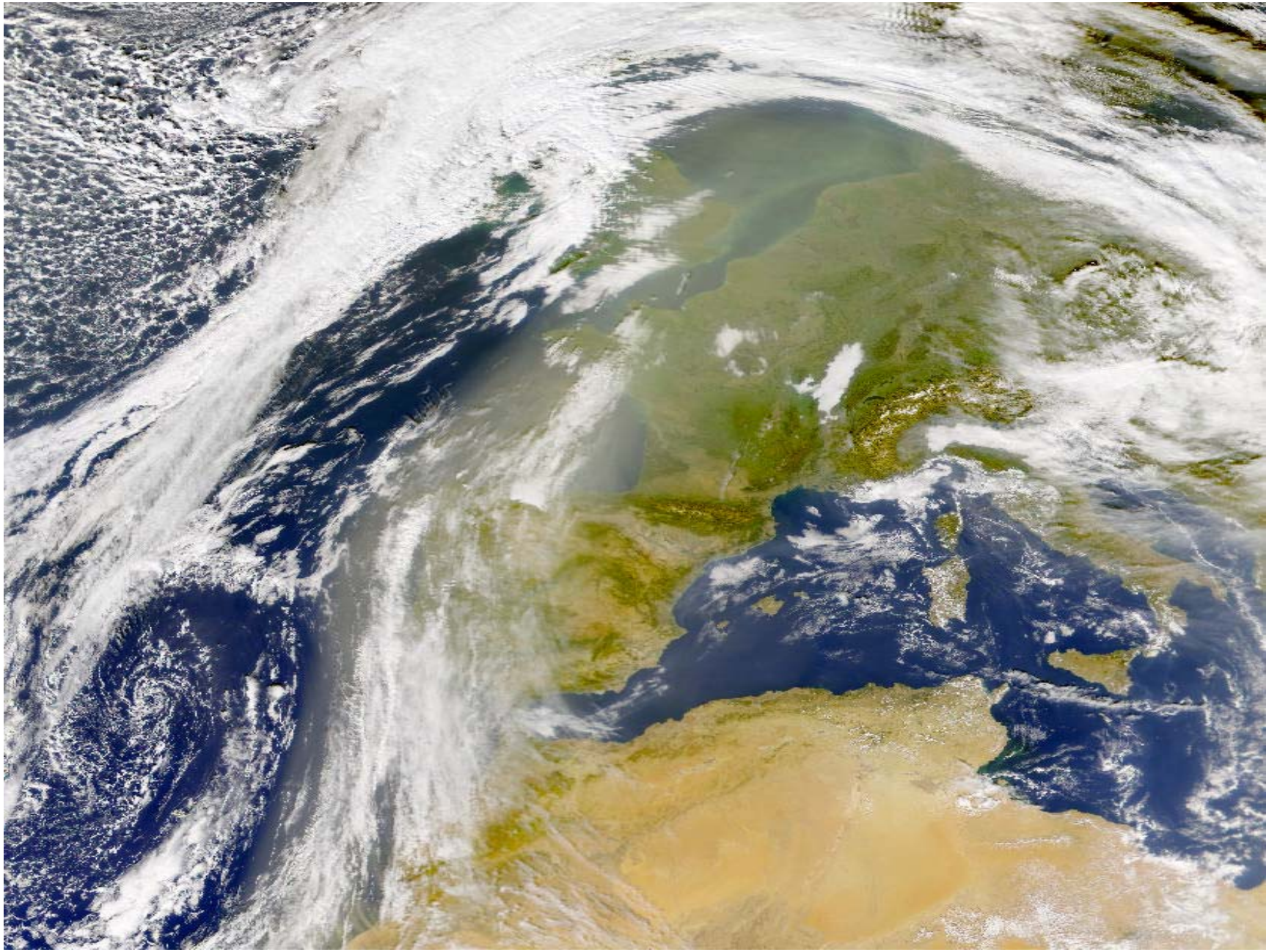
BIOGEOCHEMISTRY OF NUTRIENTS, TRACE METALS AND ORGANIC MICROPOLLUTANTS IN THE NORTH SEA

	Inorganics and generic organics	*Specific organics*
Atmosphere and precipitation	**UA (Van Grieken)** **Air-sea exchange of nutrients and inorganic micropollutants**	**UG (Van Langenhove)** **Biogeochemistry of organic micropollutants**
Aqueous phase	**VUB (Baeyens)** **Biogeochemistry of nutrients and trace metals**	
Solid phase	**ULB (Wollast)** **Biogeochemical behaviour of particulate trace elements**	



Subproject: Air-sea exchange of nutrients and inorganic micropollutants above the North Sea, contract MN/DD/10

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Micro and Trace Analysis Centre

University of Antwerp

Heavy metals (like Cd, Pb, Cu, Zn)
Nutrients (nitrogen limiting for eutrophication)

METHODOLOGY (and methodological improvements in this project):

-SAMPLING OF AEROSOLS, RAIN, GASES (optimisation of gas sampling with active denuders and passive diffusion tubes)

-ANALYSIS:

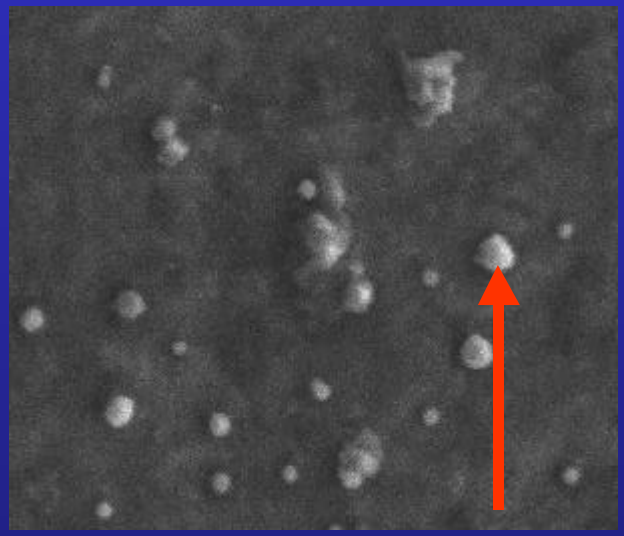
*bulk analysis by ion chromatography (IC) (optimisation of sample preparation), X-ray fluorescence, inductively-coupled plasma emission spectrometry (optimisation of analysis conditions), etc.

*single aerosol particle analysis by electron microprobe or microscope analysis (EMPA) ⇒ ⇒

Electron microprobe analysis on single environmental particles

- High resolution images, and elemental composition via X-ray emission analysis
- Very fast automated analysis
- Application of statistical data handling

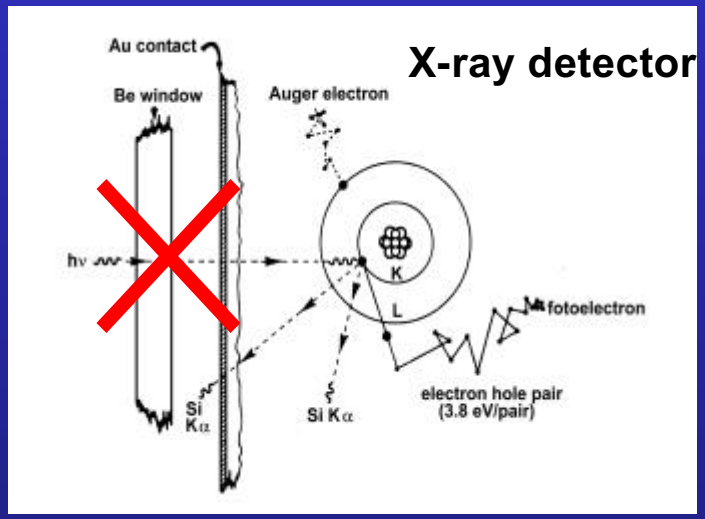
⇒ better source identification !

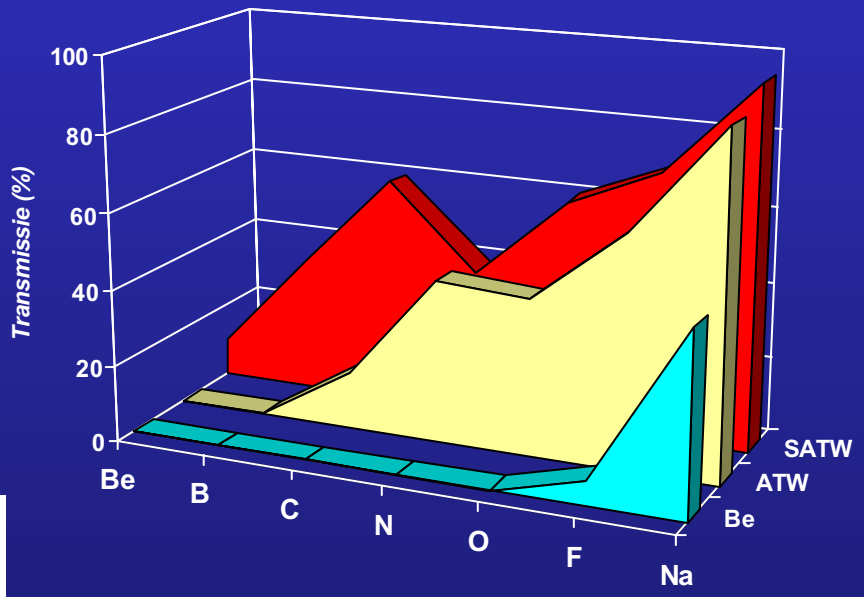


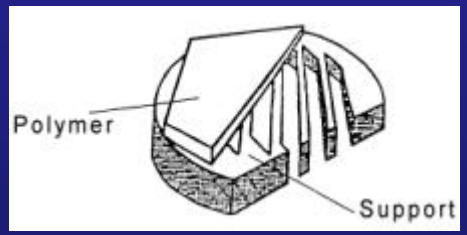
New methodologies for this project (see also poster):

