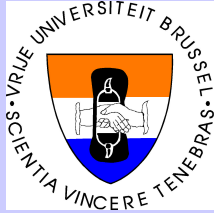




BIOGEOCHEMISTRY OF NUTRIENTS, TRACE METALS AND ORGANIC MICROPOLLUTANTS IN THE NORTH SEA.

SUBPROJECT: BIOGEOCHEMISTRY OF NUTRIENTS AND TRACE METALS IN THE NORTH SEA.

✉ **Vrije Universiteit Brussel**
Dienst analytische en milieuchemie
Prof. Dr. W. Baeyens, S. De Galan, M. De Gieter,
Dr. M. Leermakers, Dr. N. Brion



Objectives:

▶▶ **our research : biogeochemical cycling in aquatic systems**

T North Sea

T Scheldt estuary

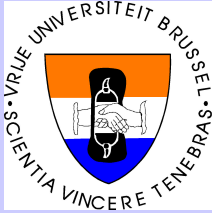
T Scheldt and tributaries

T marine biota in the North Sea

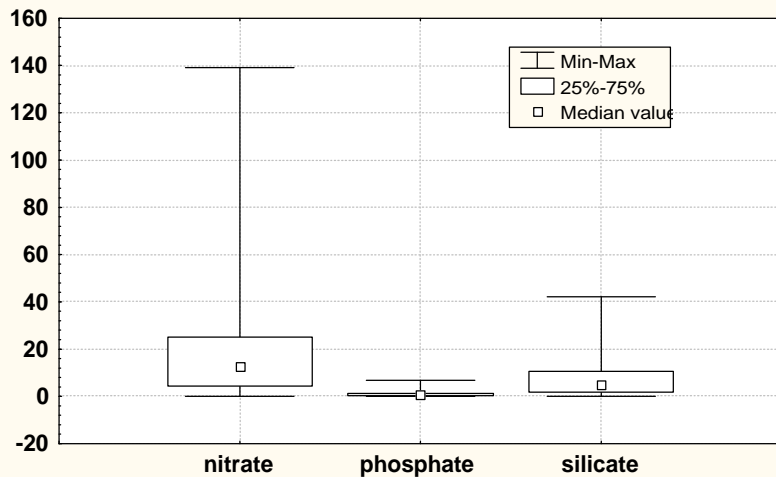
- quantification and qualification of the nitrogen cycle
- study of dissolved trace metals in the water column
- special attention for biogeochemical cycling of Hg and As

North Sea:

spatio-temporal trends in nutrient concentrations

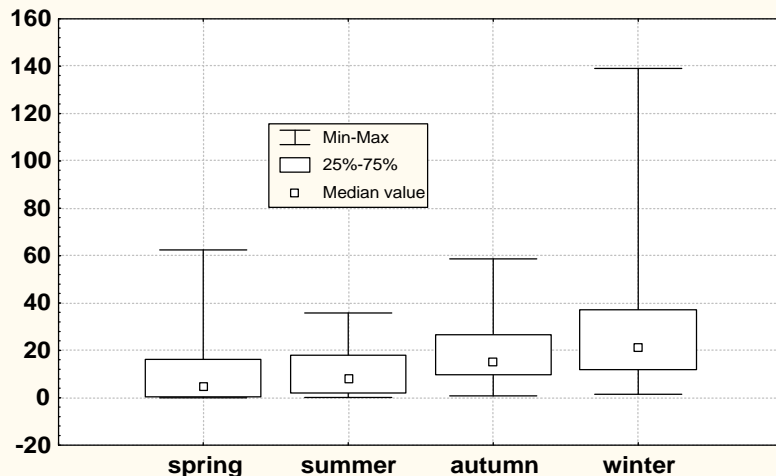


Variation in Nutrient concentrations in the Southern Bight of the North Sea



- ◆ nitrate concentration: shows high variation
 - average : 18.3 μM - range: DL - 139 μM
- ◆ phosphate concentration :
 - rather low throughout the year
 - average: 0.8 μM
- ◆ Silicate concentration:
 - average: 8 μM - range: DL -32 μM

Seasonal variation of nitrate in the Southern Bight of the North Sea



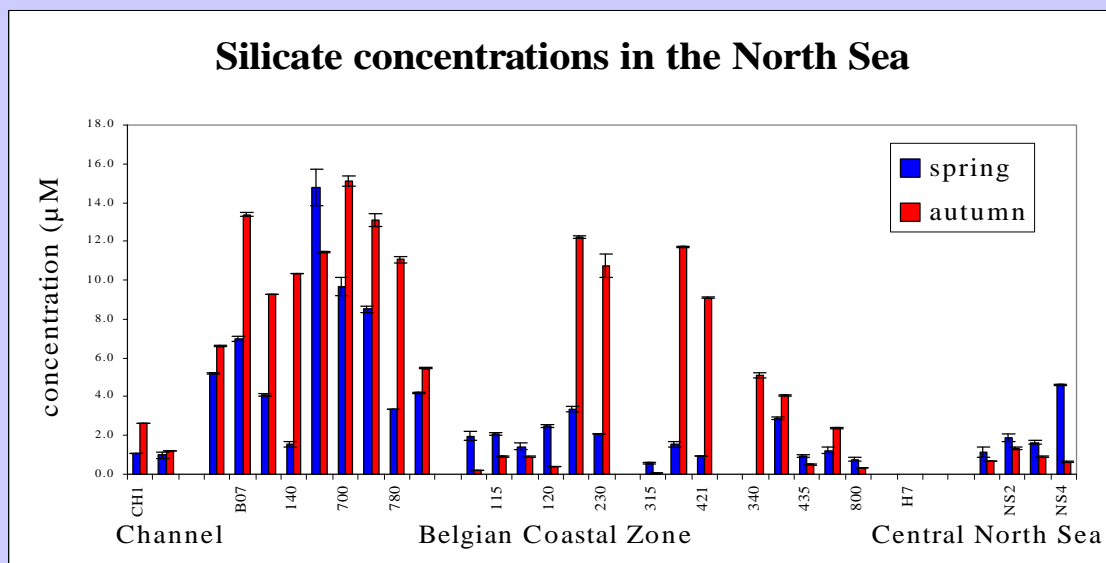
- ◆ temporal behavior: -example: nitrate
 - clear seasonal trend : highest [nitrate] in winter, lowest in spring and summer
 - ▶▶ reconstitution of winter stock
 - ▶▶ biological activity



North Sea:

spatio-temporal trends in nutrient concentrations

Example : dissolved silicate



◆ Low salinity zone is strongly influenced by the Scheldt outflow and coastal inputs

▶▶ significantly higher nutrient pools compared to the high salinity zone

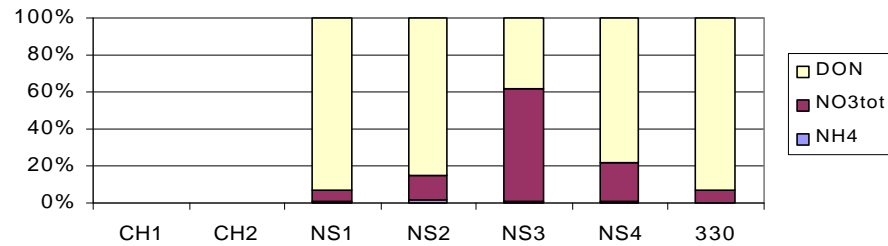
◆ Channel and central North Sea: low nutrient pools

▶▶ clear seasonal and spatial variation in nutrient concentrations in the North Sea

Nitrogen pools in the North Sea

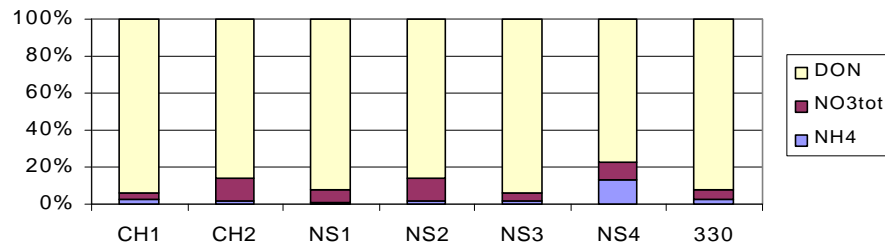


spring



◆ The ammonium pool is almost negligible

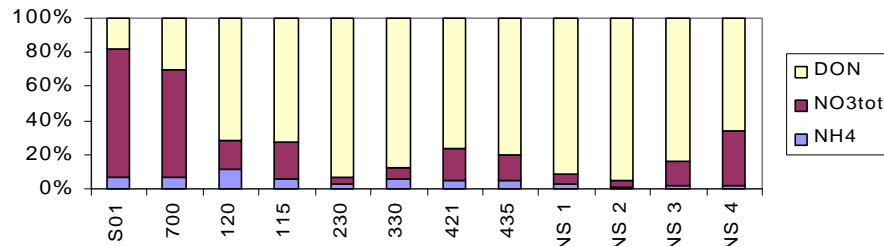
summer



◆ Most of the time: the dissolved organic nitrogen pool (DON) is dominant

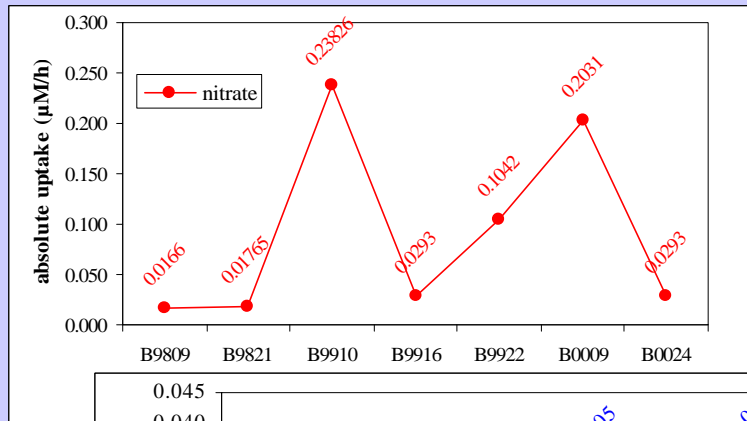
◆ The DON pool can account for up to 95% of the N pool

