PARTITIONING AS A GEOCHEMICAL FINGERPRINT FOR IDENTIFYING CONTAMINANT SOURCES IN WELL-MIXED ESTUARIES

Reid, M. K. and Spencer, K. L.
Geography Department
Queen Mary, University of London

Queen Mary
University of London

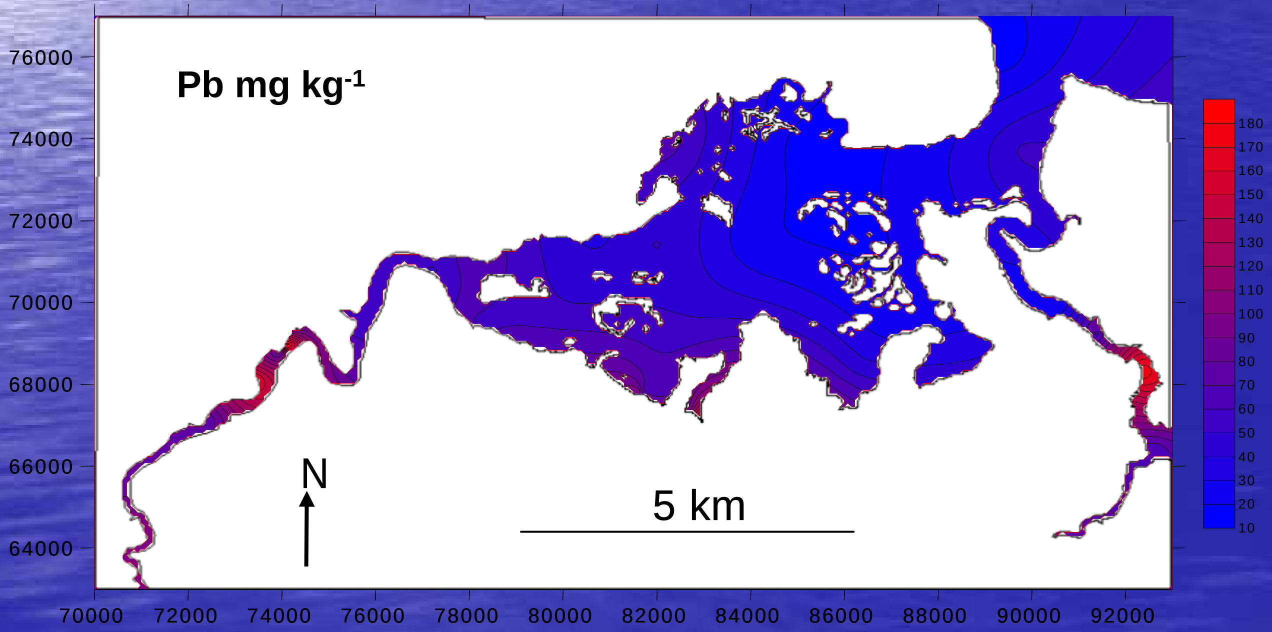
Background

- Estuaries are areas of intense industrial activity and waste disposal
- As a result, many estuaries around the world are areas of contaminant enrichment
- In order to prevent, regulate and remediate against contamination, it is vital to be able to identify the source and fate of contaminants
- Biomarkers (sterols), geochemical fingerprinting

Identifying sources of contamination in macro-tidal estuaries

Macro-tidal estuaries: tidal range > 4 m, high energy, salt water flows dominate.

Results in mixing of both waters (little variation in pH/salinity) and sediments



Spatial distribution of Pb in surface sediments of the Medway Estuary, UK.

