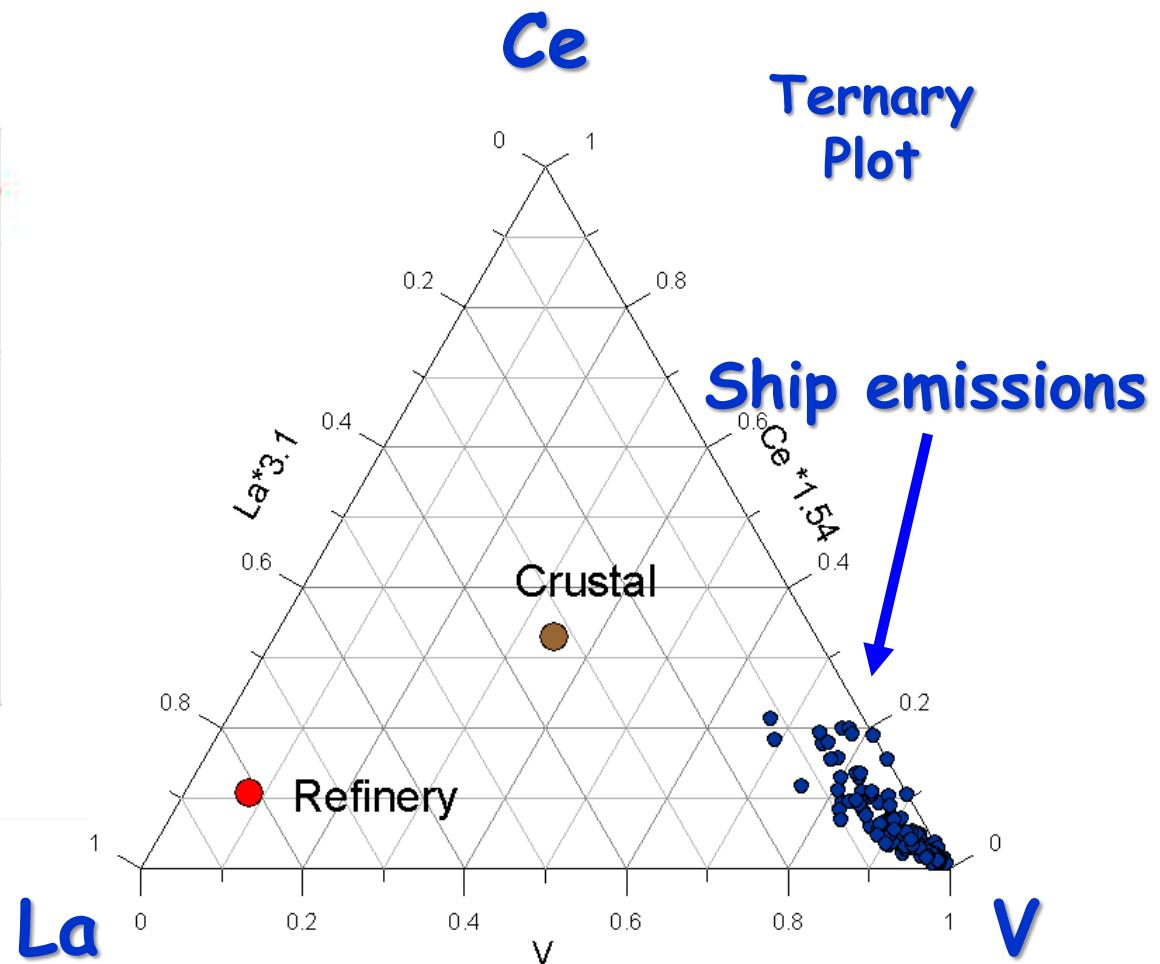
To assess the contribution of ship emissions to the aerosol budget over the Mediterranean Sea in order to address European authorities toward efficient and cost effective policies for atmospheric particulate management.



Ship emission characterization



Ni



Ce

Ternary
Plot

Ship emissions

La

V

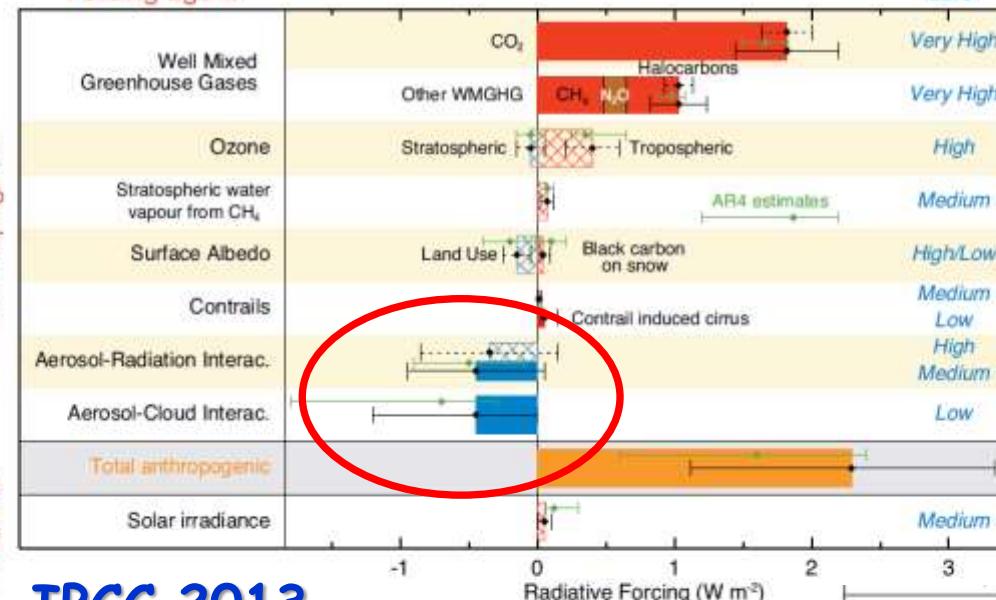
Mediterranean Sea measurements (Lampedusa Island):

Average % nssSO₄²⁻ from ship : 32.5%

Max value: 7.2 µg/m³ (66.3% of total nssSO₄²⁻ - 32.4% of PM10 mass)