autumn



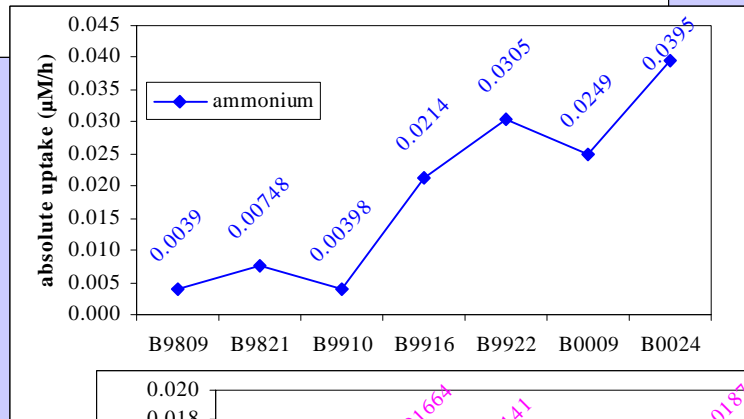
▶▶ The DON pool in the North Sea plays an important role in the nitrogen cycle

Absolute uptake rates

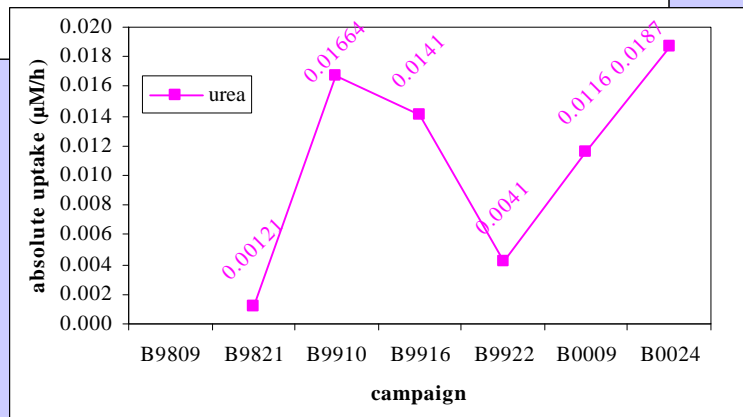


◆ selected station: 330

◆ Nitrate uptake rates are higher than those for ammonium and urea



◆ - highest nitrate uptake in spring
- highest ammonium uptake at the end of summer



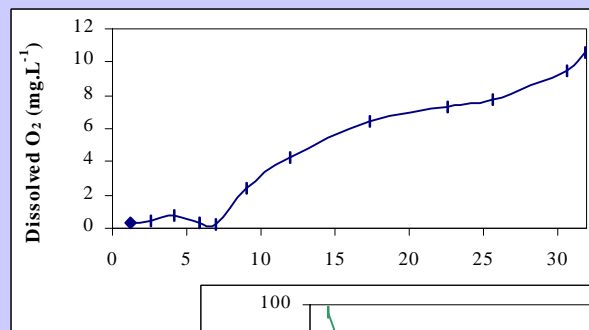
◆ low ammonium uptake rates

◆ lowest urea uptake rates

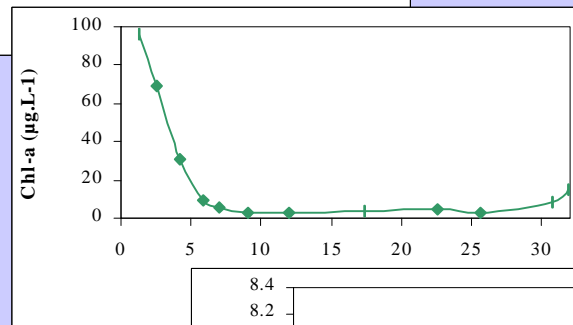
The Scheldt estuary:

The Scheldt receives high amounts of waste (mostly untreated)

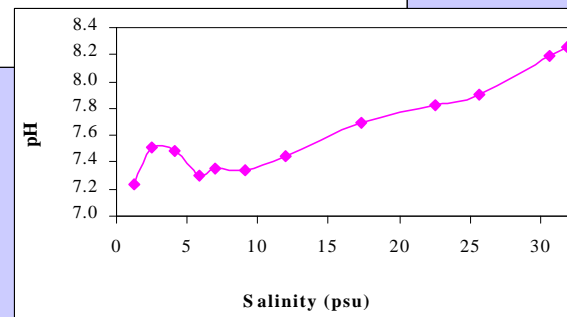
► causes high microbial activity and anoxic conditions upstream



u oxygen depletion



u high chlorophyll-a levels

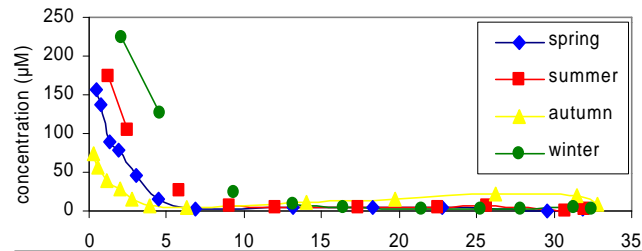


u shift to lower pH

gradients of O₂, pH and ionic strength influence mass transport to the sea

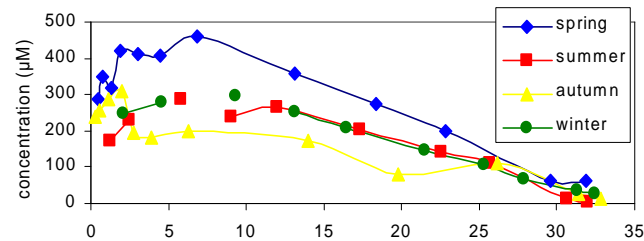
Nutrient distribution in the Scheldt estuary

ammonium in the Scheldt estuary



◆ Trend in NH_4 significantly related with oxygen depletion

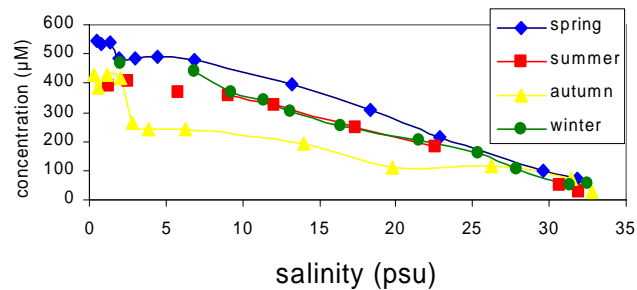
nitrate in the Scheldt estuary



◆ nutrient concentrations are very high

◆ decreasing concentrations with increasing salinity

TDN in the Scheldt estuary



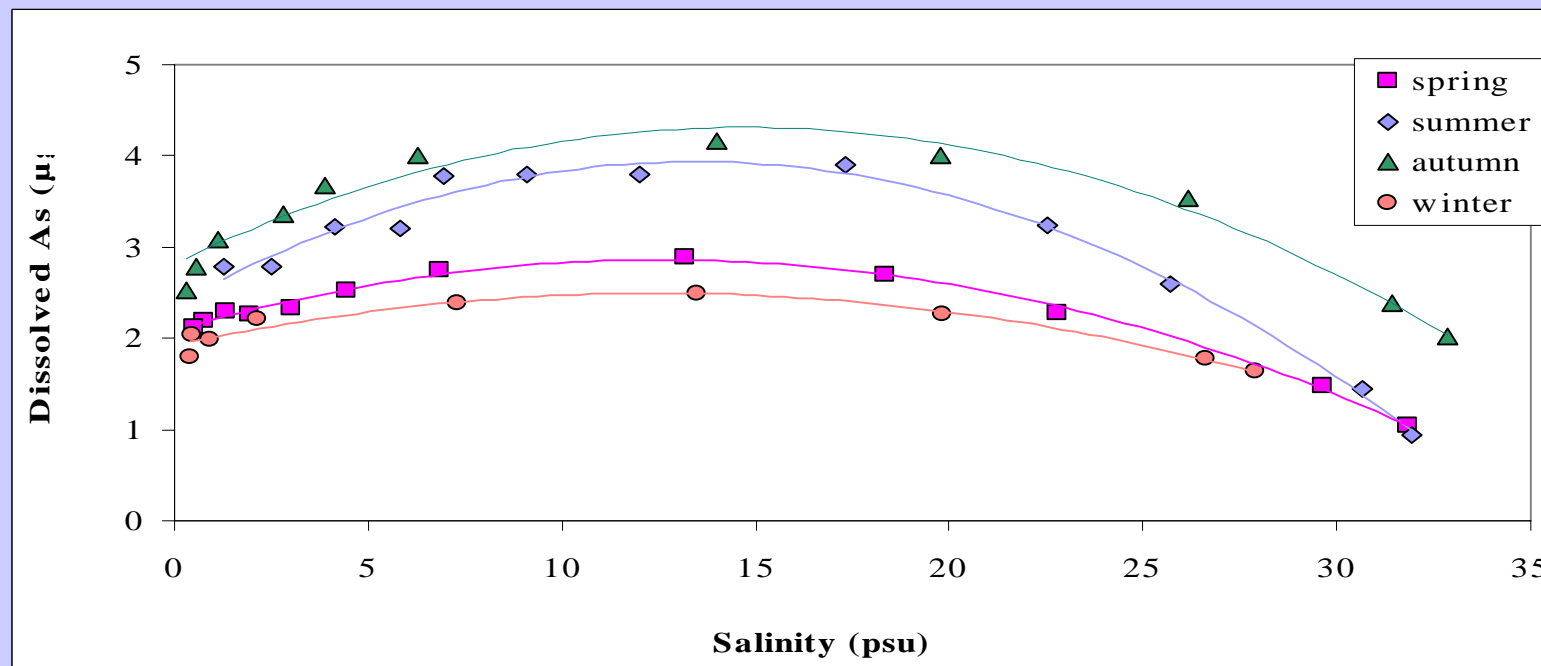
◆ longitudinal profile has a linear shape