- Liquid nitrogen cooling for volatile particles
- Variable energy electron beams for particle surface layer analysis
- Quantitative low-Z element analysis (like C, N)

Thin-window electron microprobe analysis for low-Z elements







Beryllium window (7.67 µm) replaced by a thin, polymer window (0.20 µm)

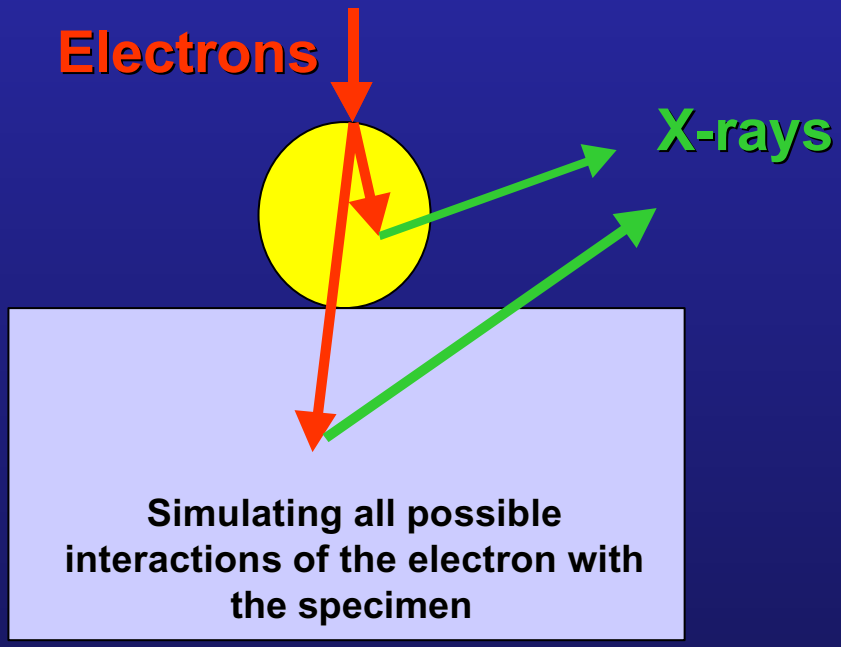
➔ Better transmission for X-rays of light elements like C, N

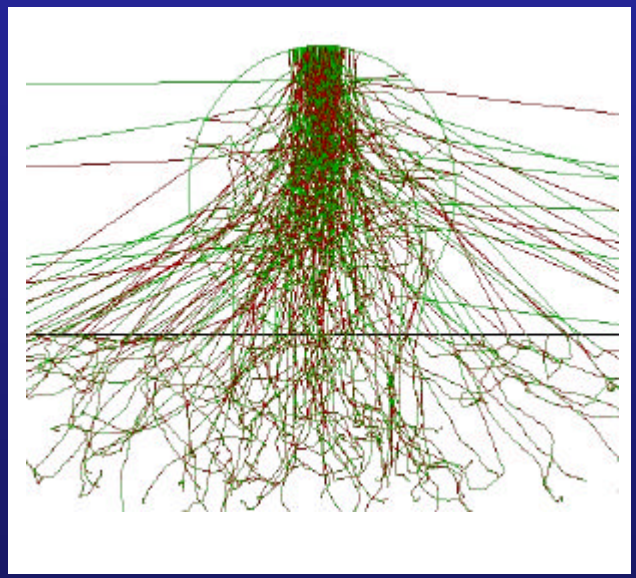
Thin-window electron microprobe analysis

What about quantification?

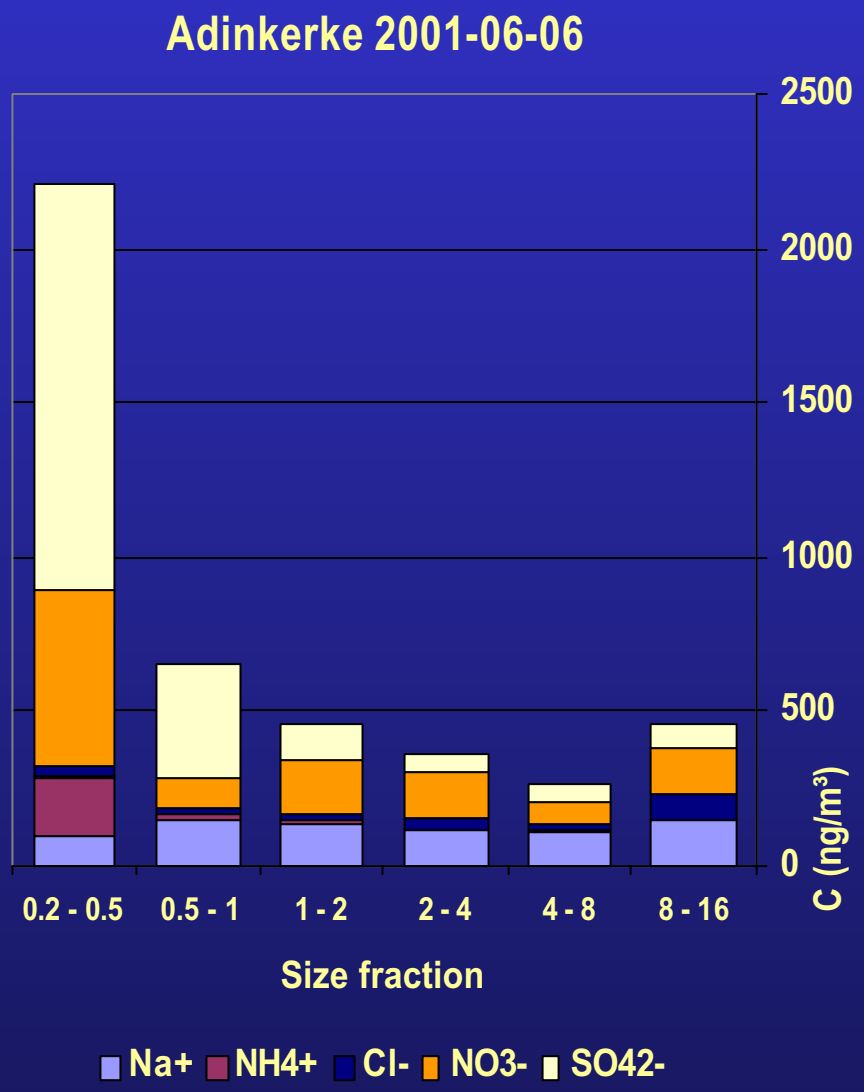
➔ low-Z element X-rays undergo enormous matrix effects !

SOLUTION: Iterative Monte Carlo simulations





Combination of IC and EMPA:



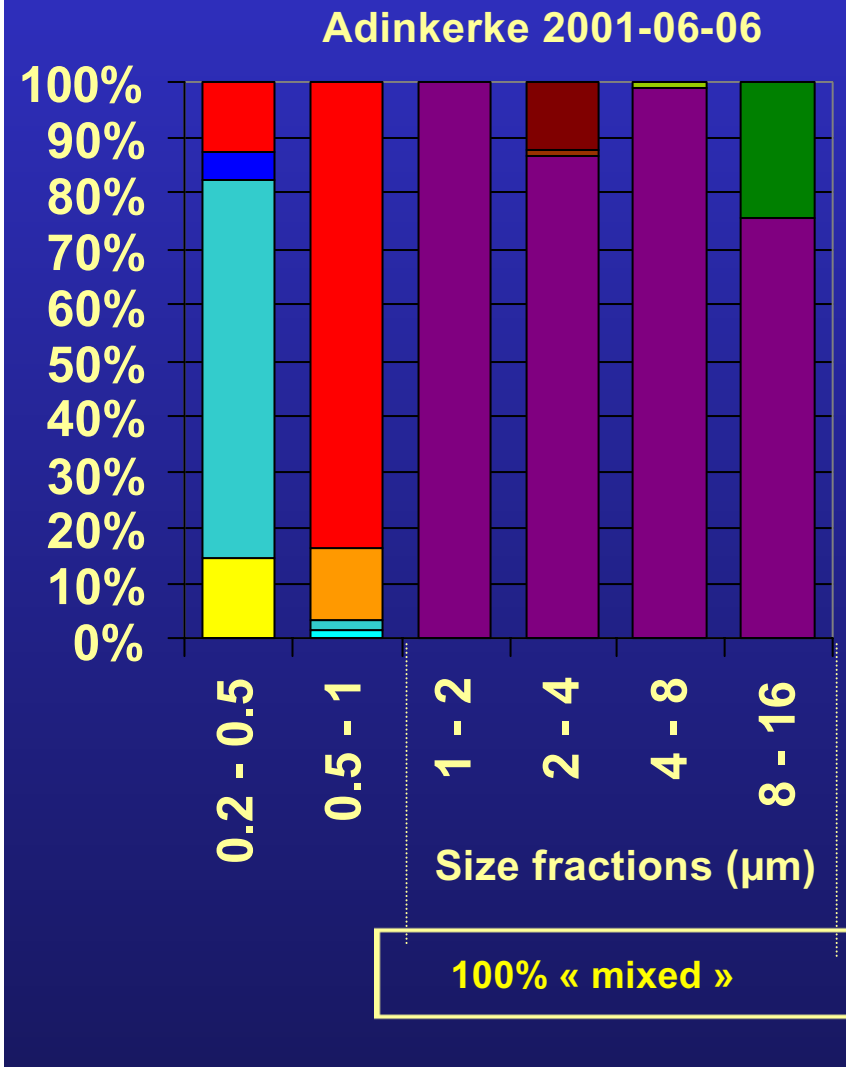
IC = Bulk ion analysis

- Quantitative (µg/m³) determination of different ions, but no speciation

BUT !