Radiative forcing of climate between 1750 and 2011

Forcing agent



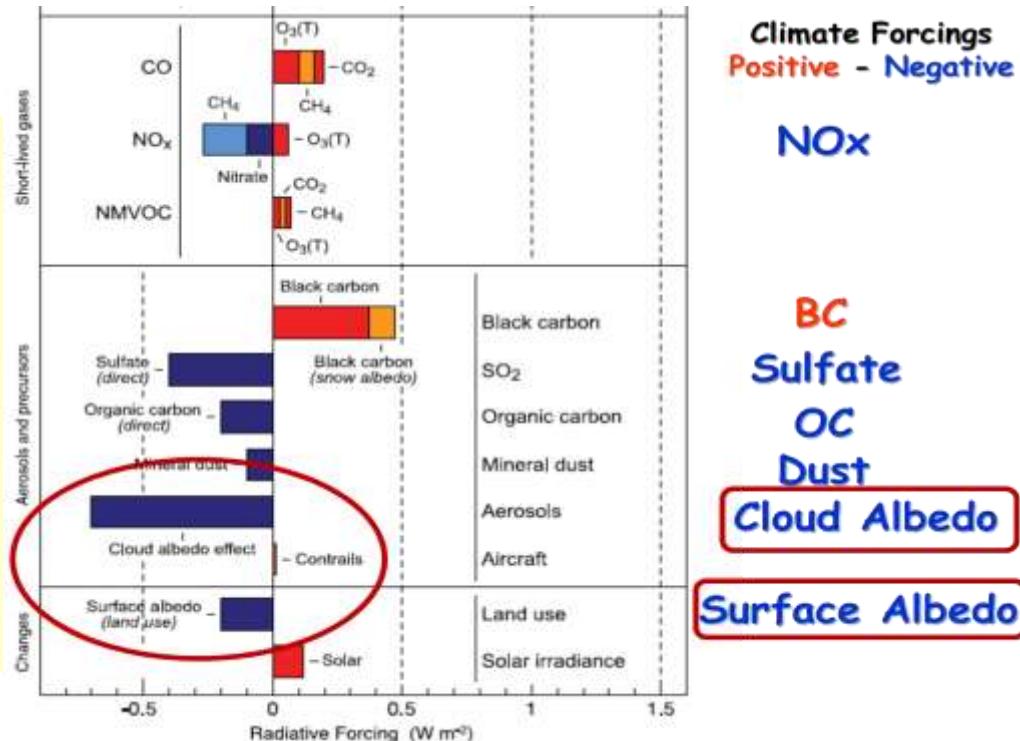
IPCC 2013

Polar Aerosol

Effective radiative aerosol forcing: cooling
But, large uncertainties,
even for the sign, especially
for polar aerosols

In the polar areas, the negative forcing of the surface albedo is higher than that of the cloud albedo and of the scattering processes.

→ Aerosol positive forcing!



Automatic Weather Station (AWS) Location Map

See <http://uwamrc.ssec.wisc.edu/aws/>
and <ftp://ice.ssec.wisc.edu/pub/biglist>
for more details.

AVHRR Image Mosaic from
USGS Map I-2560
Merge by C.A. Shuman
UMD-ESSIC



King Sejong S.

Relay Station

Dome F
Dome Fuji



DC



MZS Jang Bogo S.

Key for McMurdo Area	
1	Cape Bird
2	Ferrell
3	Fogle
4	Jimmy', Jimmy'
5	Laurie
6	Laurie II
7	Linda
8	Manning
9	Mealey
10	Minna Bluff
11	Mount Erebus
12	Nancy
13	Pegasus
14	Pegasus North
15	Pegasus South
16	Tiffany
17	White Out
18	White Island
19	Willie Field
20	Windless Bight
21	Windless Bight

Thule

Russian
Cap
Barànova
Station
Severnaya
Zemlya Is.
Ny Alesund
Svalbard
Islands



Ny Ålesund

78°56' N - 11°56' E

Spitsbergen
Svalbard (Norway)

Gruvebadet Observatory

800 m from Ny Alesund
about 50 m a.s.l.



2011-2015 Campaigns

Balloon measurements up to 1000 m altitude

Airship shape
about 15 kg payload



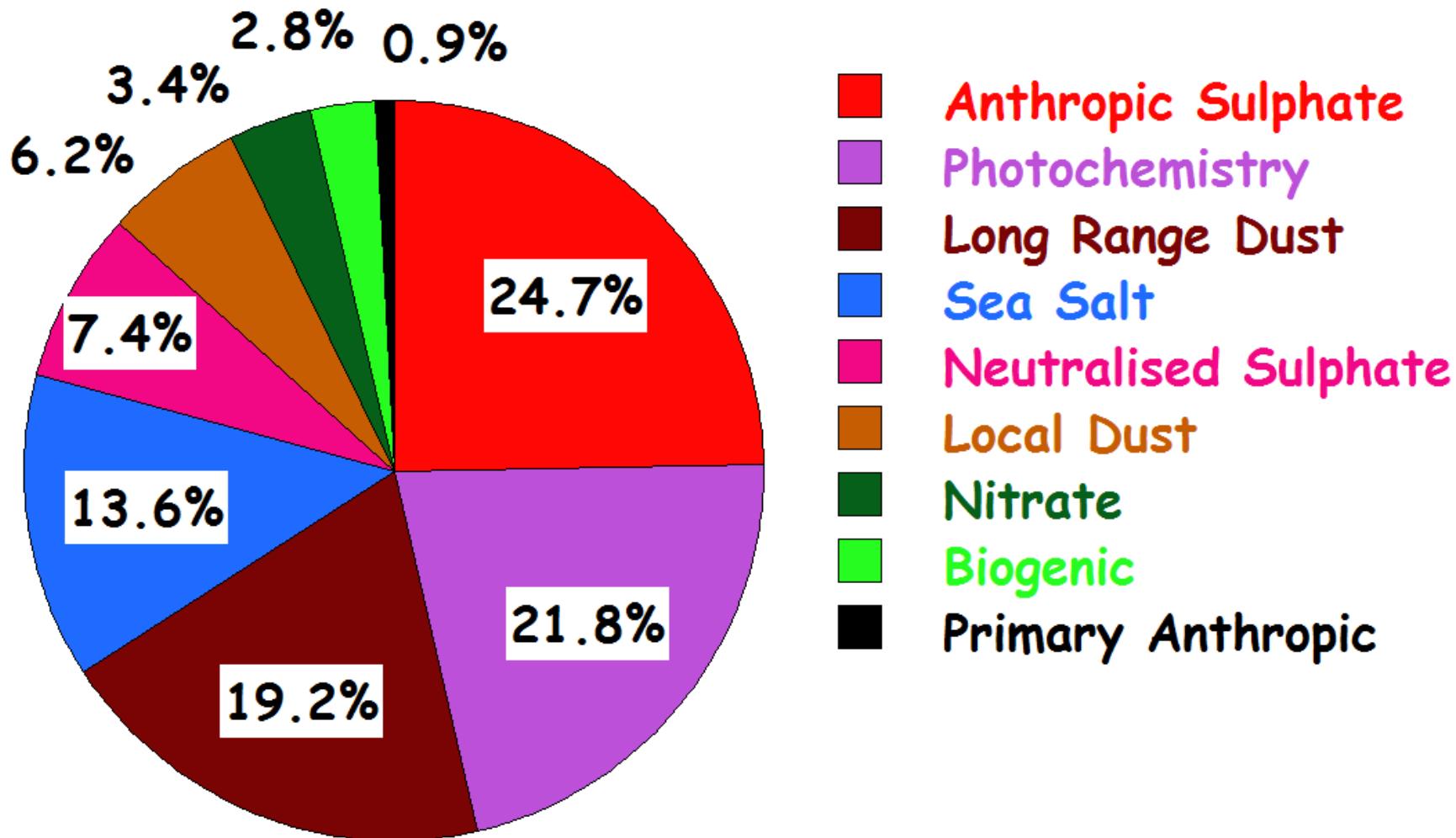
Meteo Probes
OPC measurements
Nano-Particle Count.
Nephelometer
Aerosol sampling
Ozone
Black Carbon
Video-Camera
Data Trasm. (156MHz)