Biogeochemical behavior of redox sensitive trace elements

Example : dissolved As-transport

- longitudinal profile has a convex shape

- ▶ suggests strong mobilization at freshwater/ salt water interface
- ▶ indicates influence of biological activity
- ▶ evidence was also found for influence of Fe and Mn redox chemistry





Marine Biota :

- 25 species of seafish and shellfish were investigated for total Hg and As

BUT : Hg and As occur in a wide range of species, several of them more toxic than others

THUS : speciation needed !

▶▶ speciation techniques were developed to be able to distinguish between :

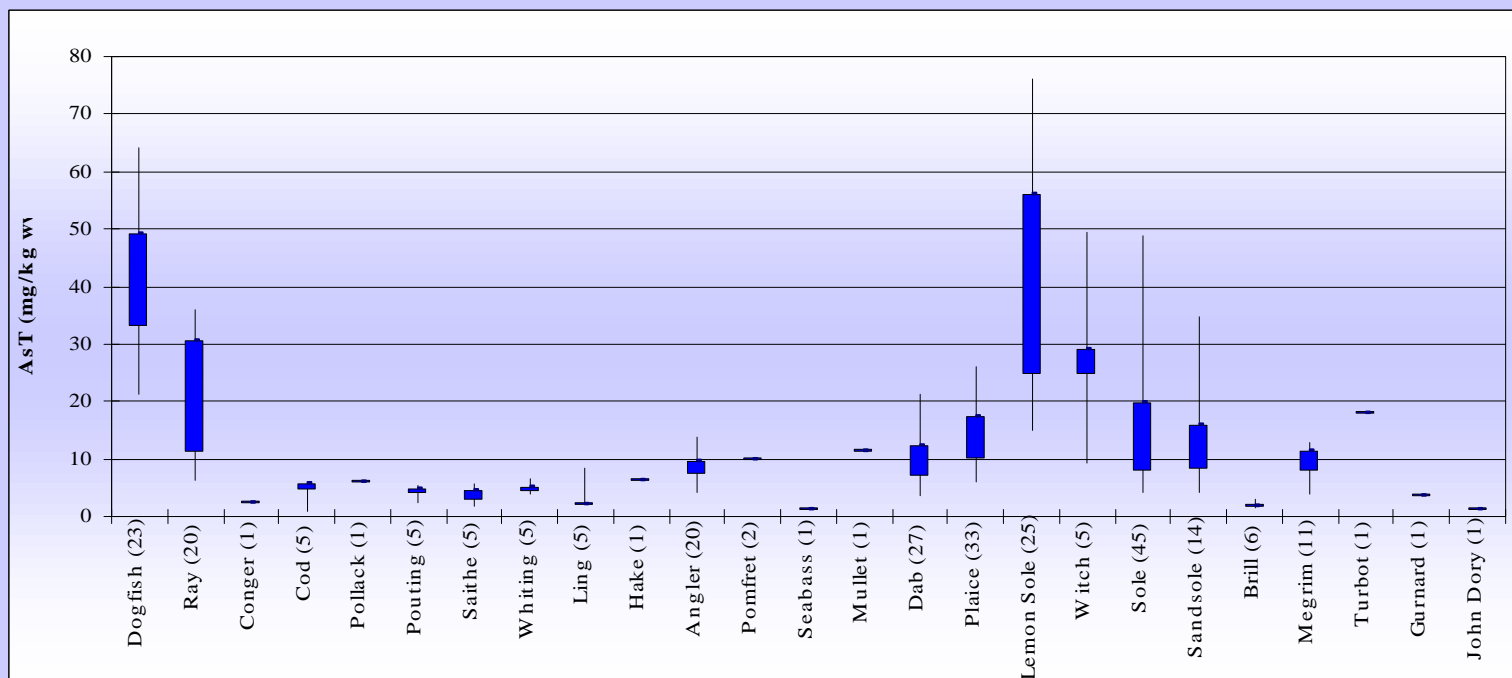
- total Hg and monomethyl Hg

- total As and arsenite, arsenate, monomethylarsonic acid, dimethylarsinic acid and arsenobetaine



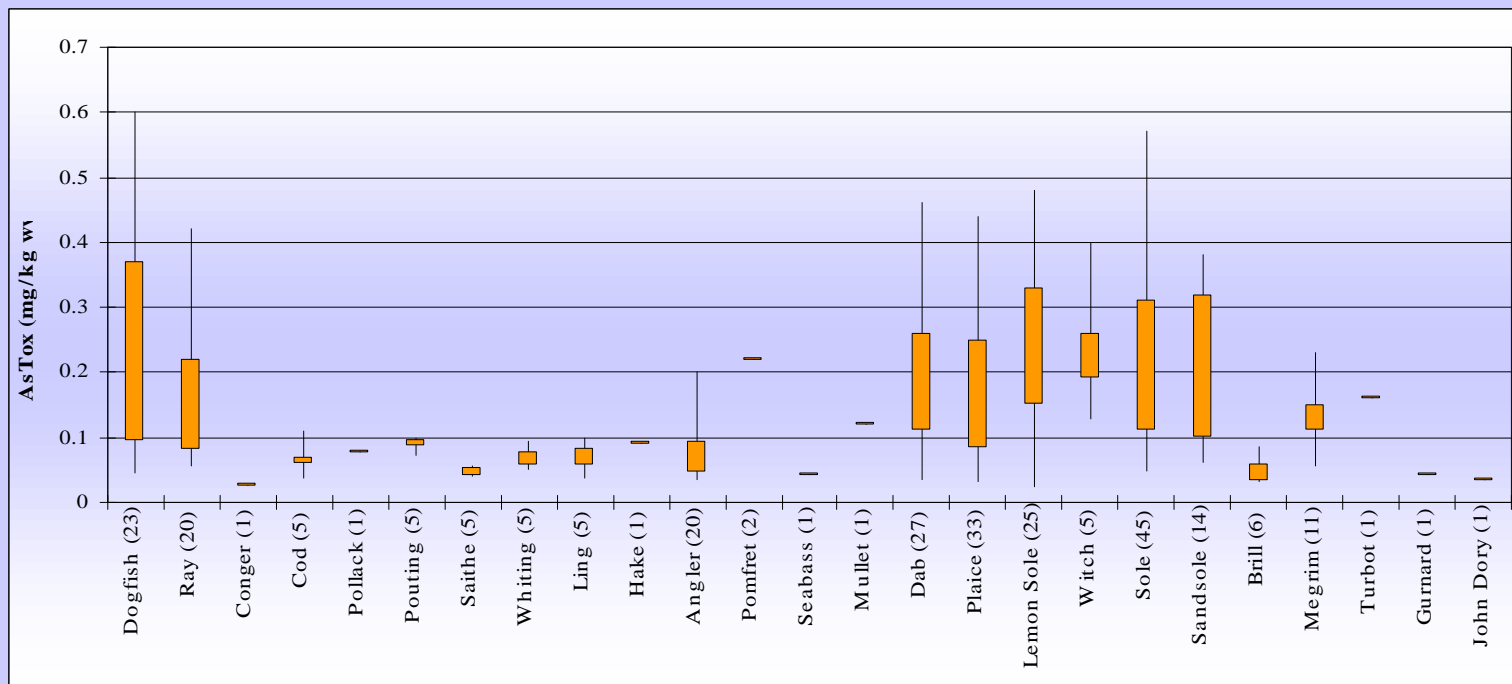
Total As

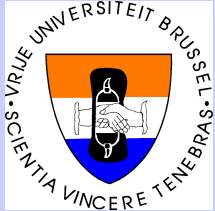
0.2-76
mg/kg ww



Toxic As

0.03-0.6
mg/kg ww





Arsenic in seafish :