Metal partitioning as a geochemical fingerprint

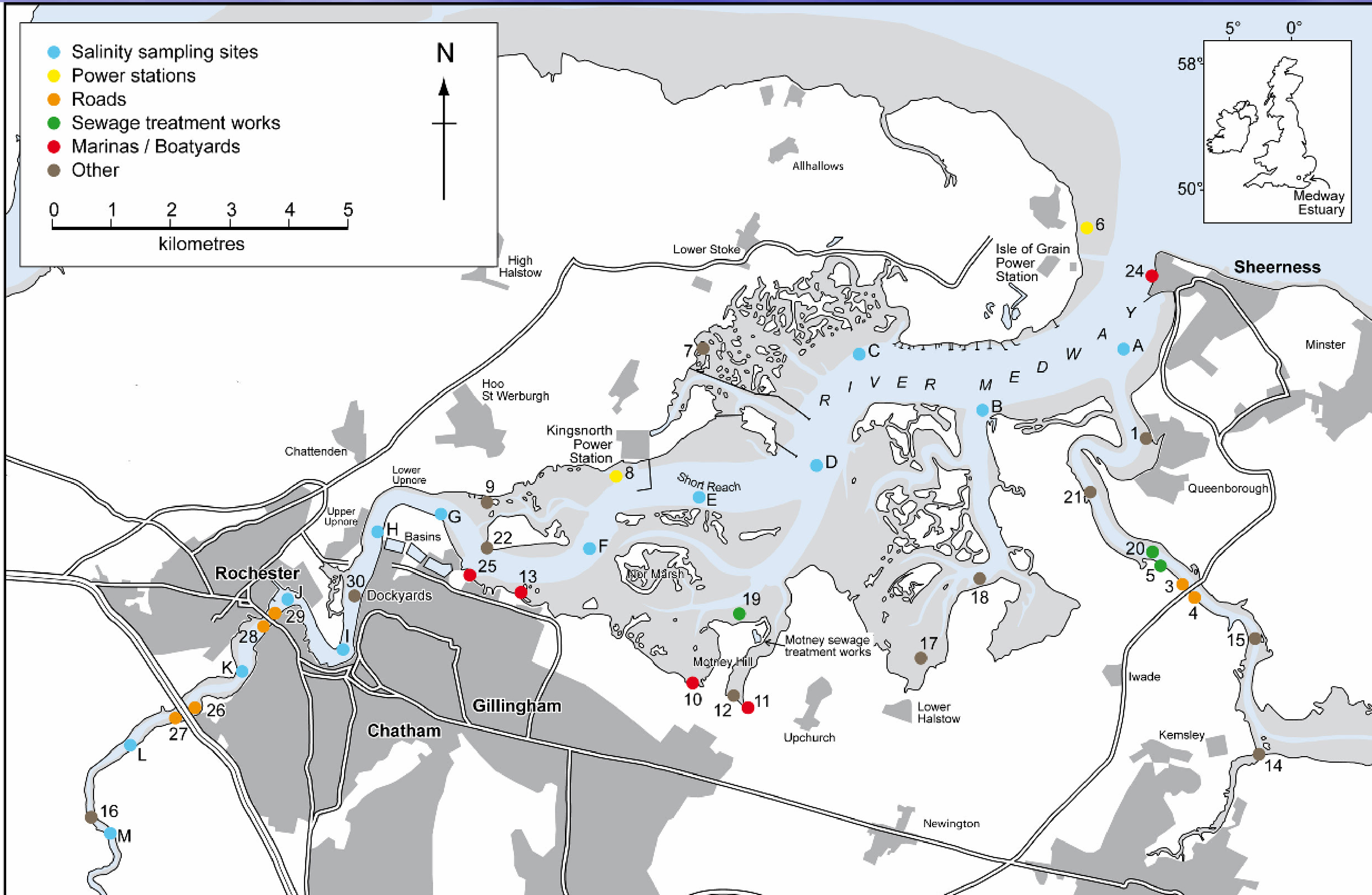
- **Aim:** to determine whether metal partitioning can be used as a geochemical fingerprint

Rationale

- Metals from different contaminant sources occur in different chemical forms
- Contaminant sources/effluent streams are heterogeneous comprising important metal binding sites
- Partitioning can provide more information on anthropogenic metals held outside the silicate matrix
- Limited studies discriminating contaminant sources using partitioning in soils

Methods

- Field study: total metals and partitioning in surface sediments from the Medway Estuary, SE England
- Samples were collected in proximity to known contaminant inputs and along a longitudinal transect
- A suite of environmental (e.g. pH) and sediment composition (e.g. Fe oxide) parameters
- Microwave assisted sequential extraction scheme
- Laboratory studies: factorial experiments to examine the influence of environmental and sediment composition parameters on partitioning of Ba, Cu, Pb, V and Zn.