- Sulphate: sodium, ammonium, or calcium sulphate?
- Nitrate: sodium, ammonium or calcium nitrate?
- Ammonium: ammonium nitrate, sulphate or chloride?

Combination of IC and EMPA:



EMPA = Single particle elemental analysis (%)

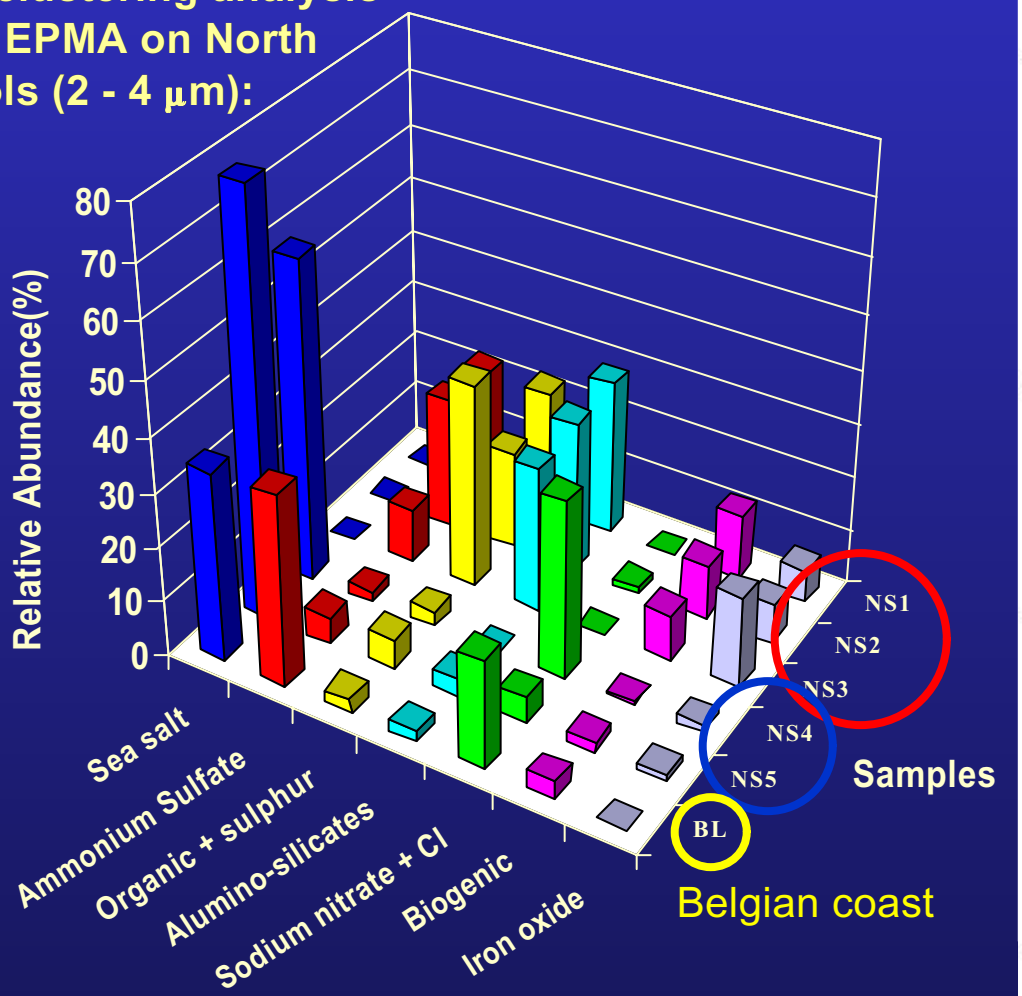
- Organic + S
- NH_4NO_3
- $(NH_4)_2SO_4$
- $NH_4NO_3 + (NH_4)_2SO_4$
- Na_2SO_4
- $NaCl + NaNO_3 + Na_2SO_4$
- *Mixed* $(Na/NH_4+Cl/NO_3/SO_4)$
- $CaSO_4$
- $CaSO_4$ + *Mixture*
- Aluminosilicates
- Alum.silic. + *Mixture*

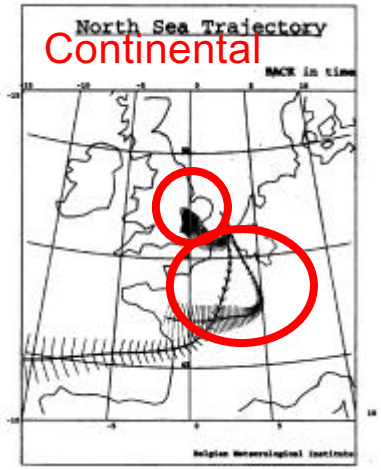
Combination with IC

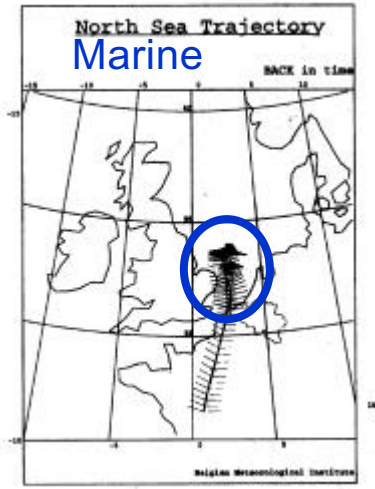
* shows « mixed » to be: 25% NO_3^-, 3% NH_4^+, etc.
* yields µg/m³

Thin-window EMPA: North Sea aerosols

Results of clustering analysis after low-Z EPMA on North Sea aerosols (2 - 4 µm):

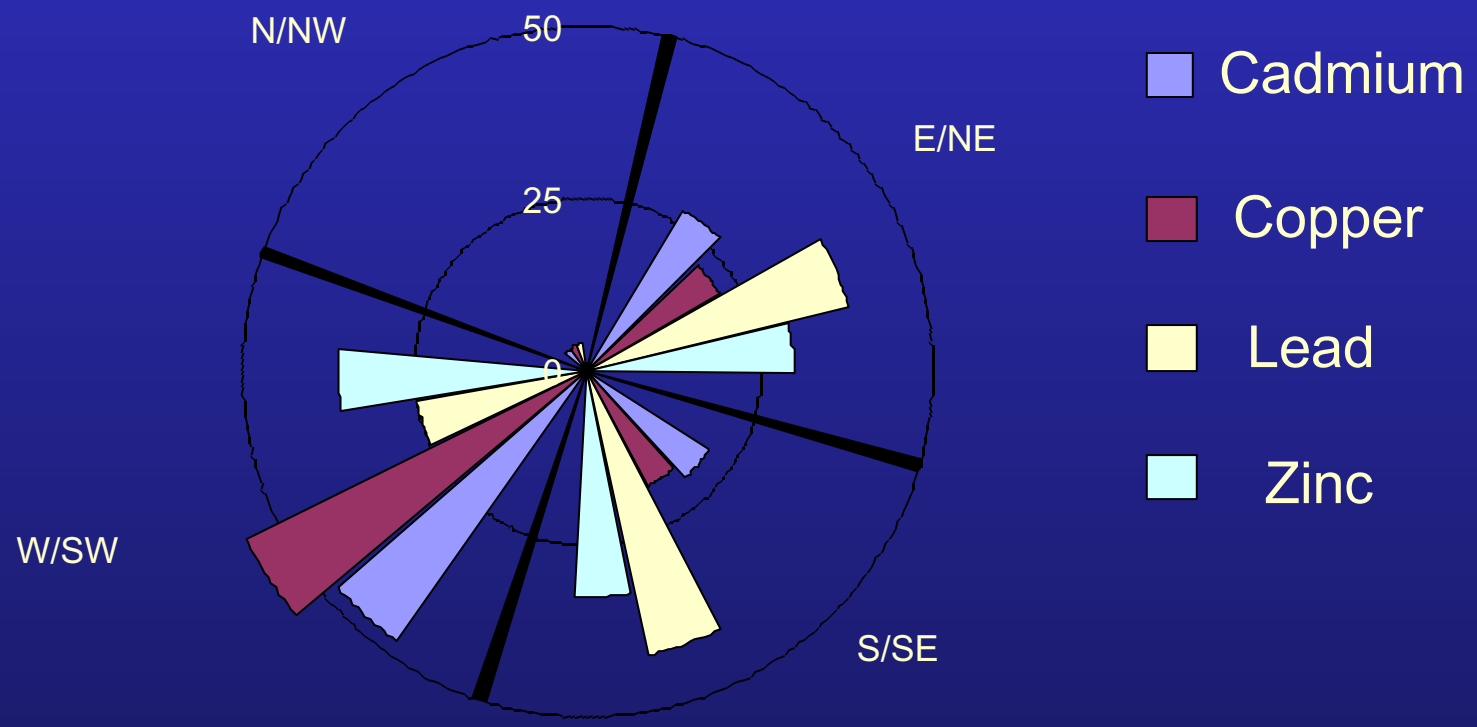






Influence of air mass origin on heavy metals

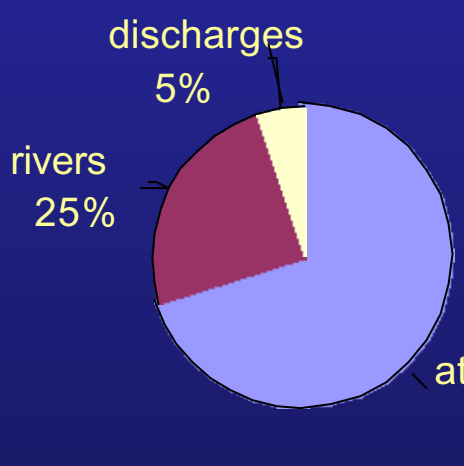
% Deposition as a function of wind direction