Source Apportionment on the reconstructed mass (74%)

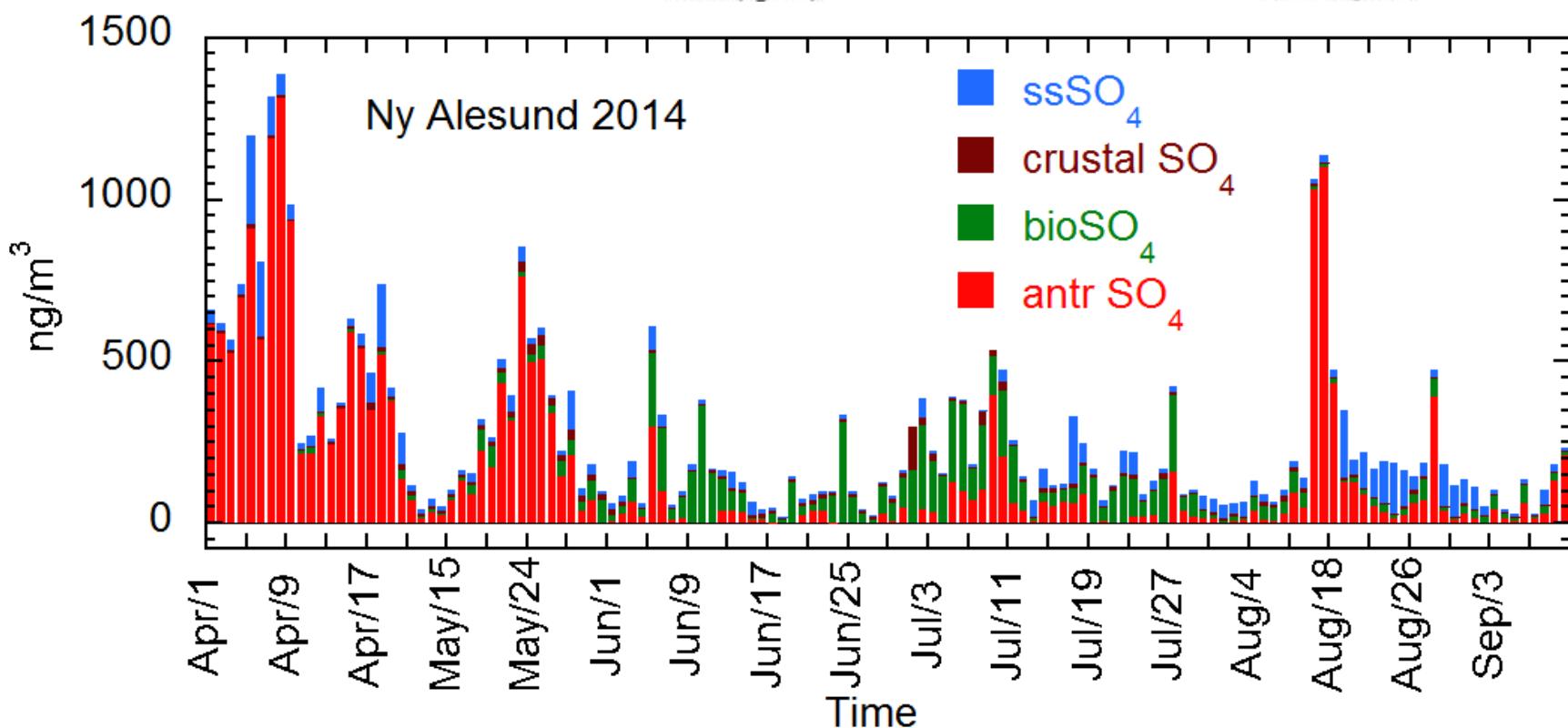
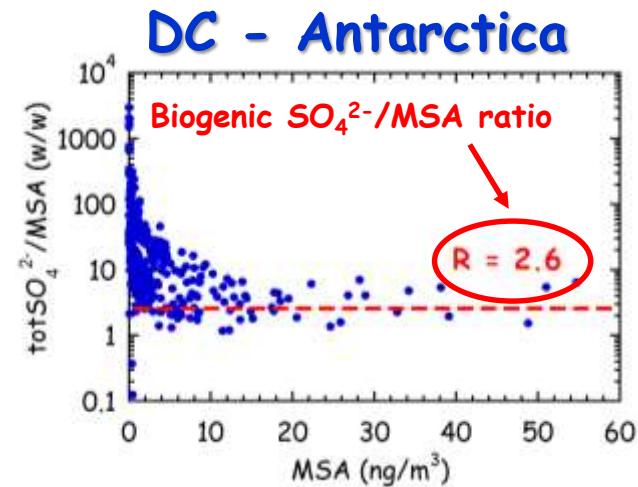
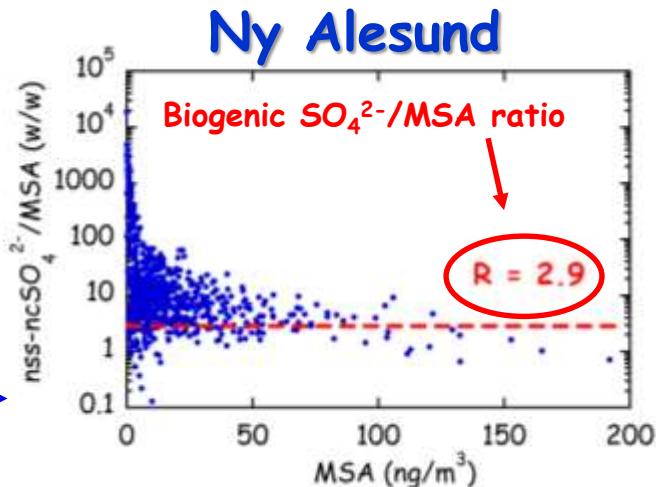
(EC-OC measurements cannot be included)