- Total concentrations are much higher than the legal limits (varying from 0.1 mg.kg^{-1} in Venezuela to 10 mg.kg^{-1} in Hong Kong)

BUT toxic fractions constitutes only 1-2 % of the total concentrations

THUS speciation information is needed to investigate possible harm of seafood ingestion to human health

- Normalization was applied to divide species in classes of harmless to harmful

▶▶ benthic fish (flatfish) generally contain more As than pelagic fish

- Differences in As-concentrations according to sampling area could be found for some species

- Unlike for Hg, no evidence of biomagnification could be found for As



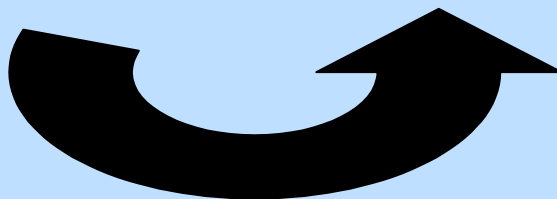
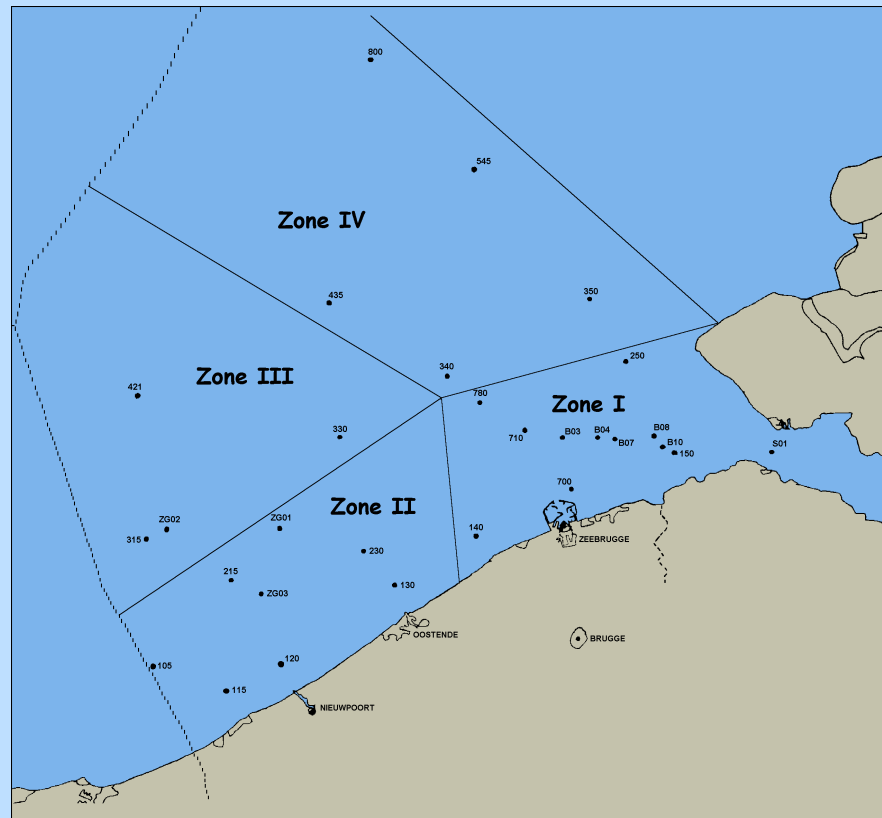
**BIOGEOCHEMISTRY OF NUTRIENTS, TRACE METALS AND
ORGANIC MICROPOLLUTANTS
IN THE NORTH SEA.**

**SUBPROJECT: BIOGEOCHEMICAL BEHAVIOUR OF
PARTICULATE TRACE ELEMENTS IN THE NORTH SEA**

**Université Libre de Bruxelles
Laboratoire d'Océanographie Chimique et Géochimie des Eaux**

R. Wollast, N. Roevros, V. Herzl, M. Loijens, B. Bastin, L. Chou

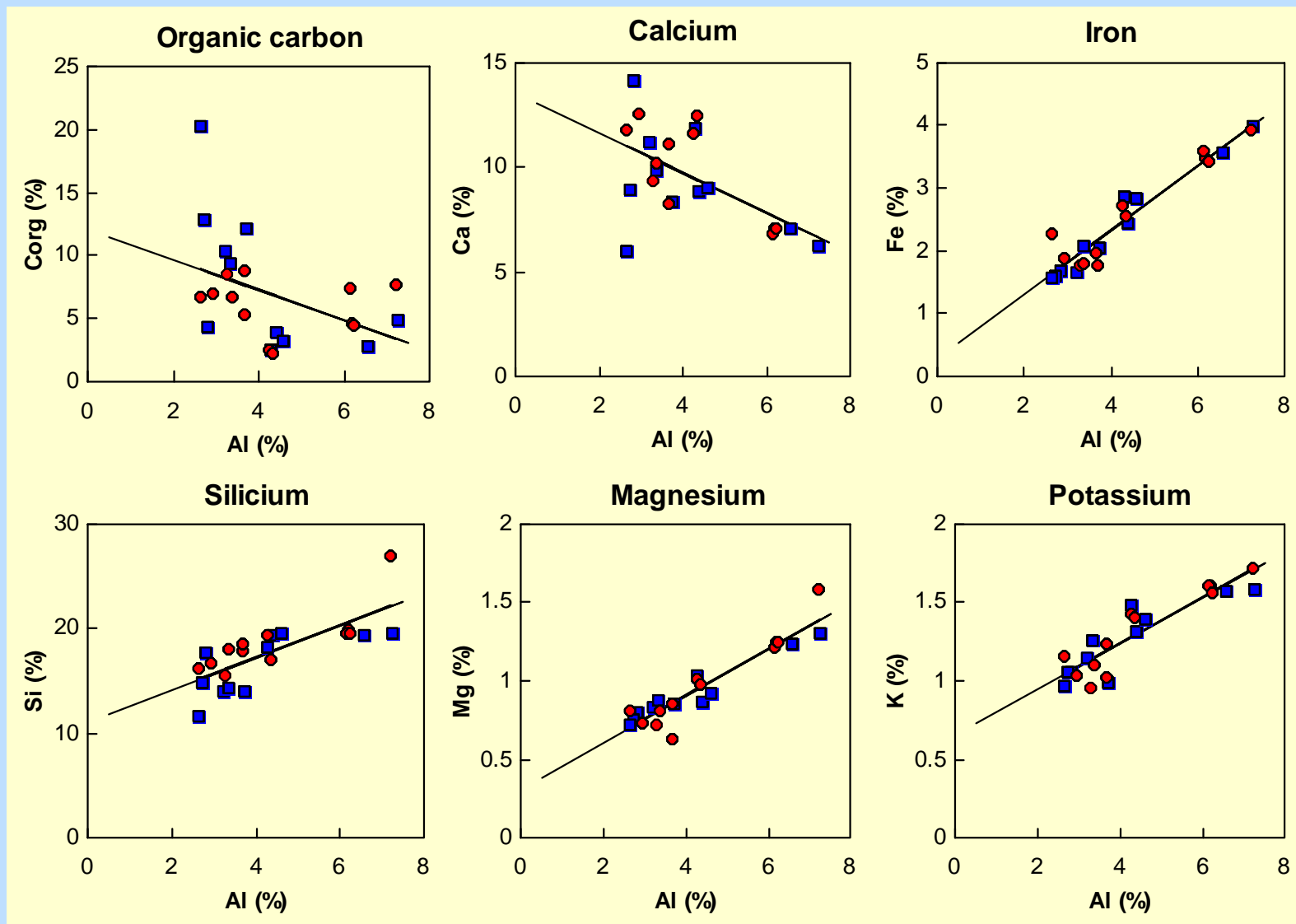
Area of Investigation



Distribution of particulate elements

Spatial and temporal variations of the composition of the suspended matter in terms of major (Na, K, Ca, Mg, Fe, Si, Al, Corg, Cinorg) and minor elements (Mn, Cr, Ni, Co, Cu, Zn, Cd, Pb) in the Southern North Sea.