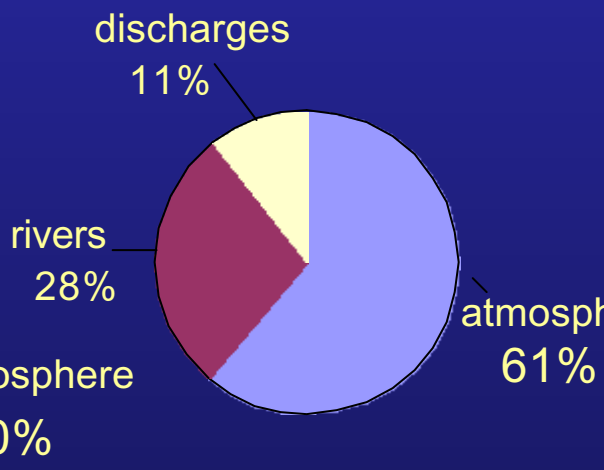
% Atmospheric contributions

in Southern Bight in 1995, for:

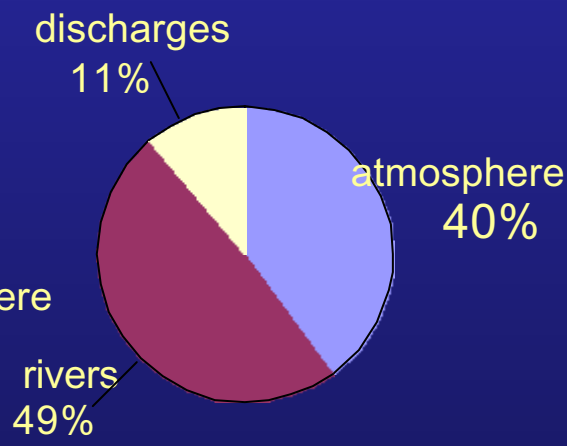
Lead



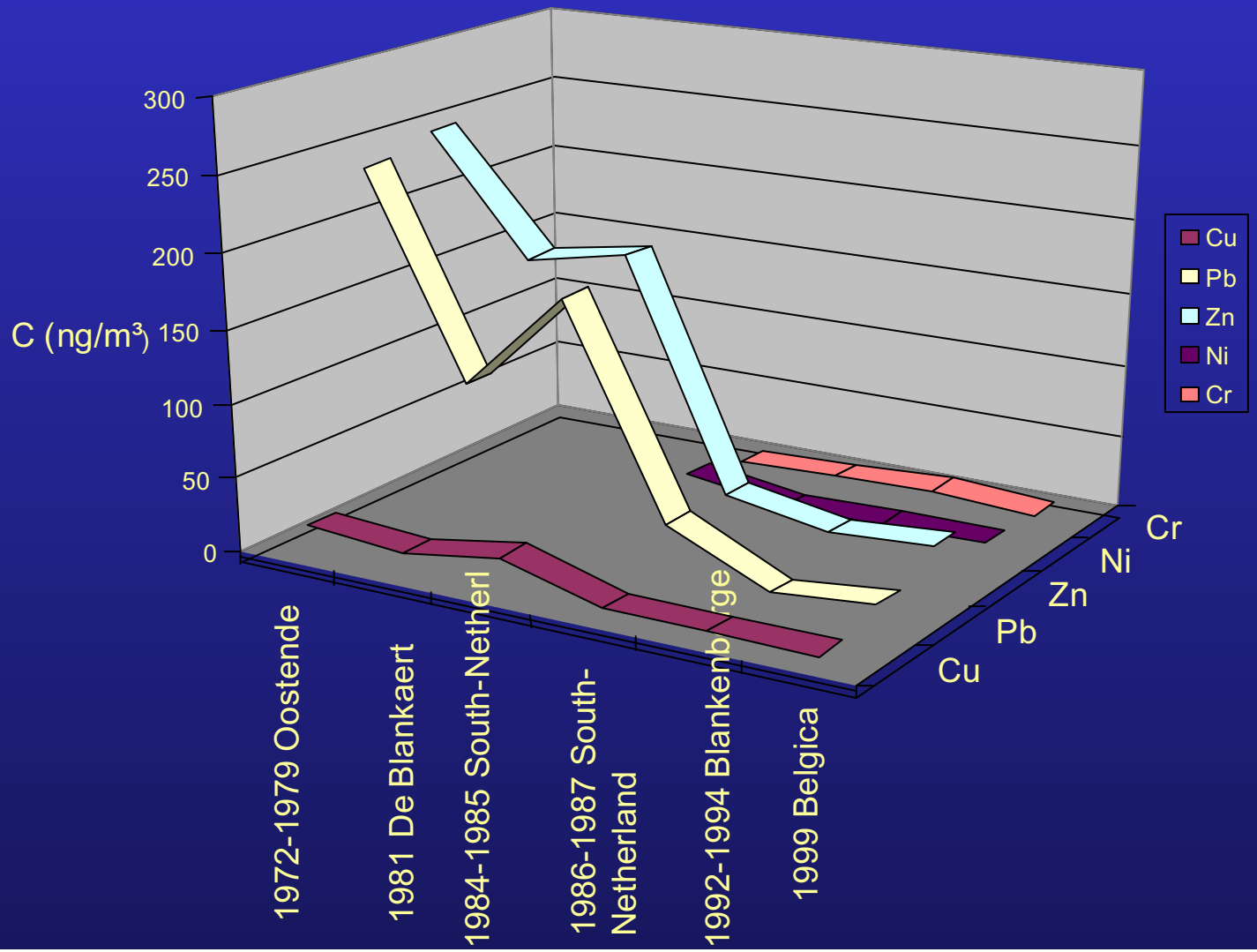
Cadmium



Copper



Trends for heavy metals with time along Belgian-Dutch coast (cfr. also QSR)



Nutrients:
Atmospheric nitrogen compounds

Sources

- Nitrogen Oxides
  ⇒ Nitrates

53%

22%

- Ammonia
  ⇒ Ammonium salts

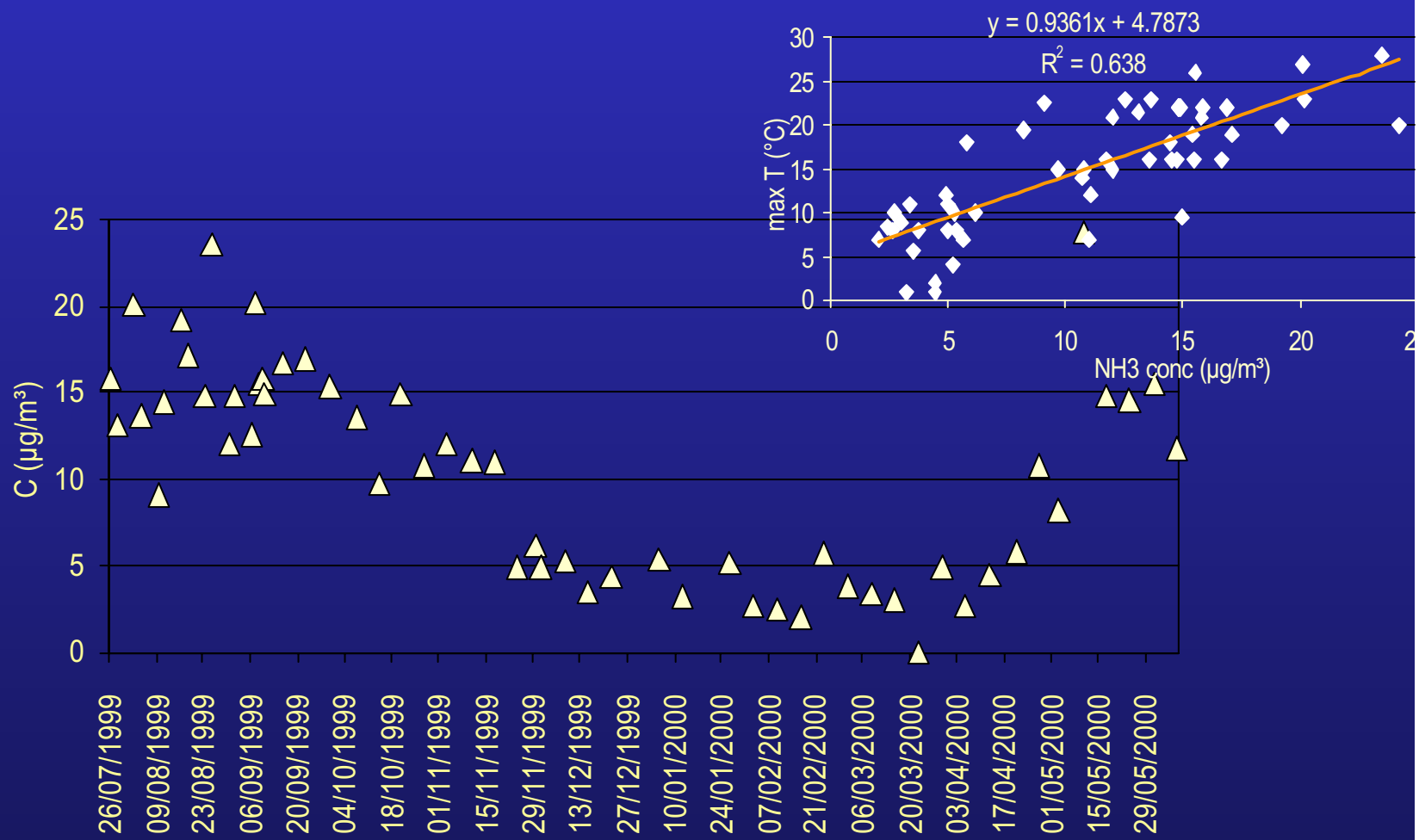
98%

- Organic Nitrogen ?