NyA 2010 - PMF Source Apportionment



Evaluation of the sulfate source fractions

ssSO_4^{2-}
 from ssNa^+
 Crust-SO_4^{2-}
 from nssCa^{2+}
 bio-SO_4^{2-}

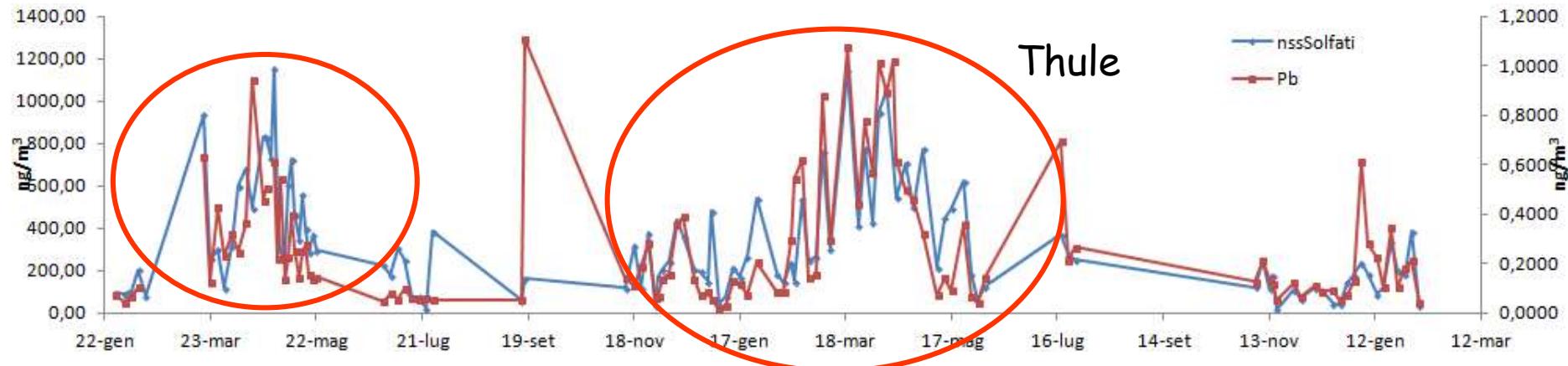
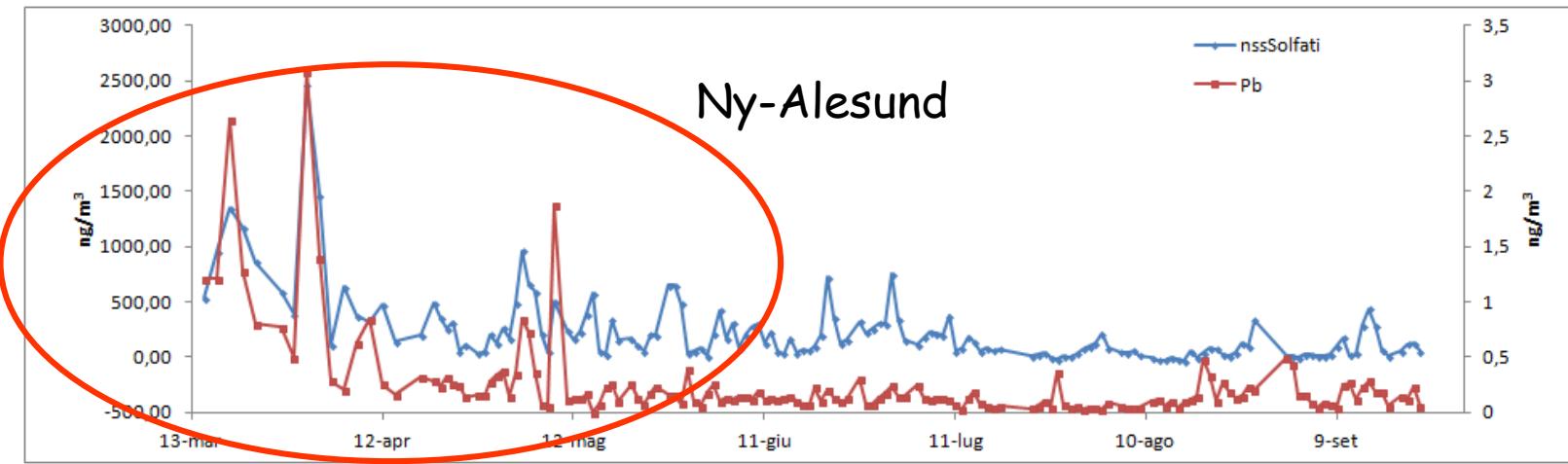



