WP4. Relationships among methods. (WP nr. 4, action nr. 2)

May 17th, 2021

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WP4. Relationships among methods

First, we need to explain what is the **dissolved** metal fraction and what is the **labile** metal fraction measured with DGT.

dissolved metal fraction ≠ **labile** metal fraction

WP4. Relationships among methods

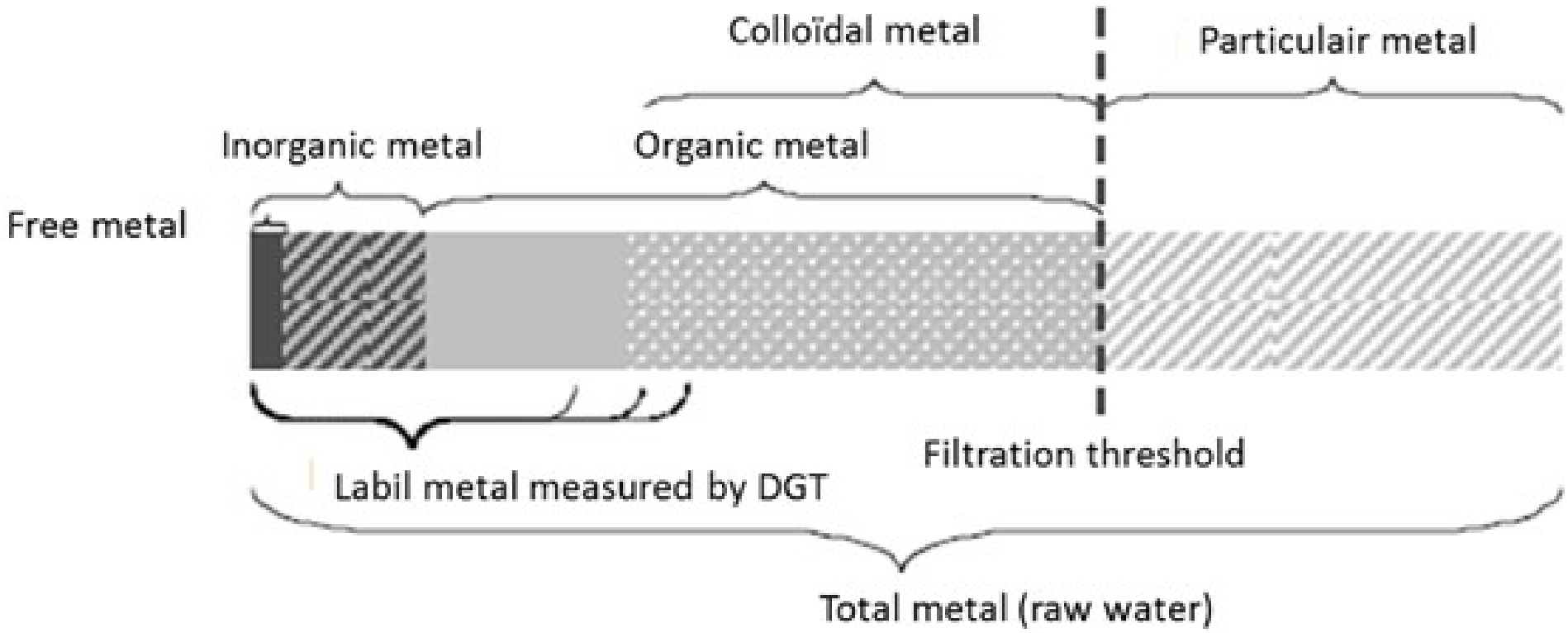
We can define the **dissolved fraction** as that which refers to the fraction after filtration, *i.e.*, once the particulate fraction has been removed.

We can define the *in situ* **labile fraction** as that which refers to the fraction measured by passive samplers (Diffusive Gradients in Thin films, DGT).

WP4. Relationships among methods

In the next slide we show the different fractions of the metal present in a water sample (in a very simplified form).