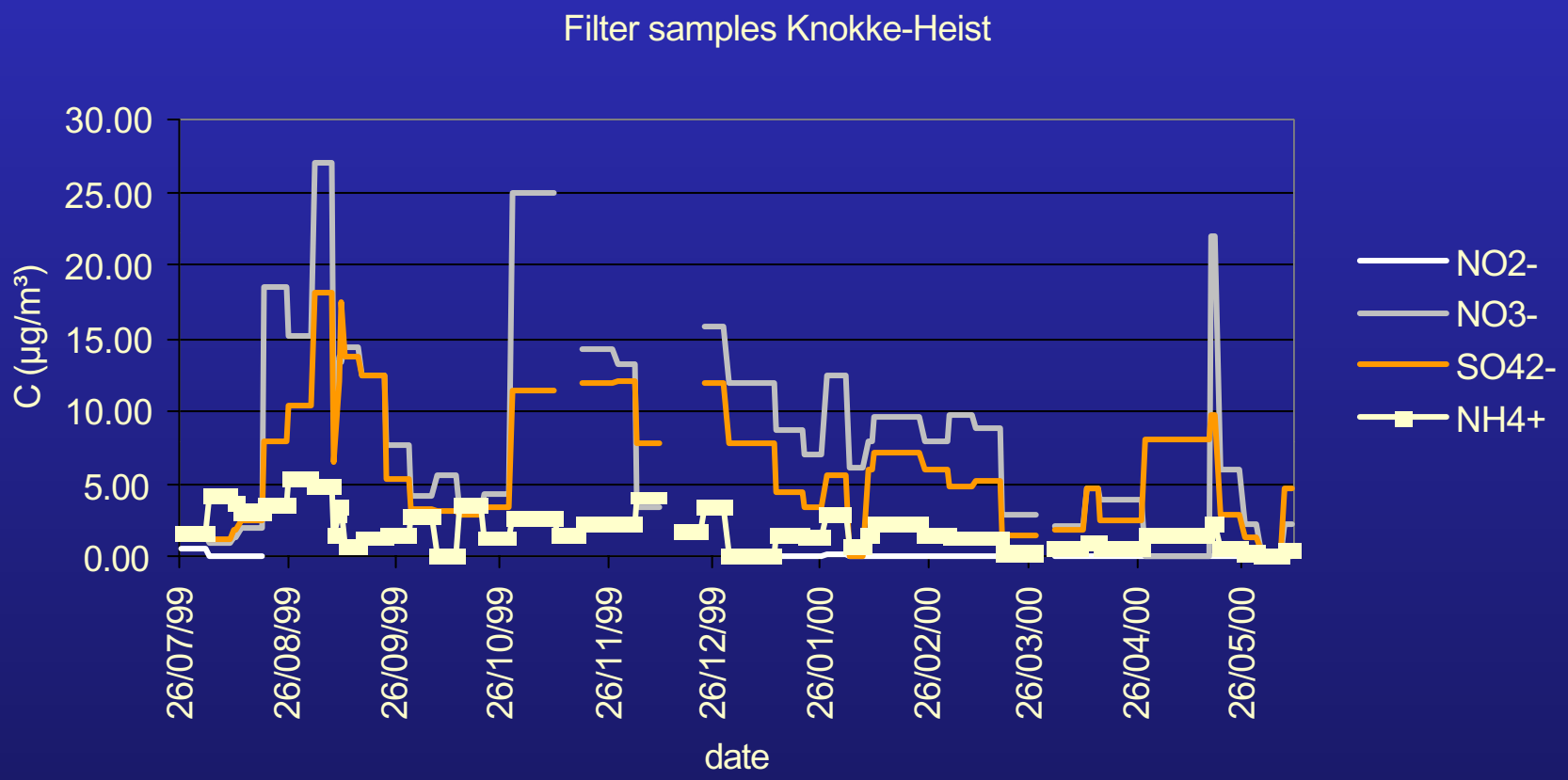
⇒ Limiting components for algae growth in the North Sea under certain conditions ?

Concentrations of ammonia at the Belgian coast

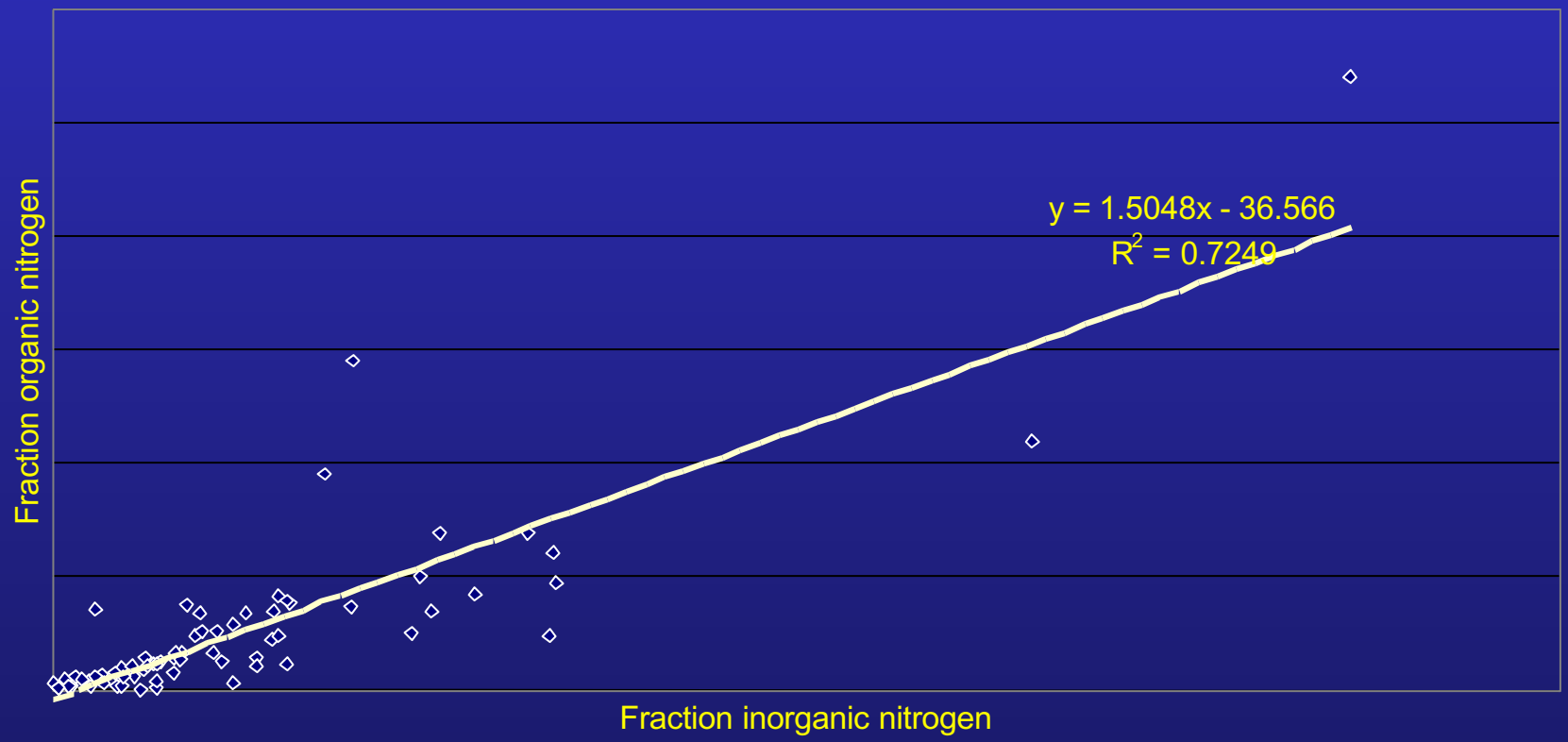
(depend on agriculture activities and temperature; highest values of the world)



Aerosol concentrations at the Belgian coast
(highly variable but with wind direction patterns)



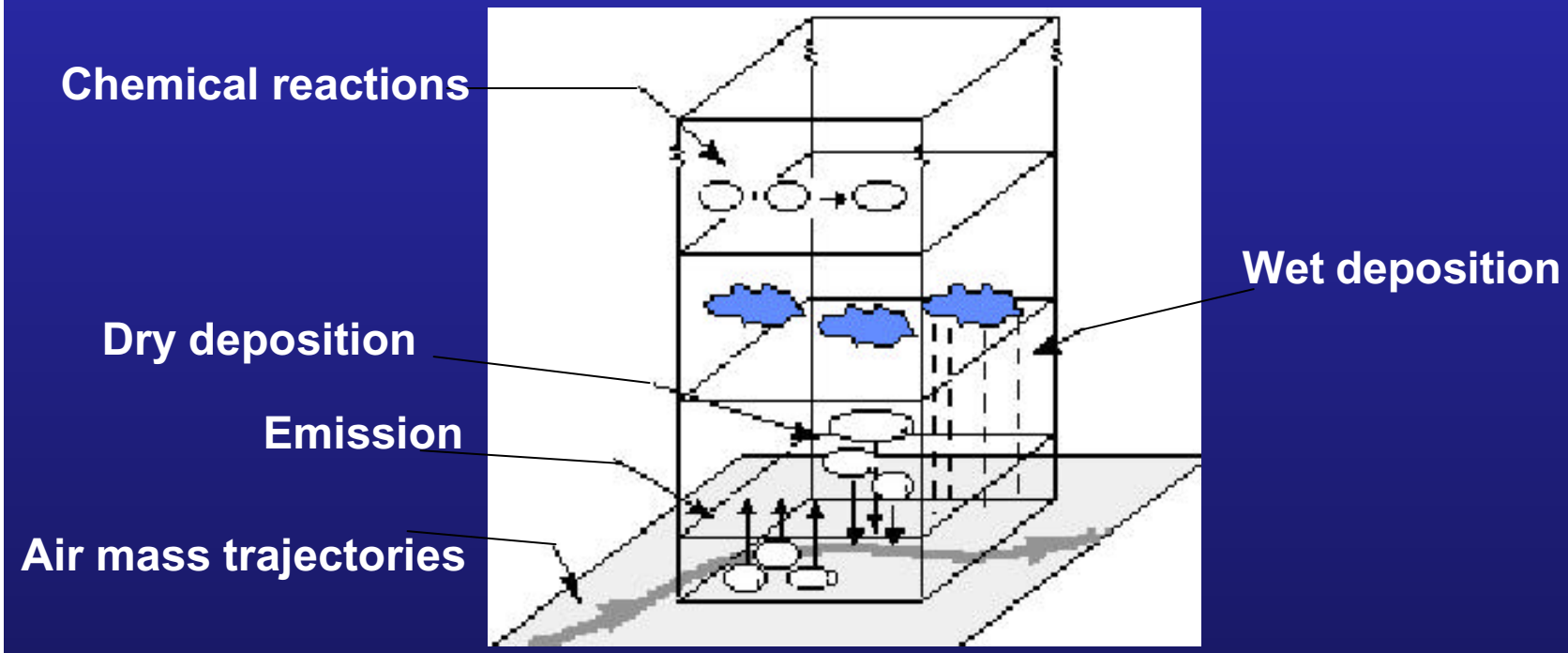
Importance of (dissolved) organic nitrogen