Correlations between Sulfate and Anthropic Metals

Same source areas and/or similar transport processes

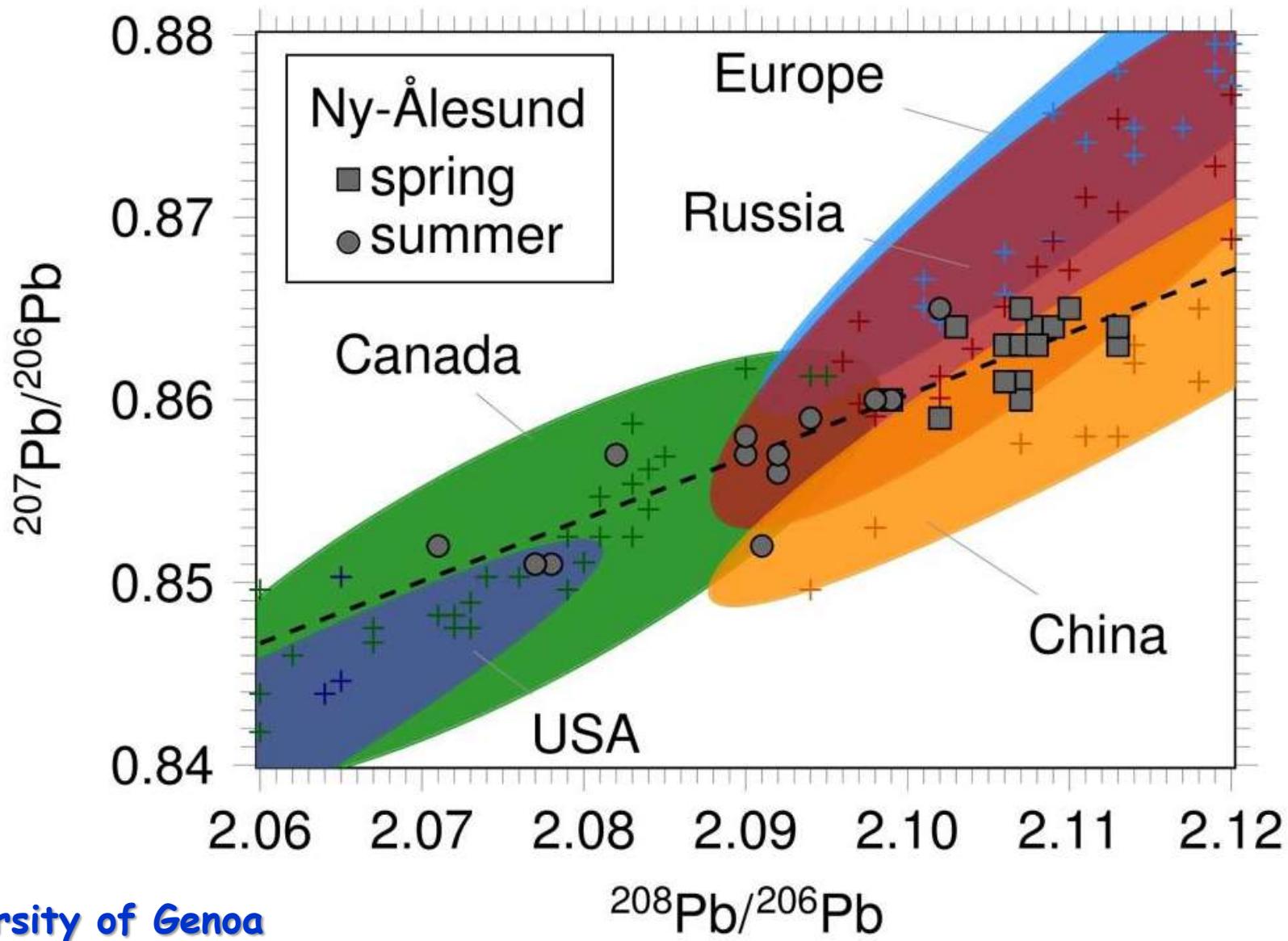
Ny-Alesund → Pb ($R^2 = 0,64$)
As ($R^2 = 0,61$)
Cd ($R^2 = 0,47$)

Thule → Pb ($R^2 = 0,49$)



Source assessment of atmospheric lead by isotope ratios

Three-isotopes plot showing potential Pb source areas in spring and summer 2012



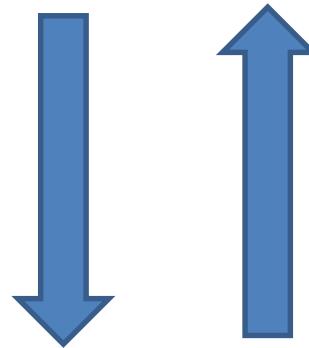
Oceanic DMS Climate Feedback

Global marine primary productivity has been declining during the last century, and is expected to decrease due to global warming. Such a decline was not observed in Arctic waters.

Climate change

Sea water stratification
in temperate regions

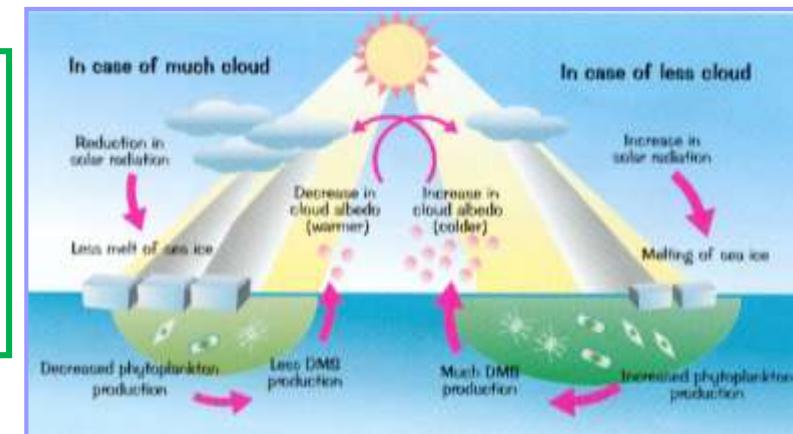
Sea ice extent
(in polar region)



**Primary
Productivity
($\text{g C m}^{-2} \text{ d}^{-1}$)**

Uptake of atmospheric CO_2
for phytoplanktonic growth

Emission of DMS, precursor
of **MSA** and nssSO_4^{2-}



January 2012

Sea Ice Extent
Jan 2012



July 2012

Sea Ice Extent
Jul 2012



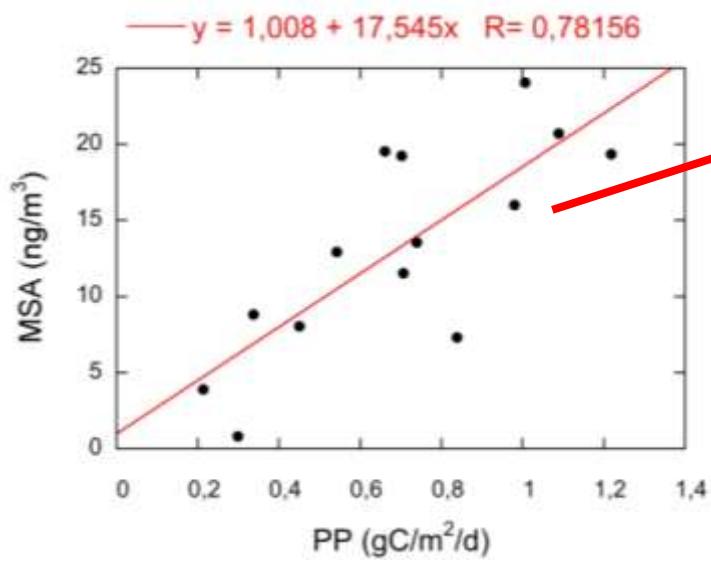
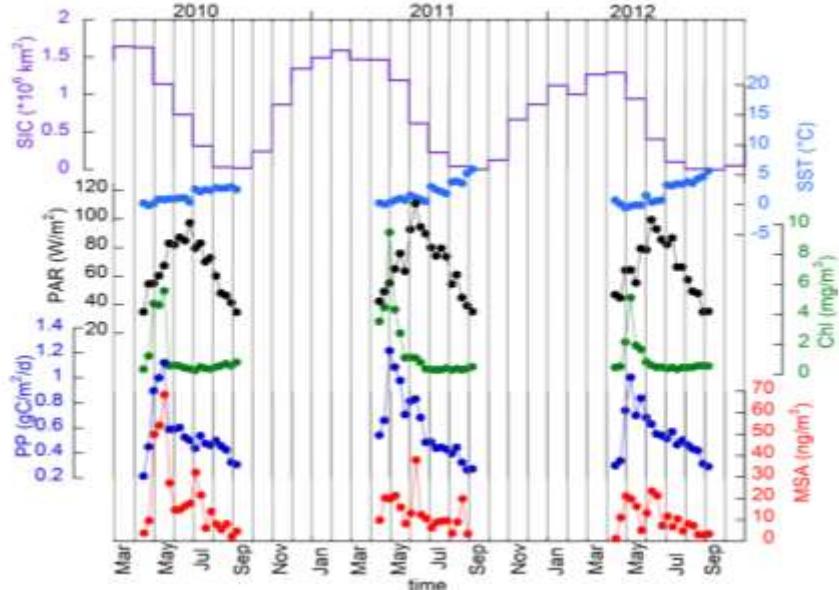
Total extent = 13.8 million sq km