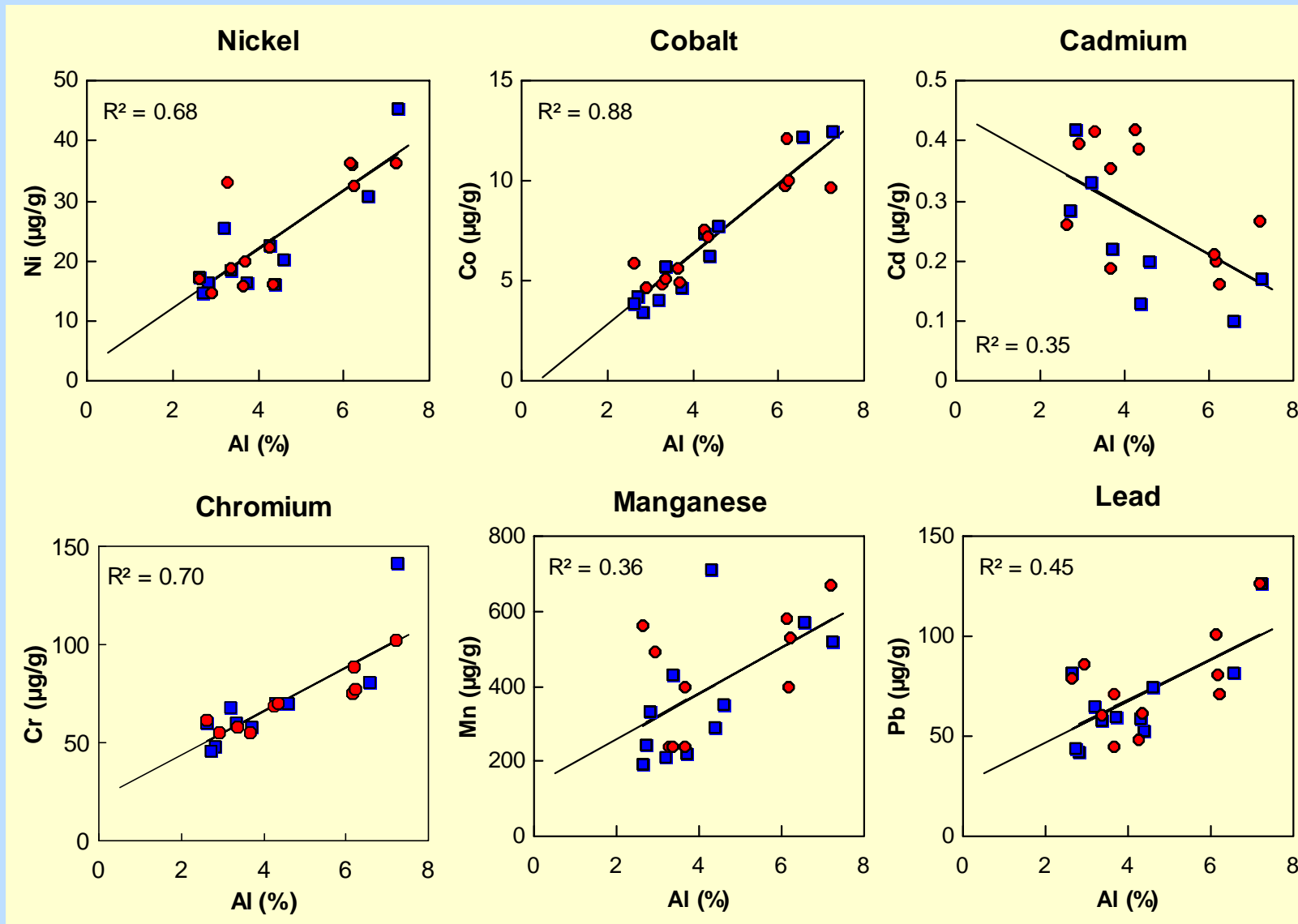
Major elements in relation with aluminium



■ April 1998

● Sept-Oct 1998

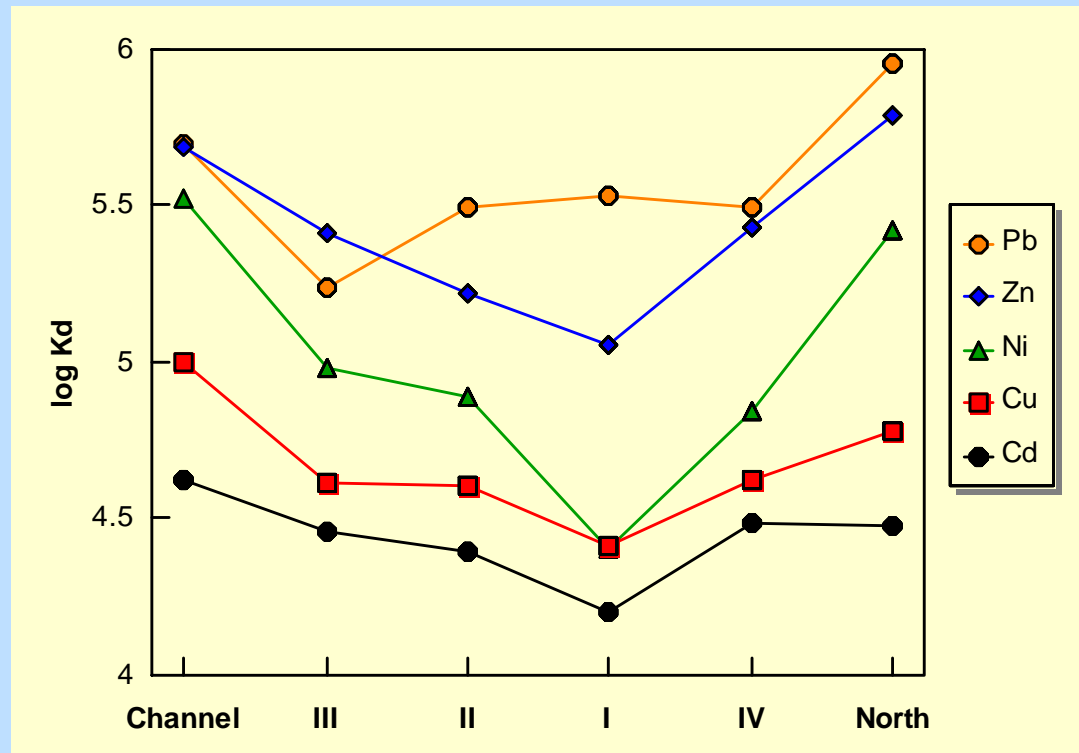
Trace metals in relation with aluminium



■ April 1998

● Sept-Oct 1998

Distribution of the log K_D

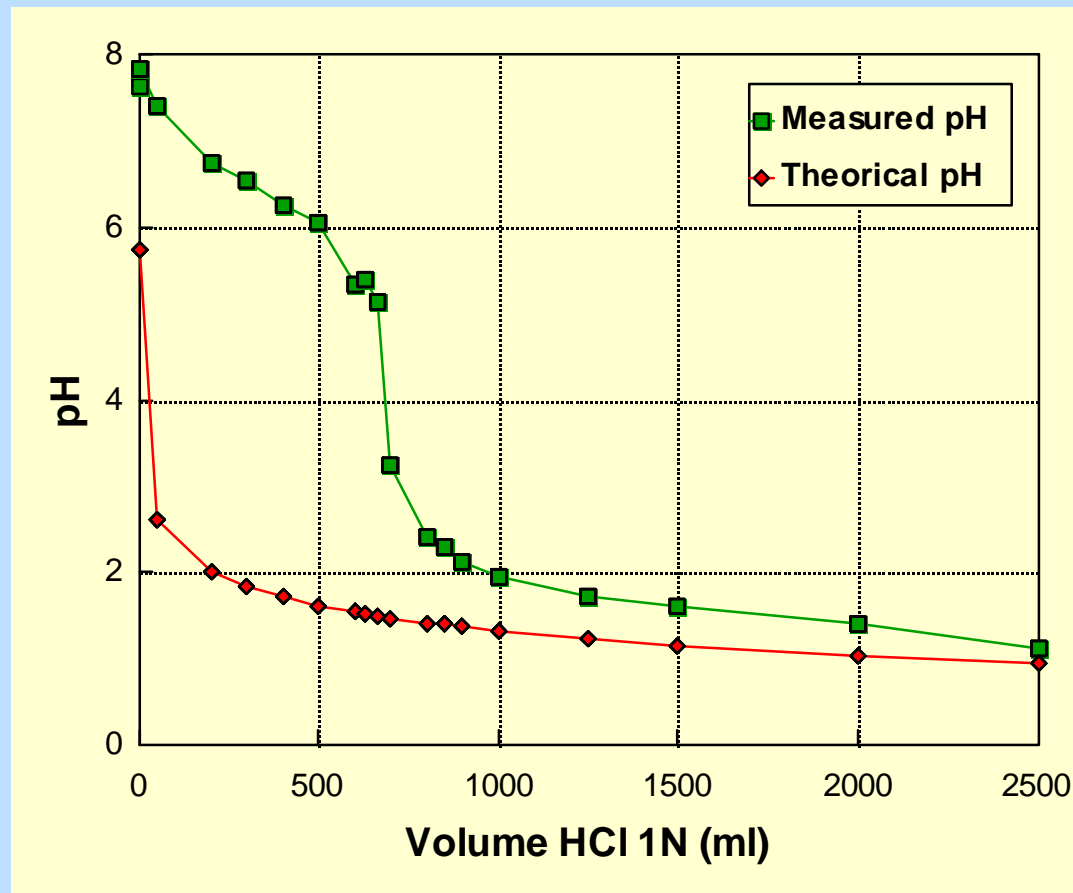


Affinity for the particulate phase:

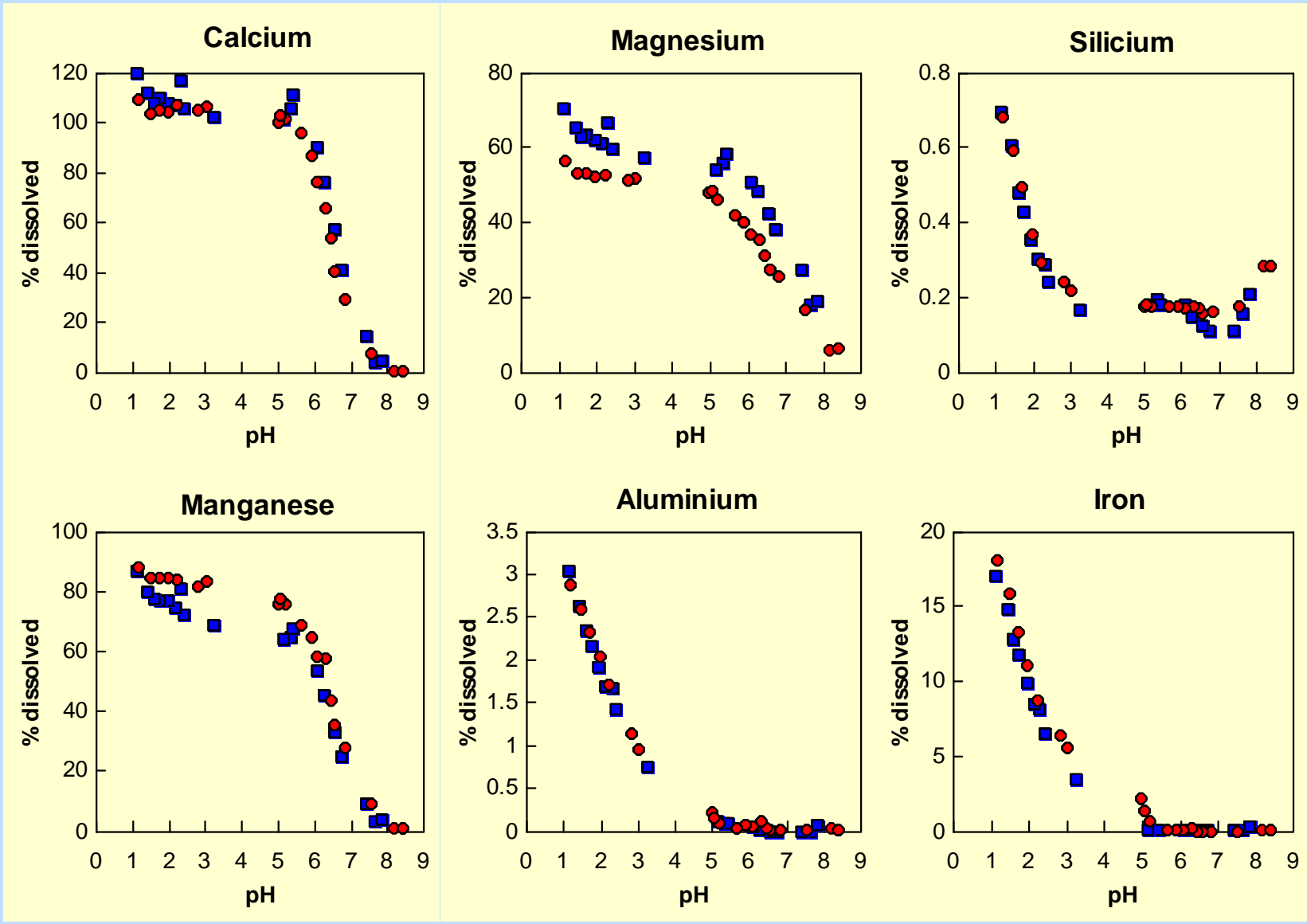
Pb > Zn > Ni > Cu > Cd

Acidimetric titration

Investigation of the mobility and thus the potential bio-availability of the particulate trace metals by performing batch titration experiments of suspended matter by a strong acid (1N HCl).