Sampling locations in the Medway Estuary

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Microwave Assisted Sequential Extraction Scheme

EXTRACT 1	Exchangeable fraction
EXTRACT 2	Bound to carbonates
EXTRACT 3	Fe Mn oxyhydroxides
EXTRACT 4	Bound to organic/sulphidic material
EXTRACT 5	Residual

Adapted from Tessier et al. (1979)

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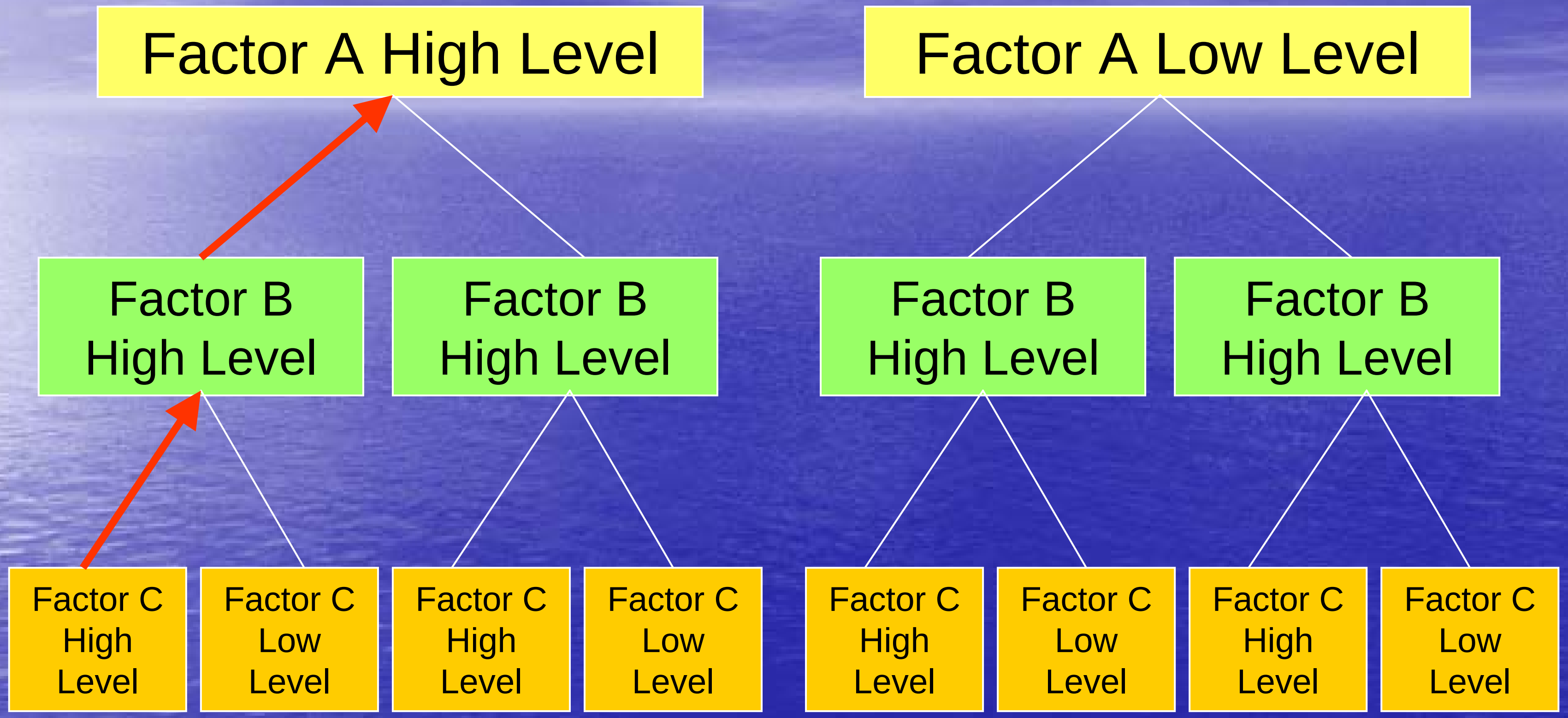
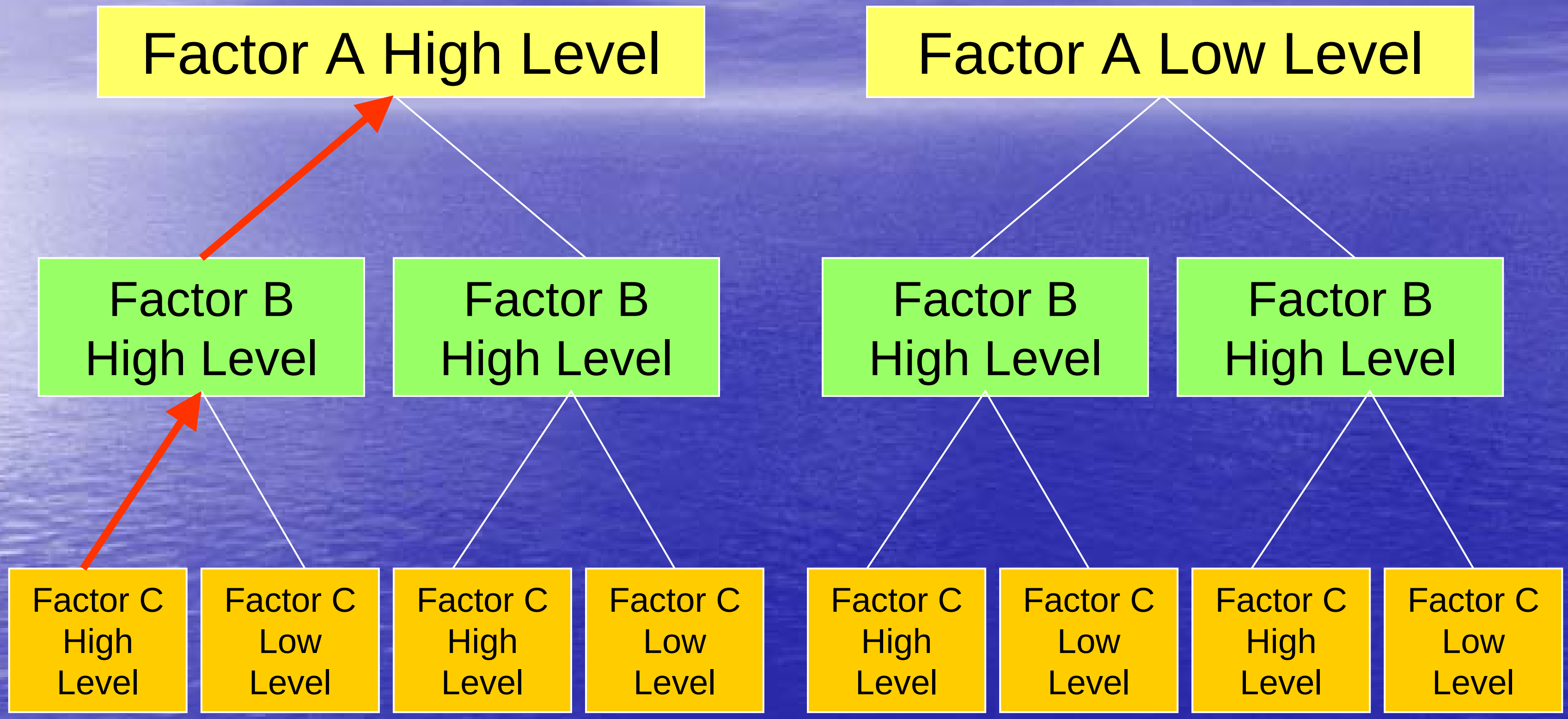
3 factor 2 level experimental design