Total extent = 7.9 million sq km

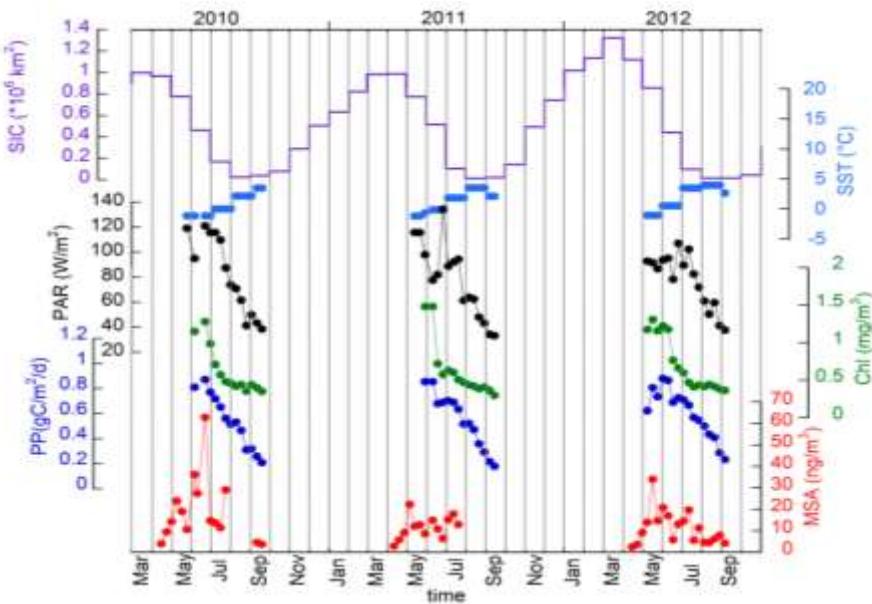
median
ice edge

Biogenic Source - MSA vs Primary Productivity

MSA Ny Alesund - PP Barents Sea



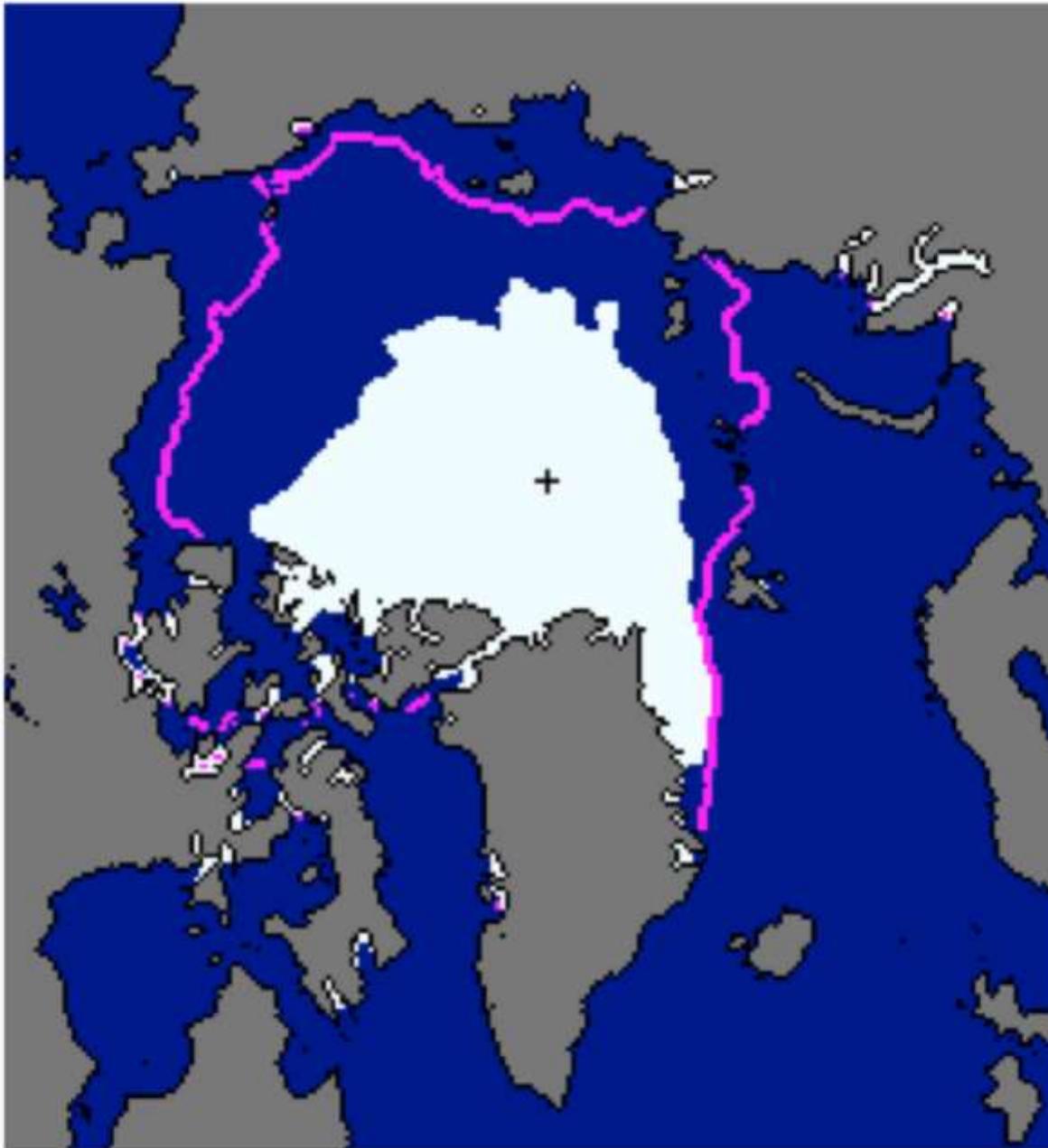
MSA Thule - PP Baffin Bay



Good correlation between MSA and primary productivity, primed by sea-ice melting.