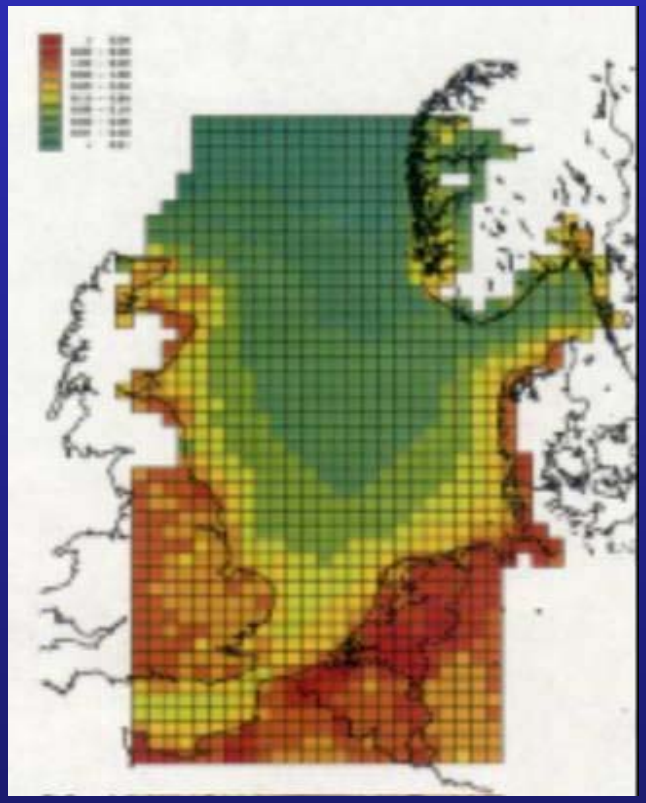
Organic fraction = 1.5 x inorganic fraction!

Flux calculations via: Modelling

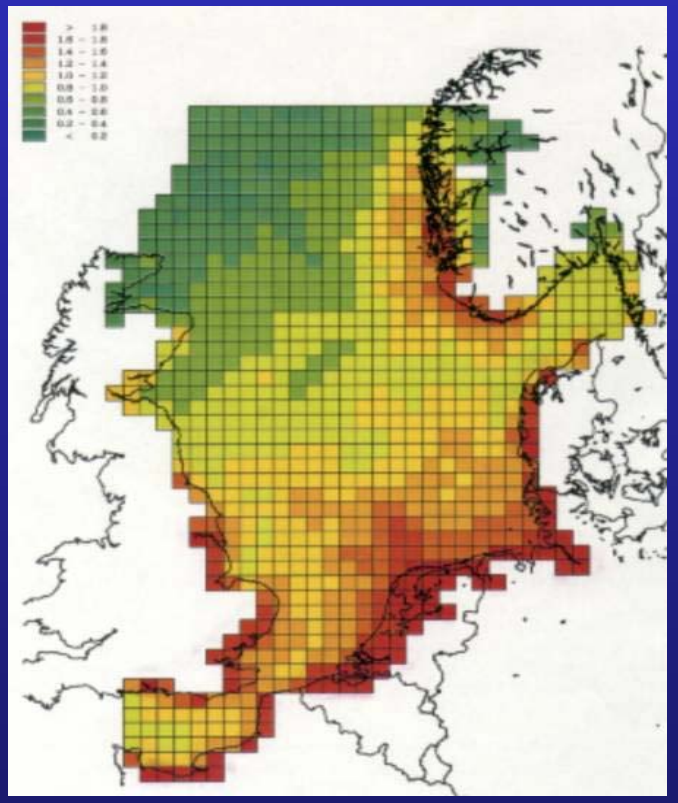
- Atmospheric and Chemical DEPosition model (ACDEP) = f(meteo, conc., chemcial reactivity, aerosol particle size, etc.)



Atmospheric N-compounds above the North Sea



NH_3-concentrations
(from >5 to <0.02 µg N/m³)



Total N-deposition (mostly wet)
(from >1.8 to <0.2 ton N/km²/y)

CONCLUSIONS

- Atmospheric deposition of heavy metals was important for the North Sea
- But: reduction of emissions over land resulted in significant improvements
- Nutrients are a newer threat
- Very high (wet) deposition of ammonium

TO BE DONE:

- Further interpretation of data
- Comparison of fluxes (nitrate, ammonium) with river supply (cfr. QSR for total North Sea); risk assessment
- Validation of models for Southern Bight

FUTURE: Organic nitrogen !!!

Project biogeochemistry of organic compounds in the North Sea (MN/DD/012)

- method validation
- quality assessment

- southern North Sea
- Scheldt estuary

Physical-chemical behaviour

of VOCs in the North Sea

Selection of target compounds from the 3rd International Conference on the Protection of the North Sea

PRIORITY COMPOUNDS

- → Mercury
- → Cadmium
- → Copper
- → Zinc
- → Lood
- → Arsenic
- → Chrome
- → Nickel
- → Drins
- → HCH
- → DDT
- → Pentachlorophenole
- → Hexachlorobenzene
- → Hexachlorobutadiene
- → Tetrachlorormethane
- → Chloroform
- → Trifluralin
- → Endosulfan
- → Simazine
- → Atrazine
- → Tributyltincompounds
- → Azinfos-ethyl
- → Azinfos-methyl
- → Fenitrothion
- → Fenthion
- → Malathion
- → Parathion
- → Parathion-methyl
- → Dichloorvos
- → Trichloorethylene
- → Tetrachloroethylene
- → Trichlorobenzenes
- → 1,2-Dichloroethane
- → 1,1,1-Trichloroethane
- → Dioxines

EXTRA PRIORITY COMPOUNDS

ALKANES

e.g. 1,1-Dichloroethane
Dichloromethane
1,1,2-Trichloroethane

ALKENES

e.g. 3- Chloropropene
1,1-Dichloroethene
1,2-Dichloroethene

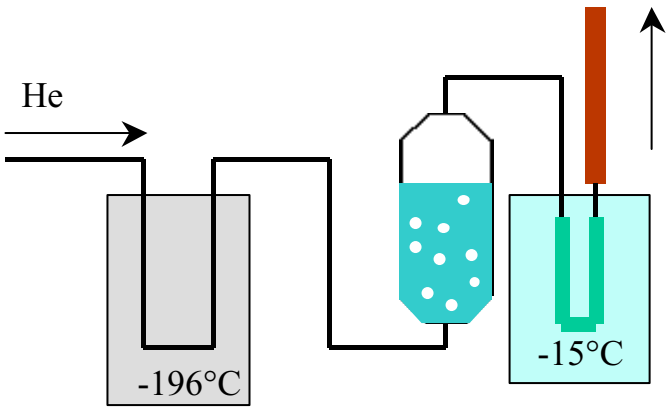
BENZENES

e.g. Benzene
Ethylbenzene
Chlorobenzene

TOLUENES en XYLENES

e.g. Toluene
m/*p*/*o* - Xylene

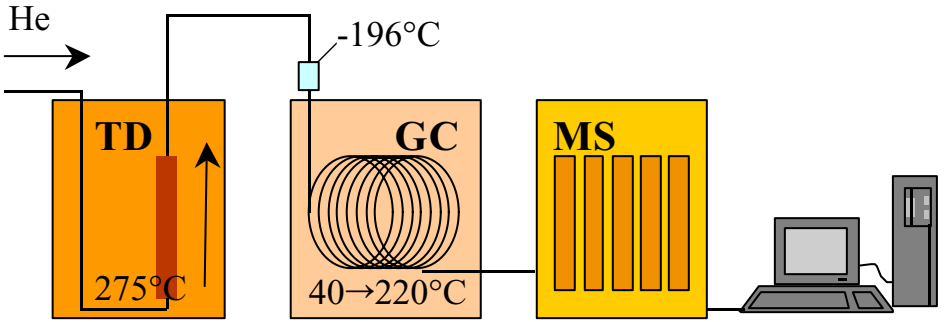
Determination of 27 VOCs in marine water samples



off-line purge-and-trap

- V_{aq} = 60 ml; T_{aq} = 45°C; Q = 50 ml min^{-1}; t = 20'
- Tenax TA/Carboxen 1000/Carboxen 1001