3 factor 2 level experimental design



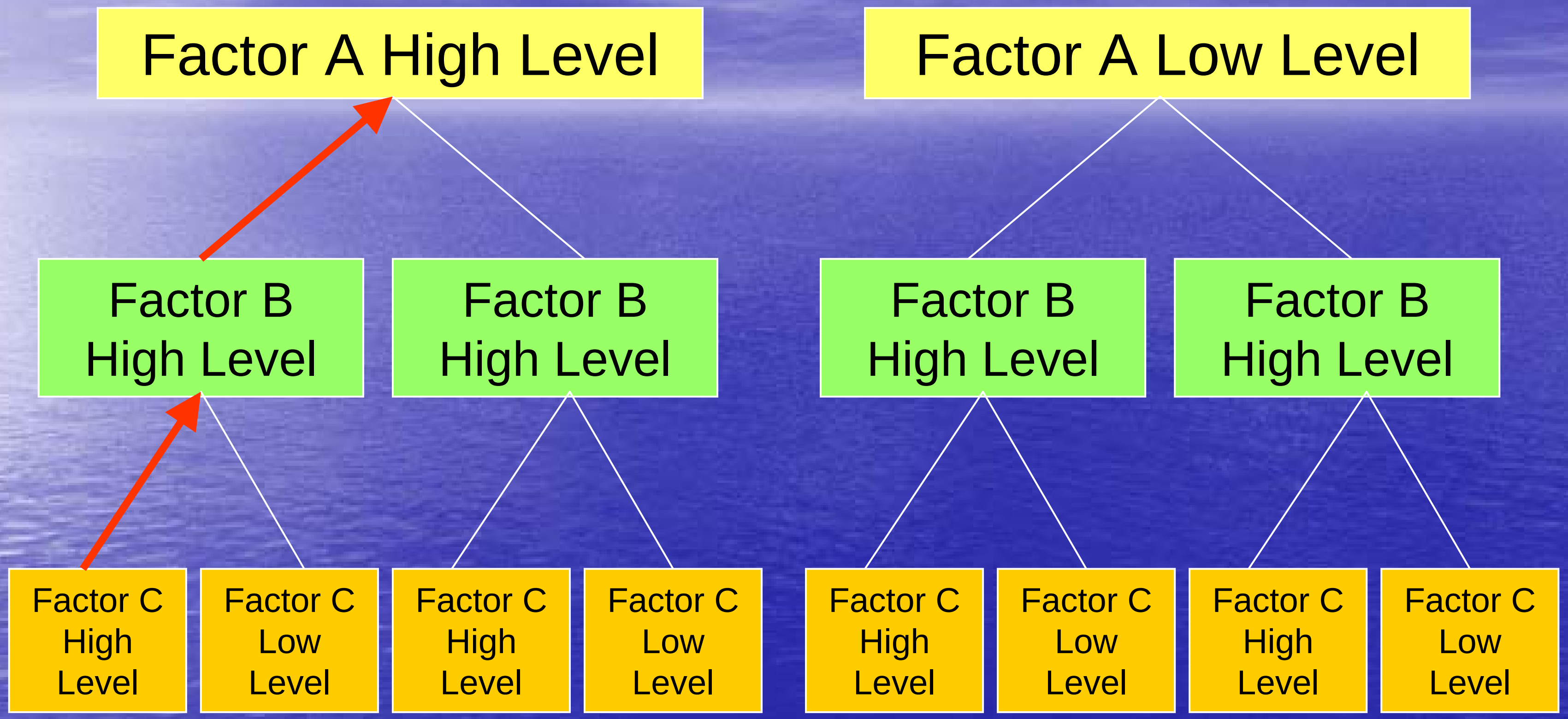
Environmental Parameters

Factor A: pH

Factor B: salinity

Factor C: time

3 factor 2 level experimental design



<u>Environmental Parameters</u>

Factor A: pH

Factor B: salinity

Factor C: time

<u>Sediment composition</u>

Factor A: Fe oxide

Factor B: carbonate

Factor C: organic matter

Source discrimination using total metal and partitioning data (field data)