Relevant result in studying the impact of climate change on marine biogenic activity in the past

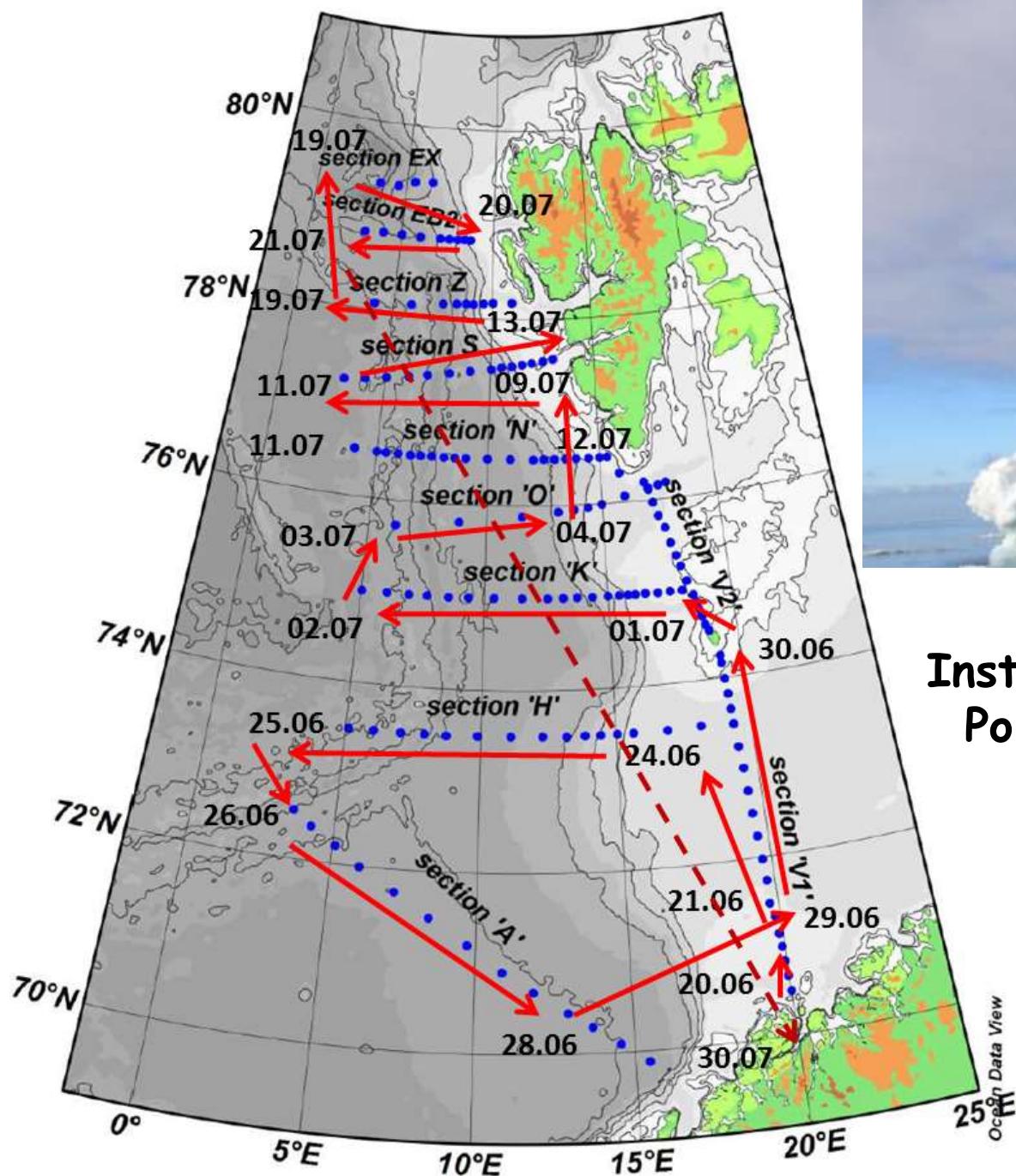
Future trans-Arctic shipping



Arctic sea ice extent
in Sept. 2012
(3.6 Mkm^2)

Magenta line indicates
mean sea ice extent
for 1979-2011.

Sept. 2012
represents a 49%
decline.