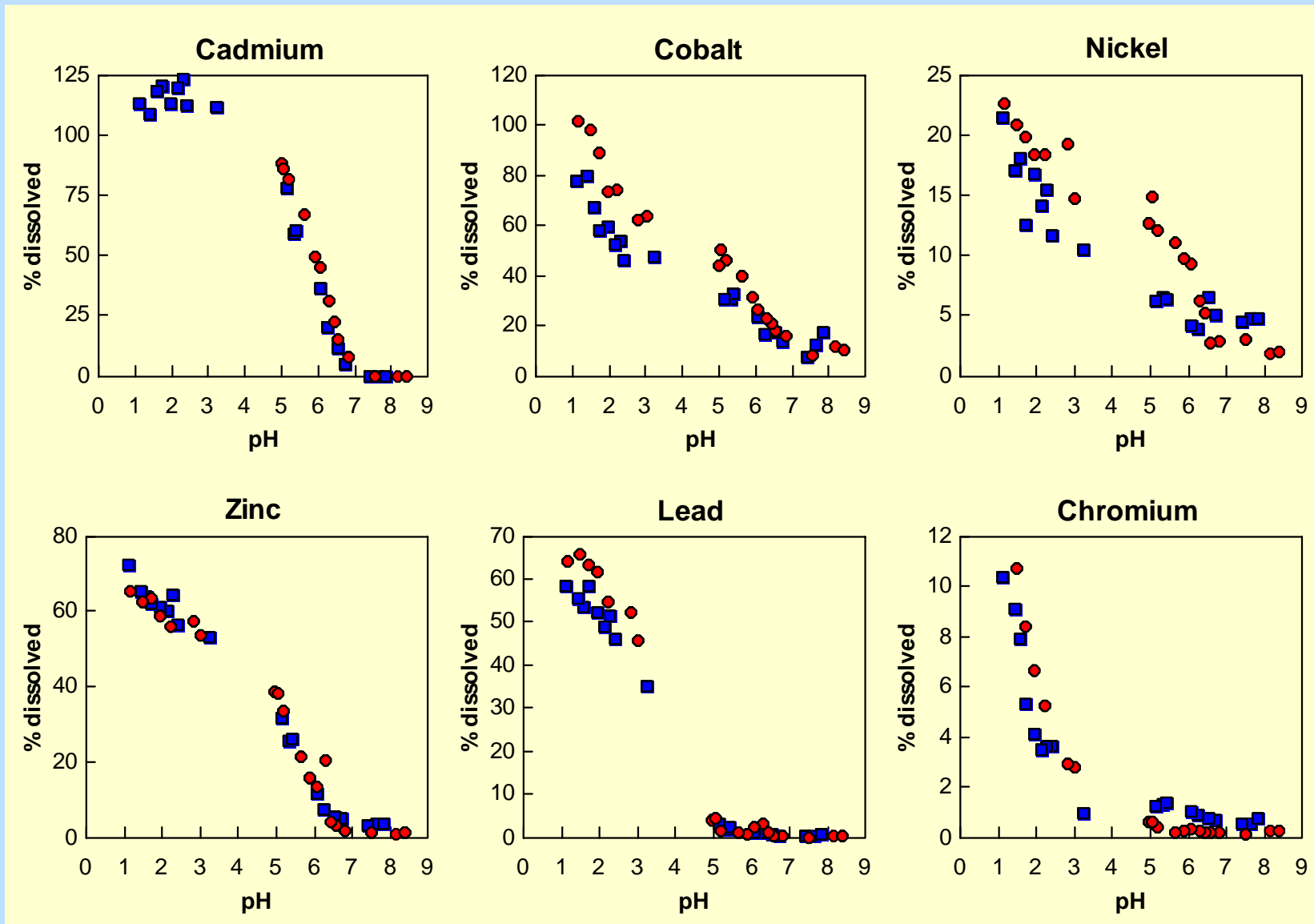
Major elements



■ April 1998

● Sept-Oct 1998

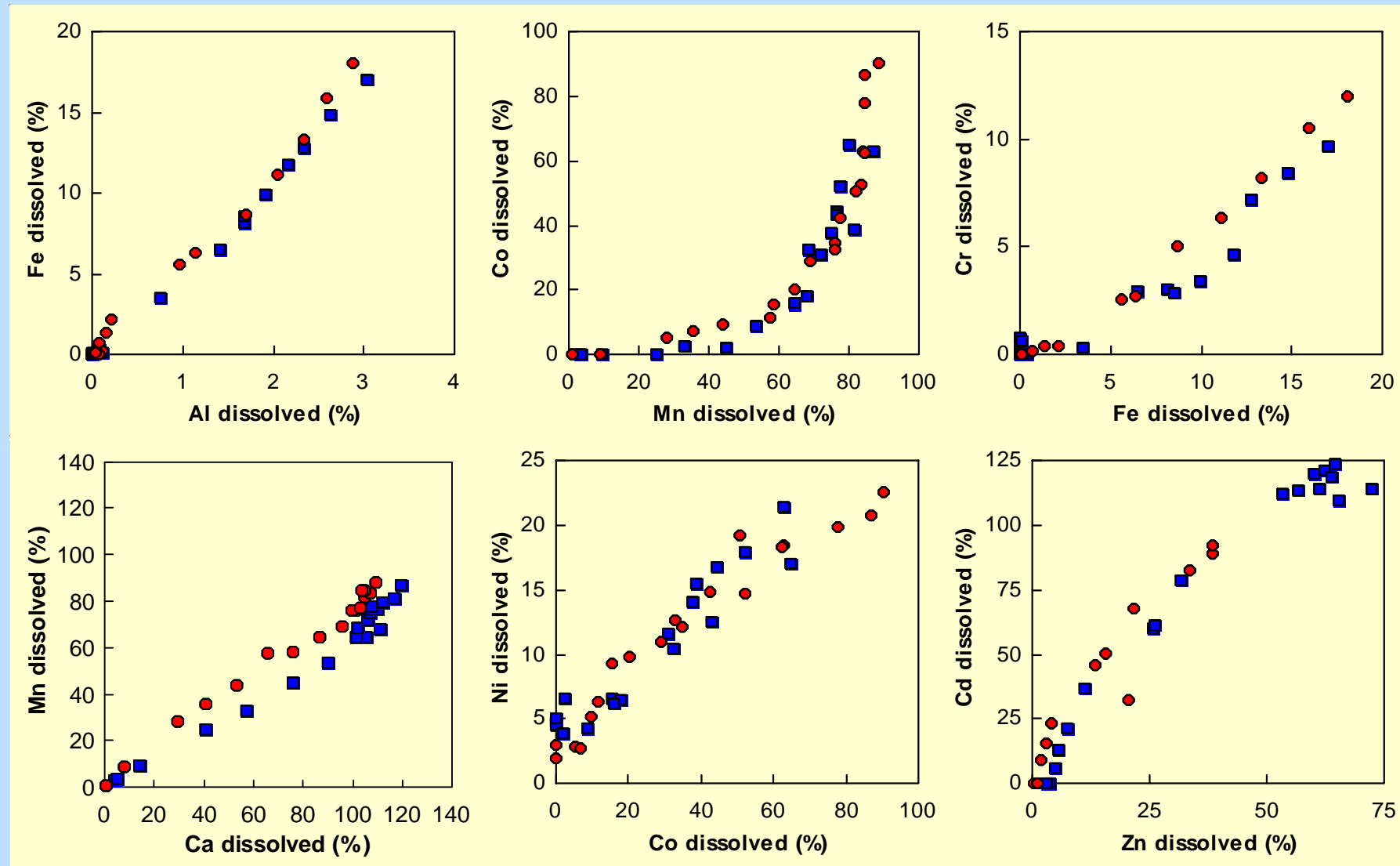
Trace metals



■ April 1998

● Sept-Oct 1998

Associated elements



■ April 1998

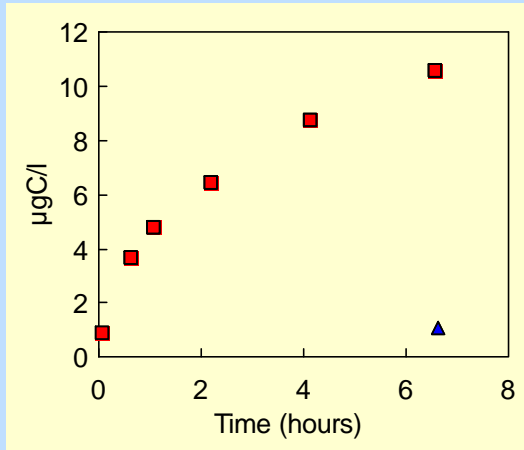
● Sept-Oct 1998

Transfer of trace elements between the dissolved and particulate phases

Study of the mechanism and rate of uptake of trace metals by suspended matter using radionuclides (^{54}Mn , ^{63}Ni , ^{65}Zn , ^{109}Cd) during incubation experiments of natural samples.

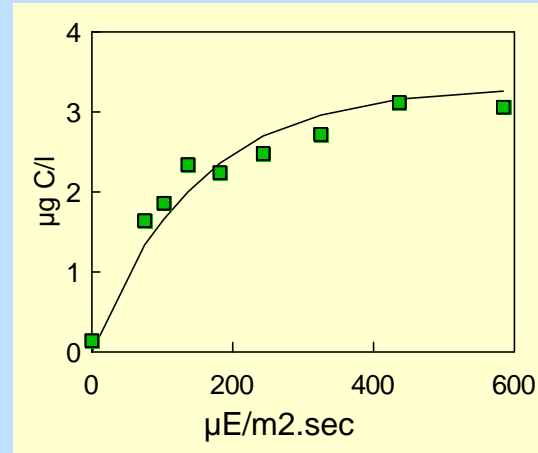
^{14}C incorporation experiments (July 1999)

Station 330



Rate: $1.0 \mu\text{g C l}^{-1} \text{h}^{-1}$

Influence of light intensity

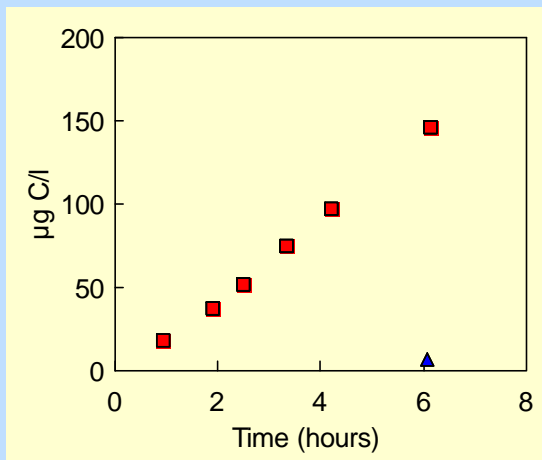


Photosynthetic parameters

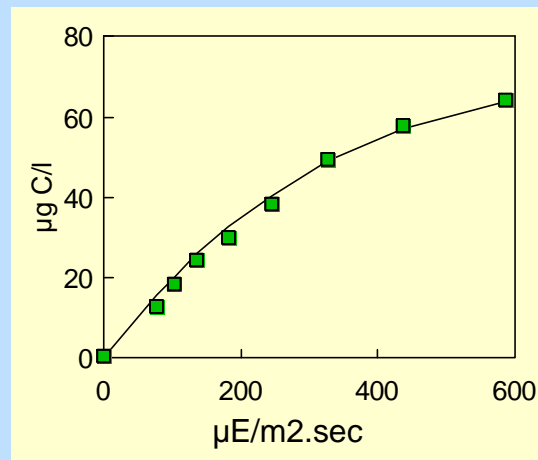
$$P_{\text{max}} = 3.33 : \text{g C l}^{-1} \text{h}^{-1}$$

$$K_t = 0.023 : \text{g C l}^{-1} \text{h}^{-1} (: \text{E m}^{-2} \text{s}^{-1})^{-1}$$

Station 700



Rate: $22 \mu\text{g C l}^{-1} \text{h}^{-1}$



$$P_{\text{max}} = 267 : \text{g C l}^{-1} \text{h}^{-1}$$

$$K_t = 0.226 : \text{g C l}^{-1} \text{h}^{-1} (: \text{E m}^{-2} \text{s}^{-1})^{-1}$$

Use of specific conditions

CONDITIONS

PROCESSES

Light

Photosynthesis

Photoreaction

Dark

Abiotic

Bacterial

short term incub.

Isotopic exchange

Use of specific inhibitors

INHIBITOR

INHIBITION

DCMU

Photosynthesis

Antibiotics

Bacterial activity

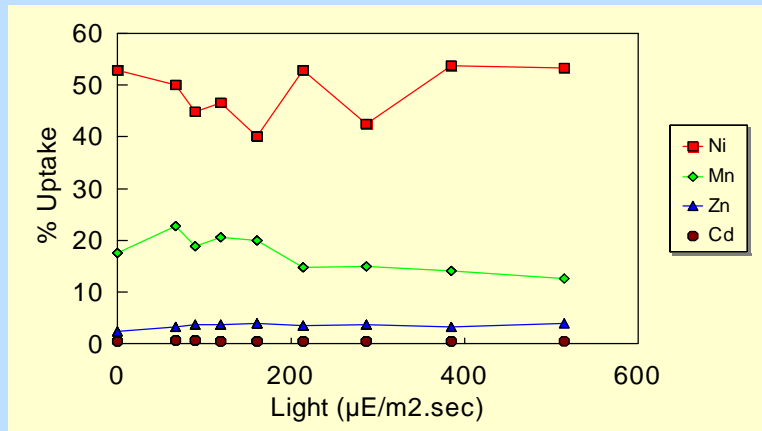
Sodium Azide

Biotic process

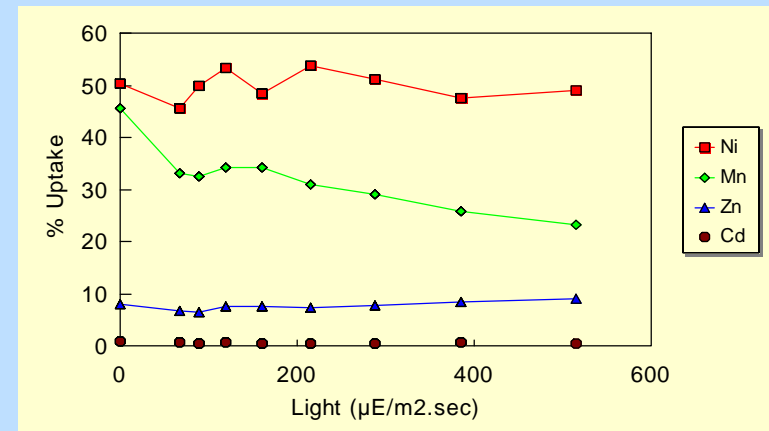
Radionuclides incorporation experiments - Trace Metals