- Identified 10 source pairs e.g. power stations and sewage treatment works
- Mann Whitney U test to discriminate between these source pairs

Total metal data	Partitioning data
• Power station and 'other' • Boating and Roads • STWs and Roads • Roads and 'other'	• Power station and 'other' • STWs and Roads • Boating and Roads • STWs and 'other' • Boating and 'other' • Boating and STWs • Roads and 'other'

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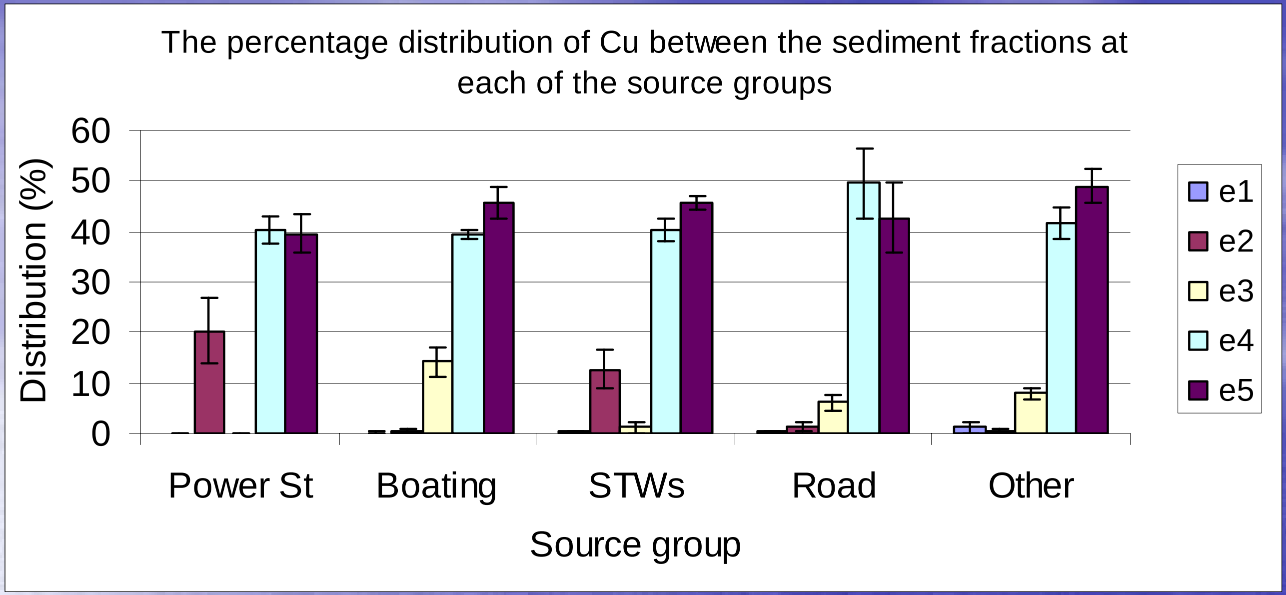
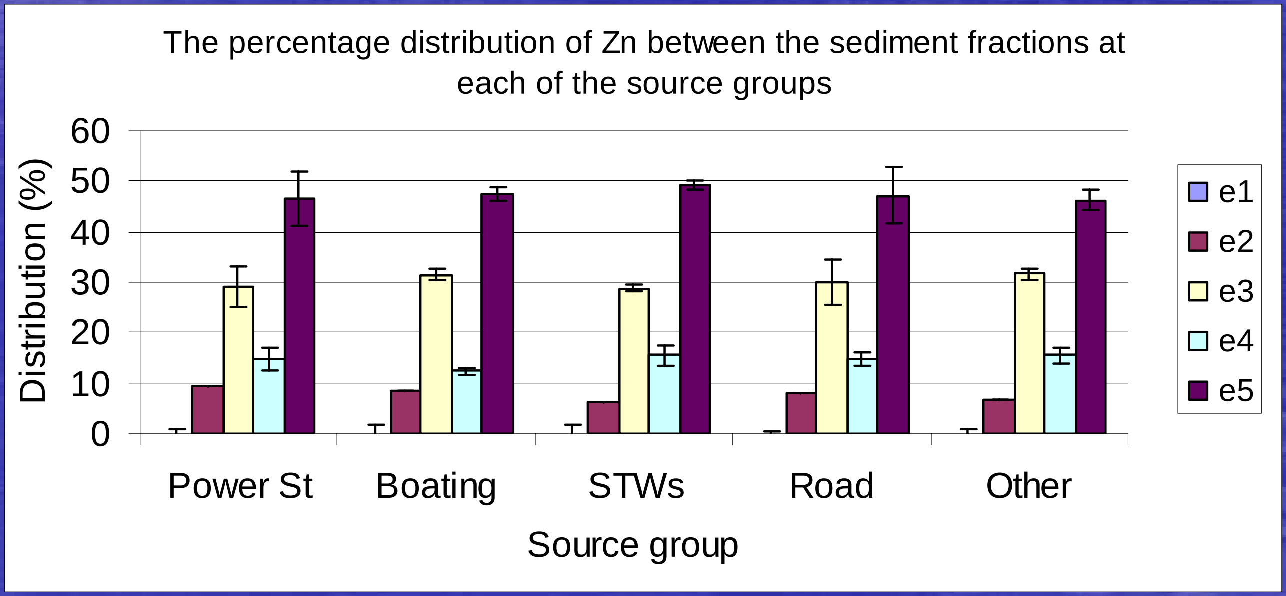
Source discrimination using total metal and partitioning data (field data)