WP4. Relationships among methods

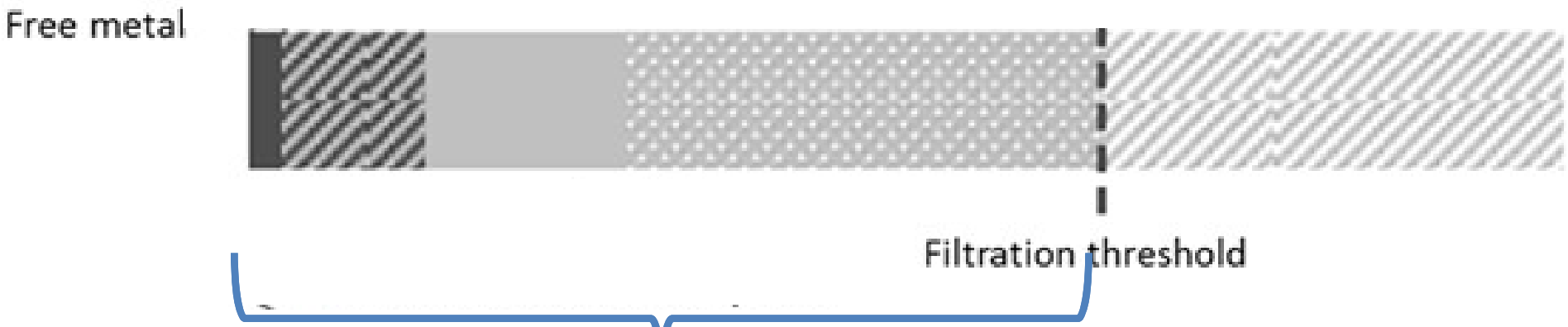


Source:

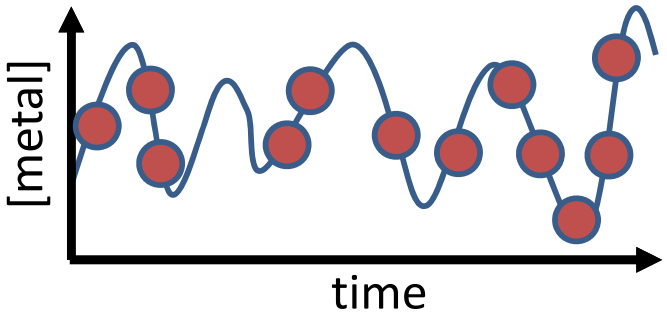
Gourlay-France C, Delmas F, Mazzella N, Tusseau-Vuillemin M-H. Que sait-on de la biodisponibilité des contaminants dissous dans le milieu aquatique ? Sci Eaux Territ 2010

Gonzalez J-L. Contribution à l'étude de la dynamique des contaminants chimiques et à la surveillance du milieu marin: apports de la modélisation et des techniques d'échantillonnage passif. Habilitation à Diriger des Recherches. 2017 .