on-line TD/GC-MS

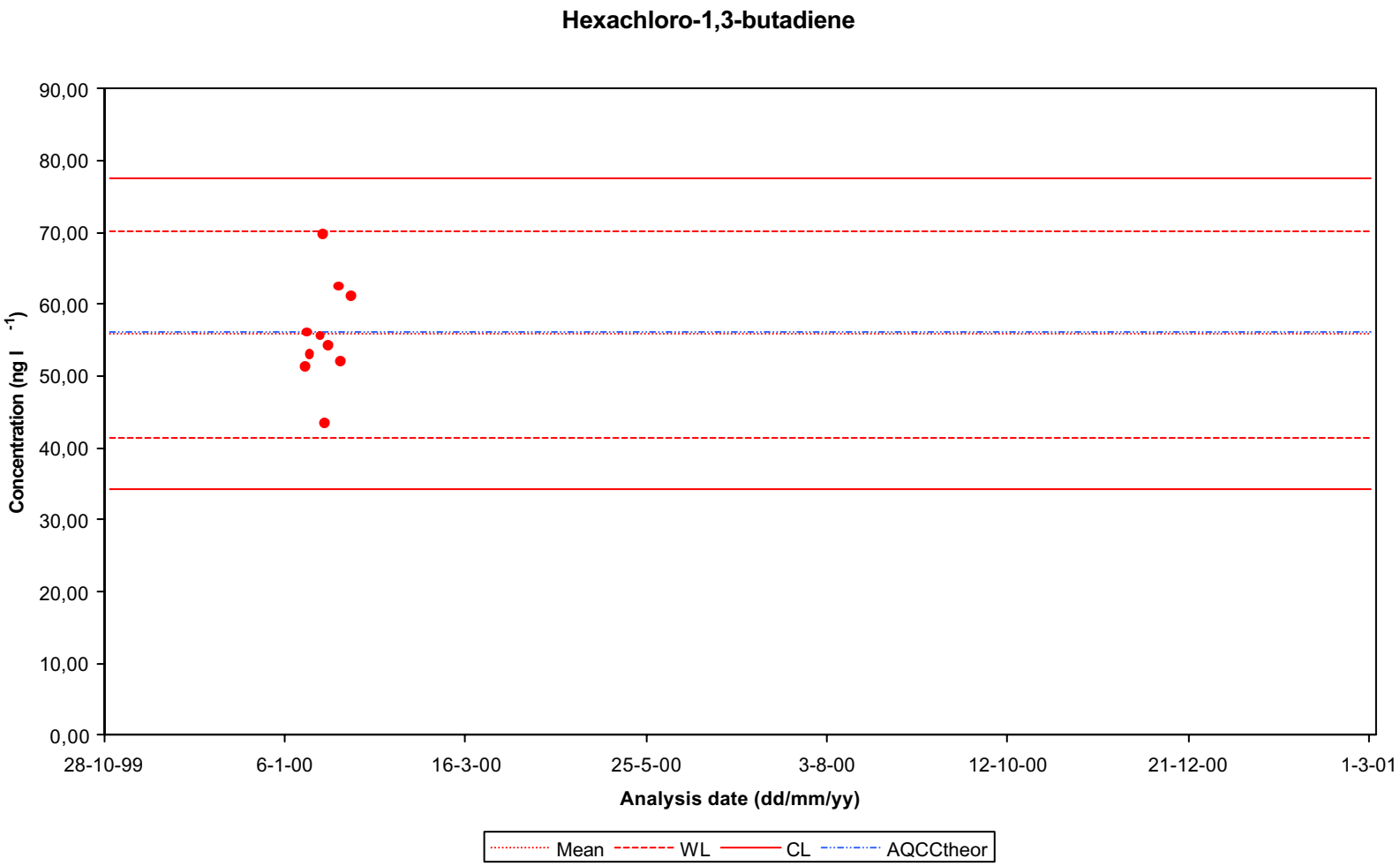


Method validation and quality assurance

- The analytical method was found reliable for 25 VOCs at a concentration level of 26 - 67 ng l^{-1}, except for dichloromethane and benzene due to high background levels

- Quality assessment and quality control by QUASIMEME (Quality Assurance of Information in Marine Environmental Monitoring Programmes in Europe)