- Partitioning data provide more detailed information about metal distribution within sediment
- Power stations higher concentrations of metals in fraction 2
- Sewage Treatment Works (STW) higher concentrations of metals in fractions 2 and 3
- Boating higher concentrations of metals in fractions 3 and 4
- Some metals were more capable of discriminating than other



- Observed partitioning may be due to source

- Observed partitioning may be due to environmental conditions and/or sediment composition



Influence of environmental parameters on metal partitioning (experimental)

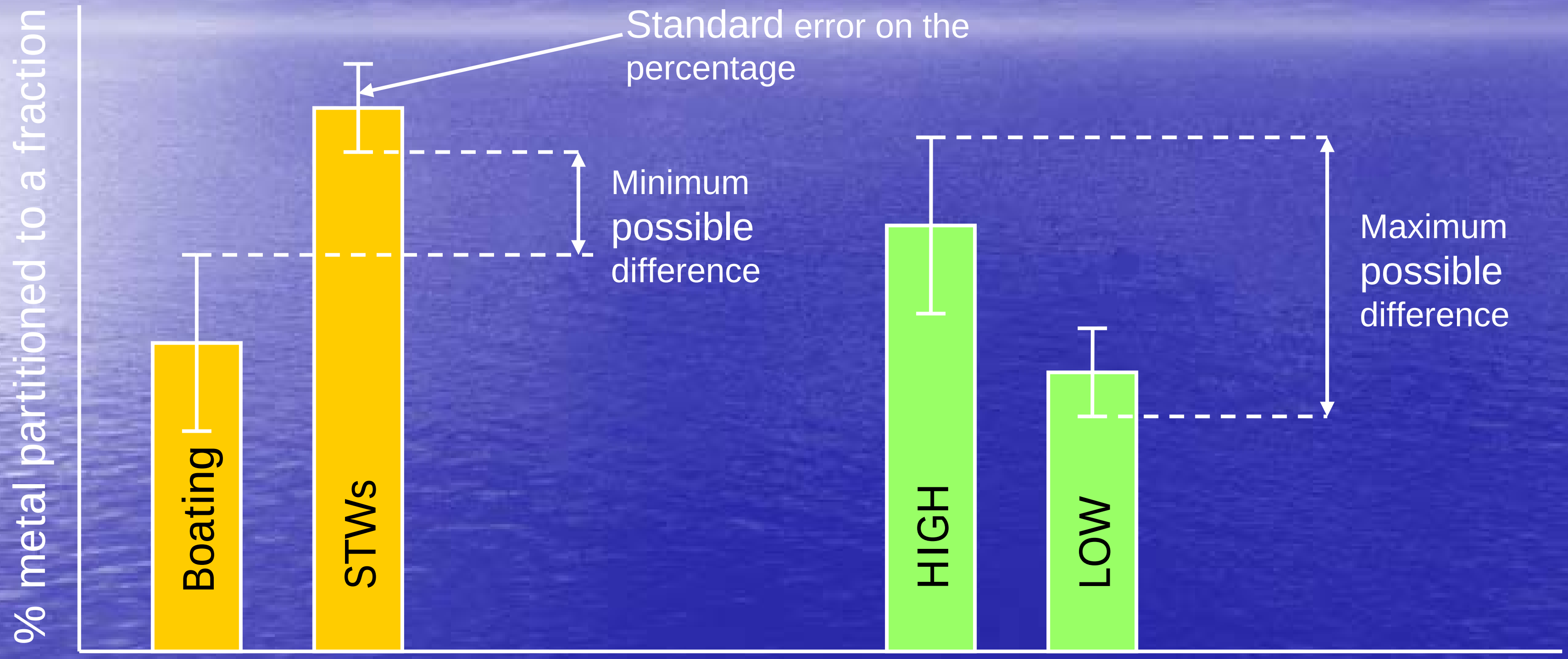
- Time > salinity > pH
- Time Pb > Zn = Cu > V = Ba
- Salinity Pb > V = Ba > Zn > Cu
- pH Zn > Ba >Cu > Pb > V

Influence of sediment composition on metal partitioning (experimental)

- Fe oxide >/= organic matter > carbonate
- Fe oxide content Pb > Zn = Cu > V > Ba
- Organic matter content Cu > Zn > V > Pb > Ba
- Carbonate content Zn > Pb > Cu > V > Ba

- Does the partitioning that we observe in the field reflect source and/or environmental parameters and/or sediment composition?
- To use metal partitioning as a geochemical fingerprint we need to quantify effect of each of these parameters on partitioning.

Comparison of the magnitude of changes in partitioning



Source

Environmental / Sediment composition

e.g. Ba in fraction 2 at the Boat and STWs

e.g. Ba in fraction 2 under high / low salinity conditions

Metal partitioning as a geochemical fingerprint

- The effect of environmental parameters and/or sediment composition on partitioning was generally greater than source
- Therefore, in estuaries where we see a full range of environmental parameters and varied sediment composition, partitioning will have limited use
- However, in the Medway and other well-mixed estuaries where environmental parameters and sediment composition vary little, partitioning could discriminate between source groups

Conclusions

- Partitioning data had a greater ability to discriminate between sediments collected in proximity to contaminant source groups in the Medway Estuary
- Time was the environmental parameter with the greatest influence on metal partitioning followed by salinity and pH
- Organic matter and Fe oxide content had the greatest influence on metal partitioning followed by carbonate content

Conclusions

- Although environmental parameters and sediment composition may have a greater influence on metal partitioning, in macro-tidal environments these parameters show little variability and therefore it may be possible to discriminate contaminant source groups

Example:

- Ba in extract 3 can discriminate between Power St and Other sites with a minimum difference of 2.87%
- The pH causes a maximum of 3.52% change in the amount of Ba partitioned to this fraction between the high (pH 8.0) and low (pH 6.5) level conditions of the experiments
- However the pH between these sites only varied on average from 7.27 – 7.35