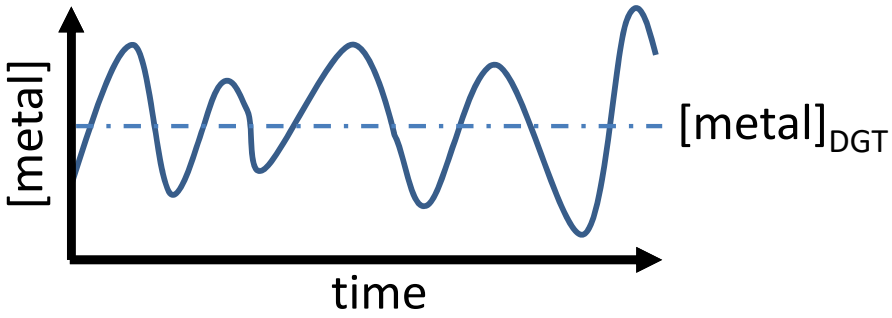
WP4. Relationships among methods

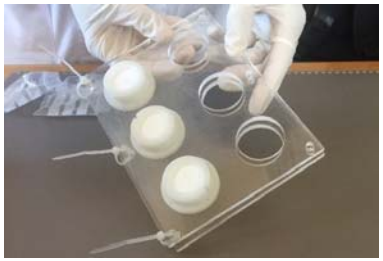


total dissolved fraction <- Spot sampling + Filtration

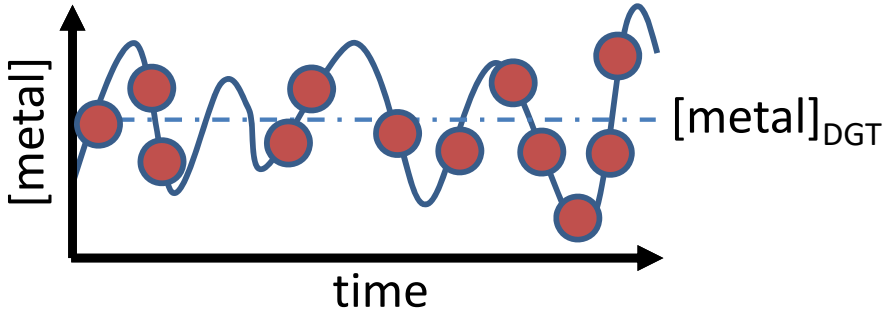


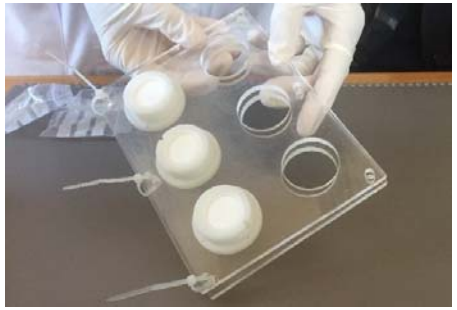
WP4. Relationships among methods





WP4. Relationships among methods





-> DGT labile fraction

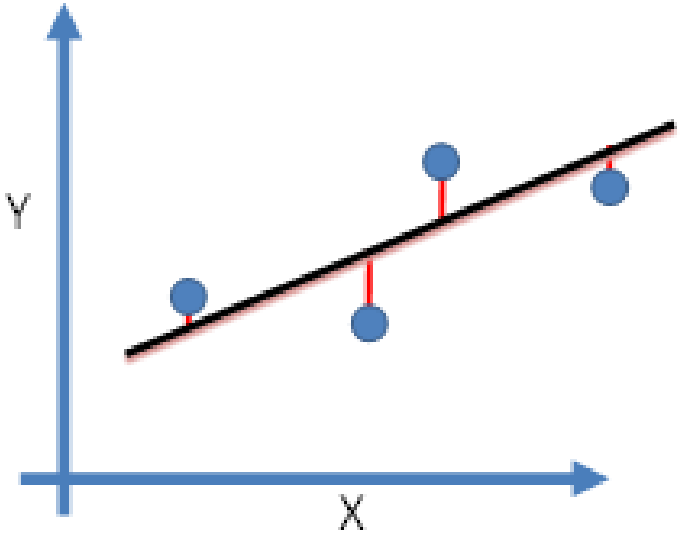
Spot sampling + Filtration -> total dissolved fraction

WP4. Relationships among methods

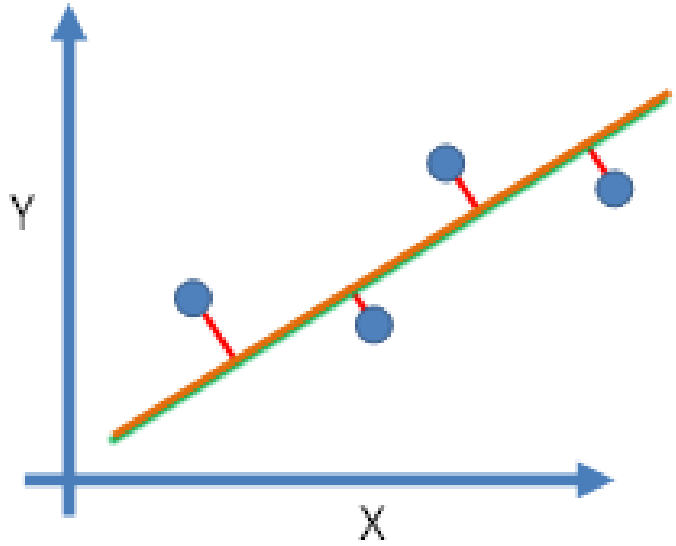
Note: as my colleagues explained, spot samples were measured by ICP-MS and voltammetry, today only ICP-MS results are shown (in the deliverables we will include both).

WP4. Relationships among methods

Type I regression: fits the line by minimizing the sum of the squares of the y-offsets (residuals). E.g., ordinary least squares regression.



Type II regression: fits the line by minimizing the sum of the squares of the offsets measured along a line perpendicular (or normal) to the regression line.

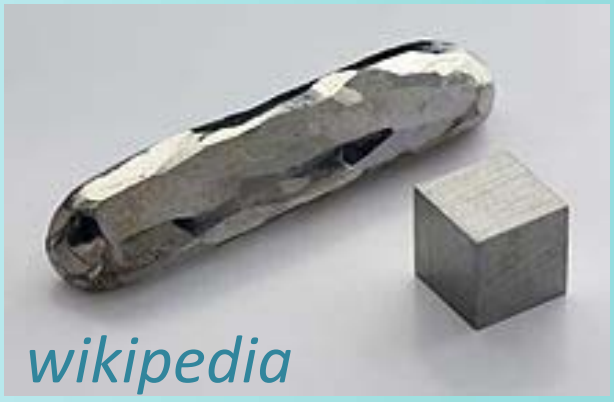


Type II regression: Neither X nor Y is an INDEPENDENT variable but both are assumed to be DEPENDENT on some other parameter which is often unknown. Neither are "controlled", both are measured, and both include some error. We do not seek an equation of how Y varies in response to a change in X, but rather we look for how they both co-vary in time or space in response to some other variable or process.