Analytical quality control chart



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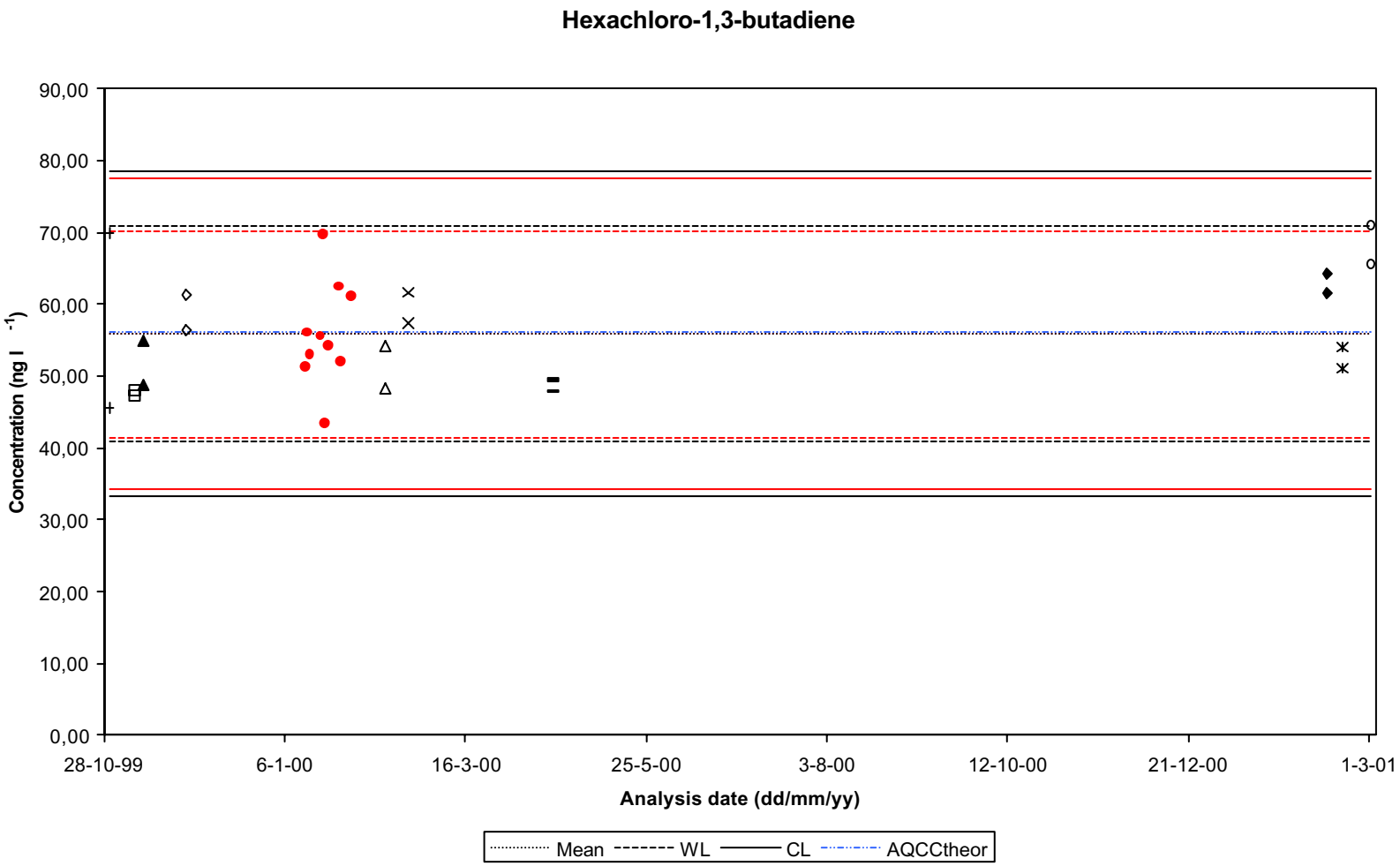
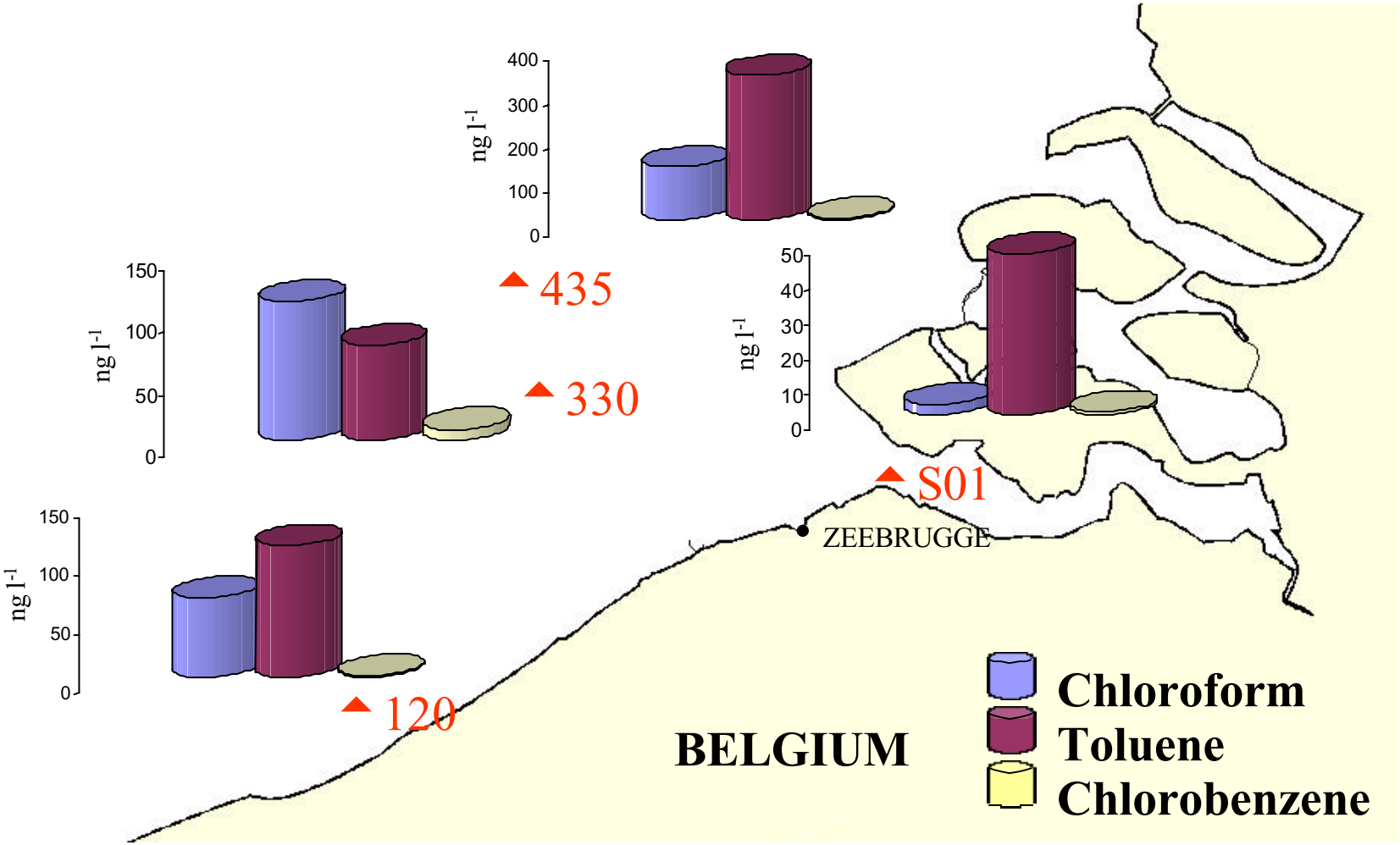
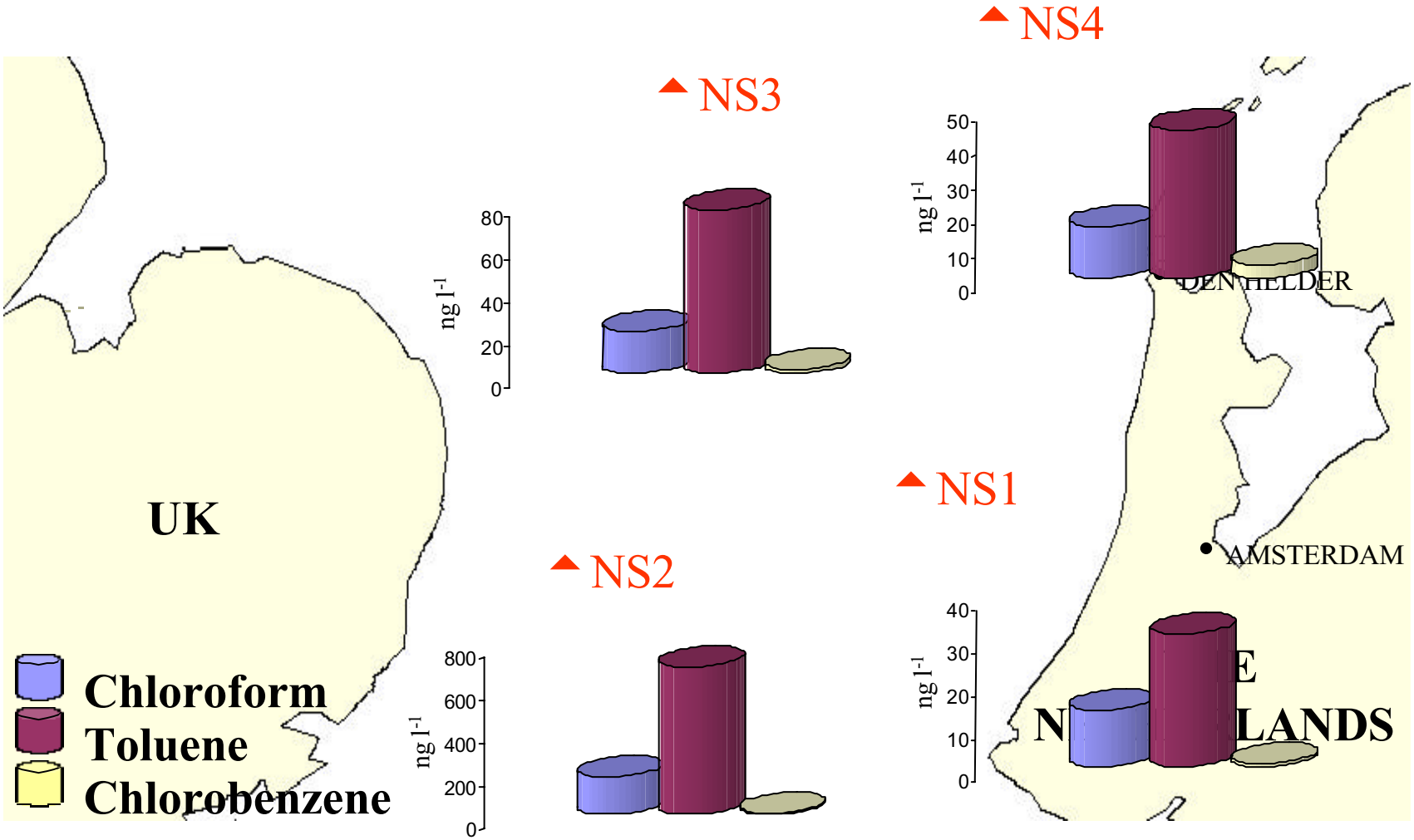


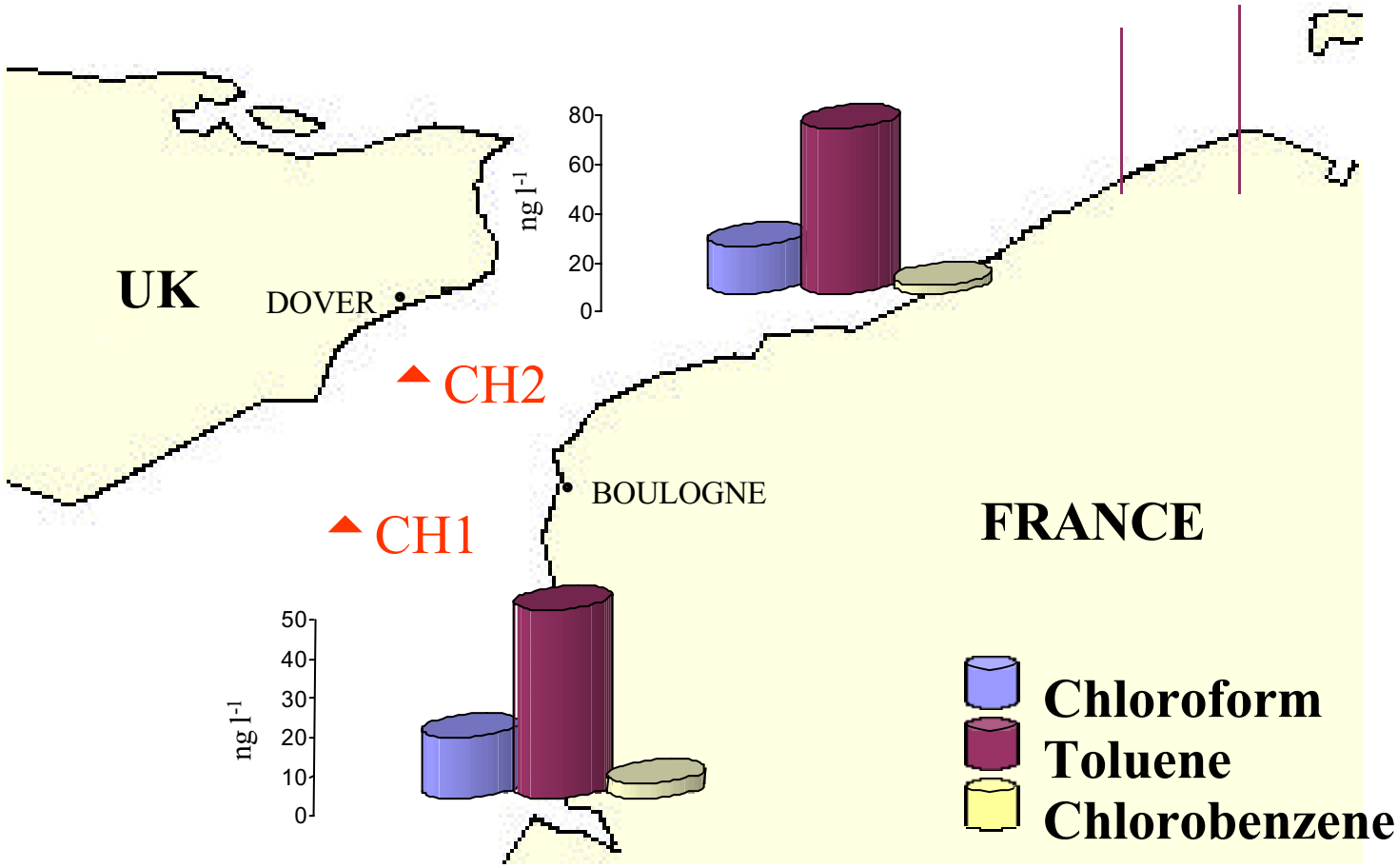
Belgian Continental Platform (October 1998)



Southern North Sea (October 1998)



The Channel (October 1998)



Concentration-profile of chloroform in the Scheldt estuary (October 1998)