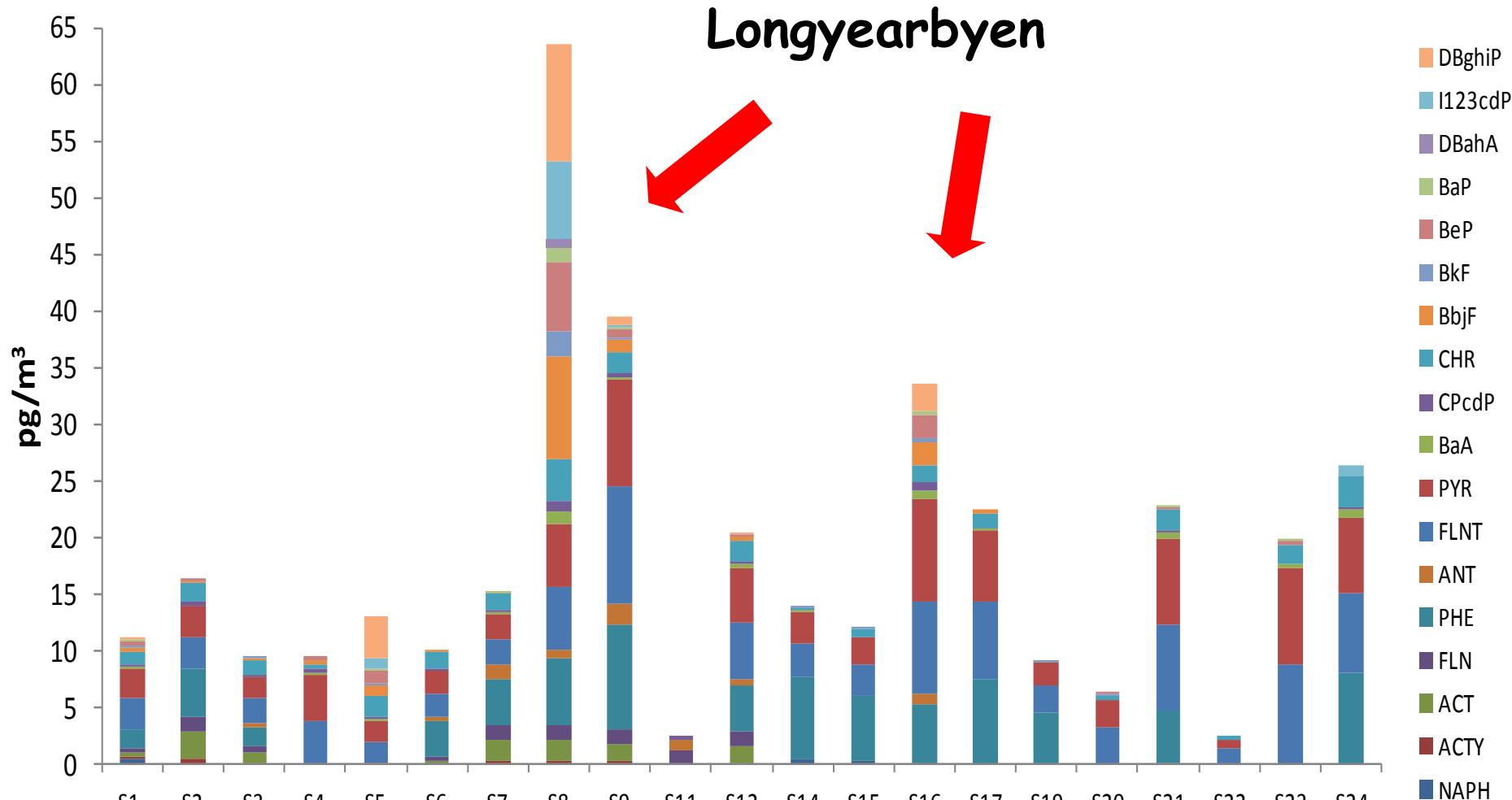


**Polish Ship
Oceania**

Collaboration with
Institute of Oceanology of the
Polish Academy of Sciences

Longitudinal and
Latitudinal transects
from Tromsø to
Svalbard Islands
during the
AREX 2011 Cruise

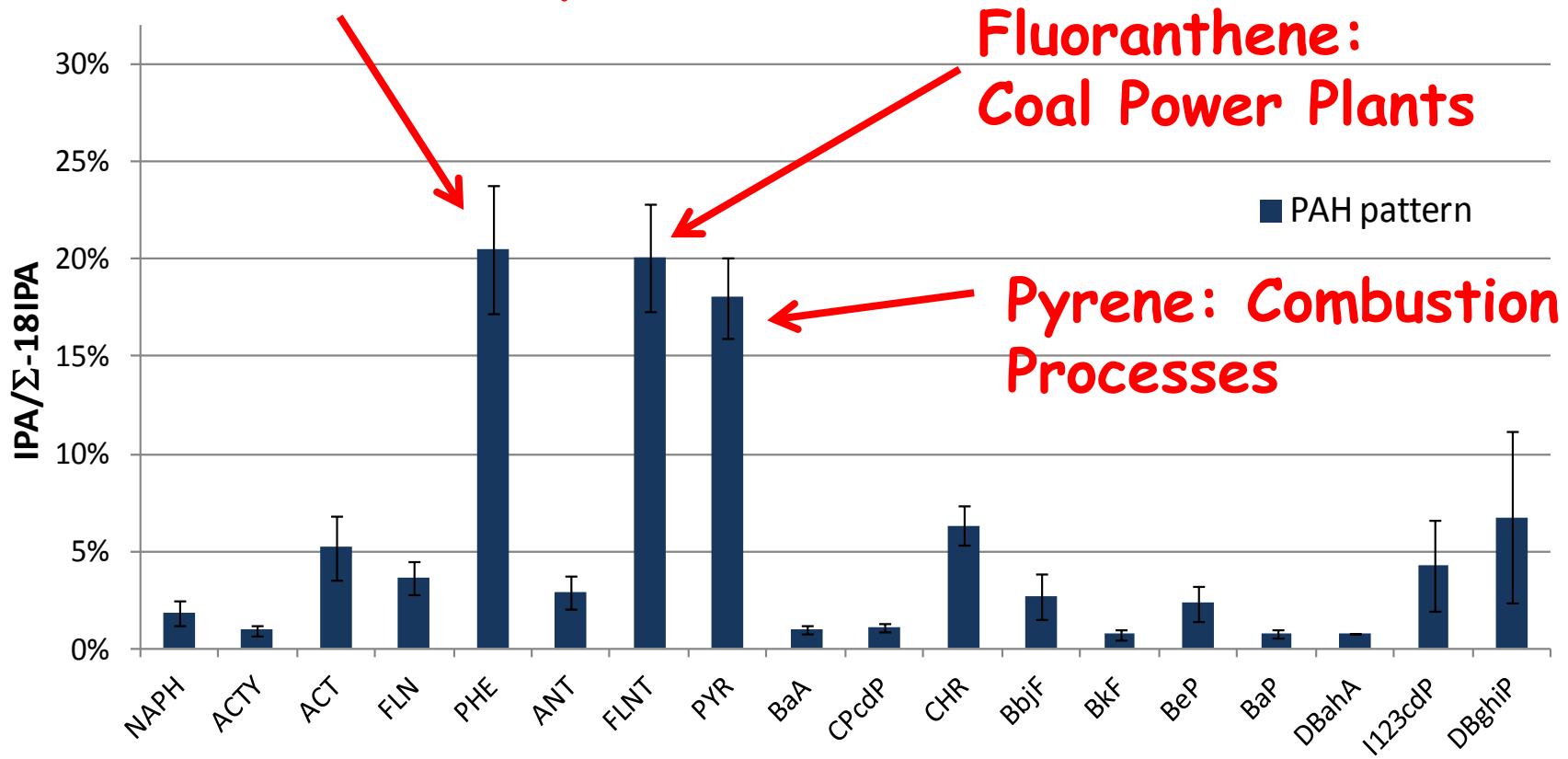
PAH species and spatial distribution



$$\Sigma 18 \text{ PAH species} = 18.1 \pm 14.0 \text{ pg/m}^3$$

Percentage contribution of PAH species

Phenanthrene: Heavy Fuel Oil



Fluoranthene:
Coal Power Plants

Pyrene: Combustion
Processes

Phenanthrene, Fluoranthene and Pyrene
constitute 58% of the PAHs sum

A photograph of two snowmobiles on a vast, snow-covered plain. In the distance, a large, snow-capped mountain peak rises against a sky filled with scattered clouds. The snowmobiles are positioned in the center of the frame, moving away from the viewer towards the horizon.

Thanks for your attention !
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