Influence of light intensity

Station 330



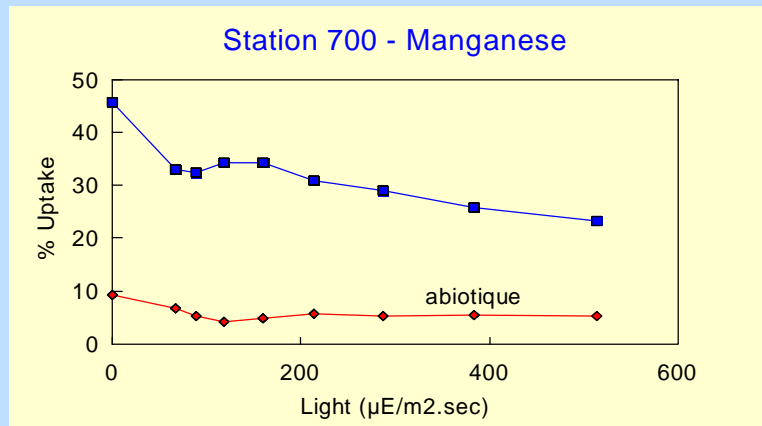
Station 700



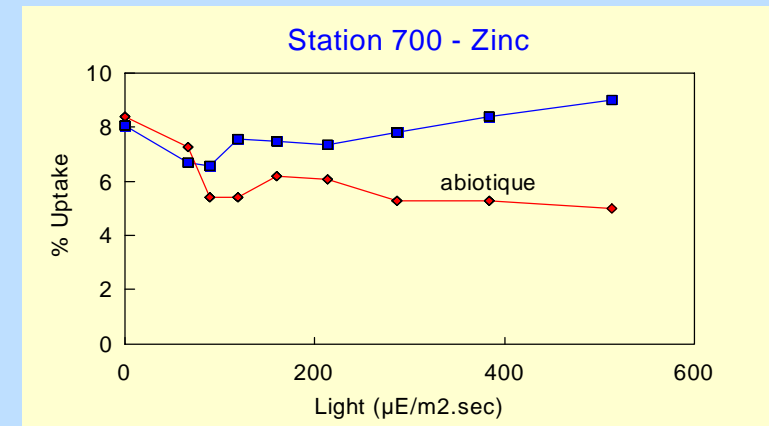
- No influence of light intensity except a slight photoinhibition of Mn transfer

Influence of biological activity - Inhibition by sodium azide

Station 700 - Manganese



Station 700 - Zinc

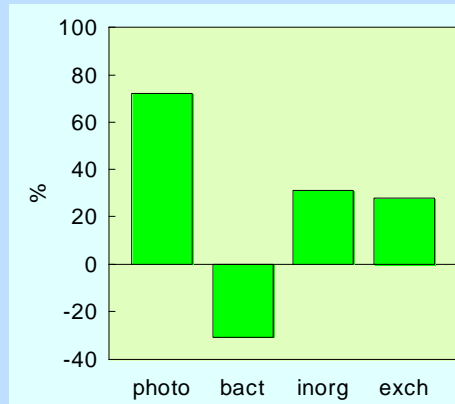


- Strong influence of biological activity on Mn uptake
- Strong abiotic uptake of Zn

SPECIFIC INCORPORATION

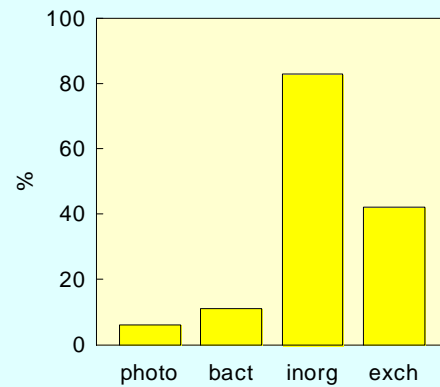
Station 330

Cd



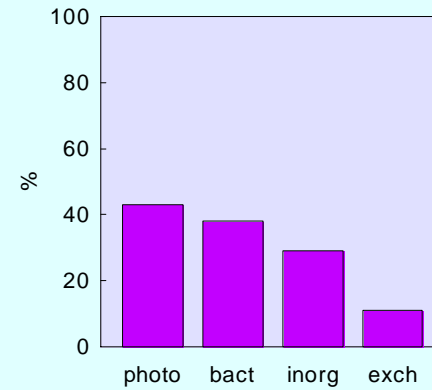
$$K = 1.3 \cdot 10^{-3} \text{ h}^{-1}$$

Zn



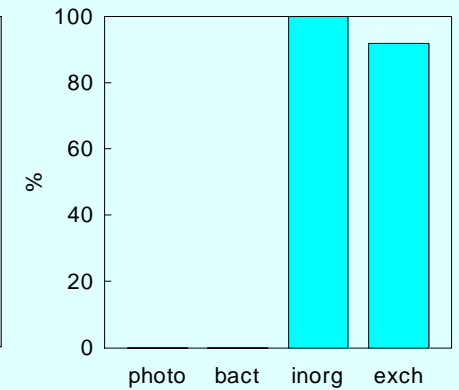
$$K = 4.2 \cdot 10^{-3} \text{ h}^{-1}$$

Mn



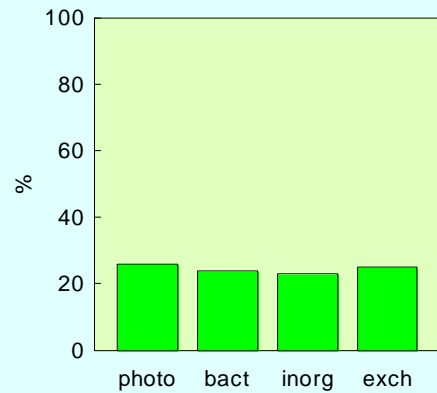
$$K = 25 \cdot 10^{-3} \text{ h}^{-1}$$

Ni

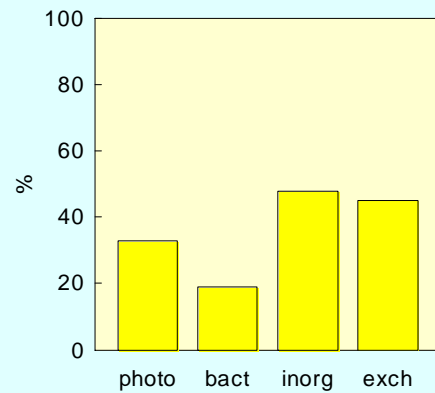


$$K = 62 \cdot 10^{-3} \text{ h}^{-1}$$

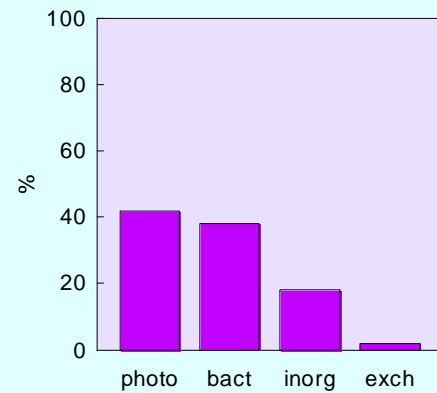
Station 700



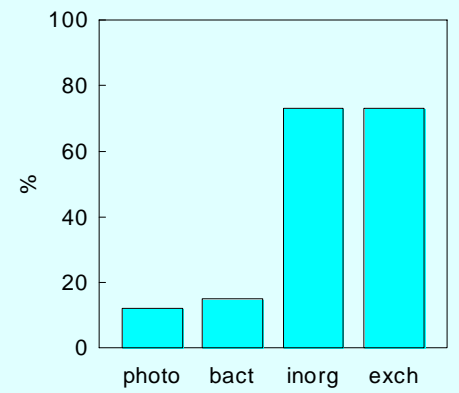
$$K = 2.5 \cdot 10^{-3} \text{ h}^{-1}$$



$$K = 15.4 \cdot 10^{-3} \text{ h}^{-1}$$



$$K = 77 \cdot 10^{-3} \text{ h}^{-1}$$



$$K = 75 \cdot 10^{-3} \text{ h}^{-1}$$

CONCLUSIONS

- In the coastal area under the influence of the Scheldt plume, the concentrations of particulate trace metals may be higher than that of the dissolved species, partly due to high values of the partition coefficient K_d . Most of the trace metals are associated with detrital alumino-silicates and Fe/Mn oxy-hydroxides of continental origin.
- Titration experiments with HCl developed during our study allowed a better evaluation of the mobility of the various particulate elements. In particular, it has been shown that the dissolution of most trace elements begins as soon as the pH drops below 7. However, in the case of Pb and Cr, the dissolution starts only at pH below 5.
- The use of radioactive trace elements allowed the assessment of biotic and abiotic fast reactions transferring the metals between the dissolved and particulate phases. As a consequence, the residence times of dissolved trace elements in surface waters are short (of the order of a few days). The particulate phase may act as a buffer to maintain the stock of dissolved elements constant.

ACKNOWLEDGEMENTS

The present research was supported by the Belgian Federal Office for Scientific, Technical and Cultural Affairs (Contract N° MN/DD/11 to Prof. W. Baeyens and Contract N° MN/DD/13 to Prof. R. Wollast). The two subprojects presented are part of a network research co-ordinated by Prof. R. Van Grieken of the Universitaire Instelling Antwerpen. We would like to thank the captain and the crew members of the RV Belgica for their logistic and technical assistance during the various cruises in the North Sea.