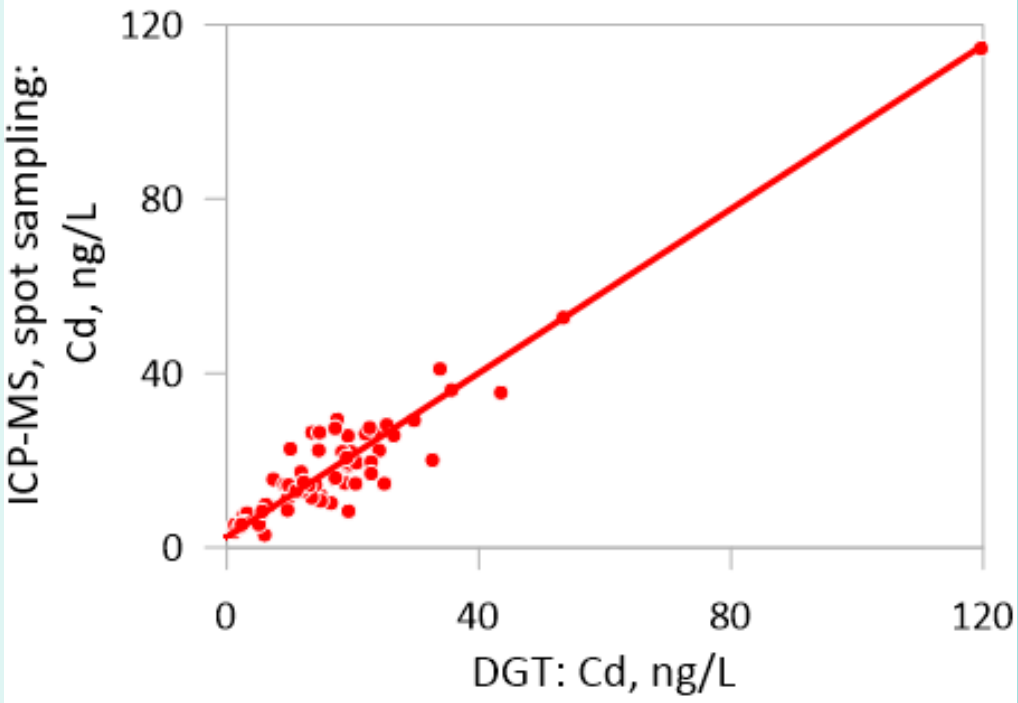
Source: https://www.mbari.org/

WP4. Relationships between methods.

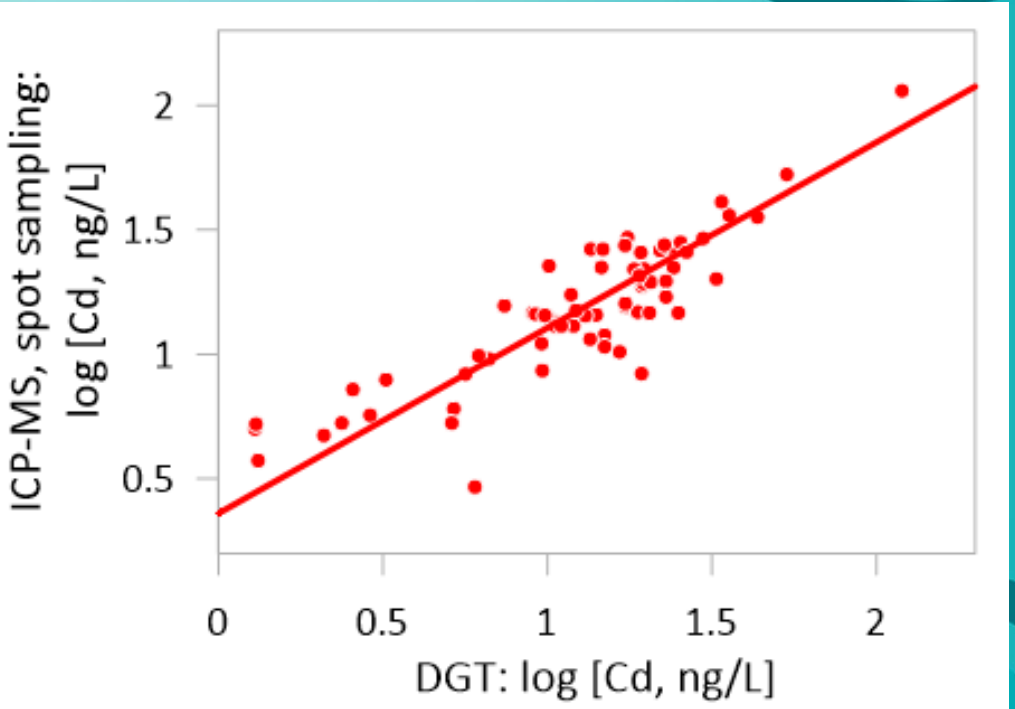
Cadmiun



WP4. Relationships among methods



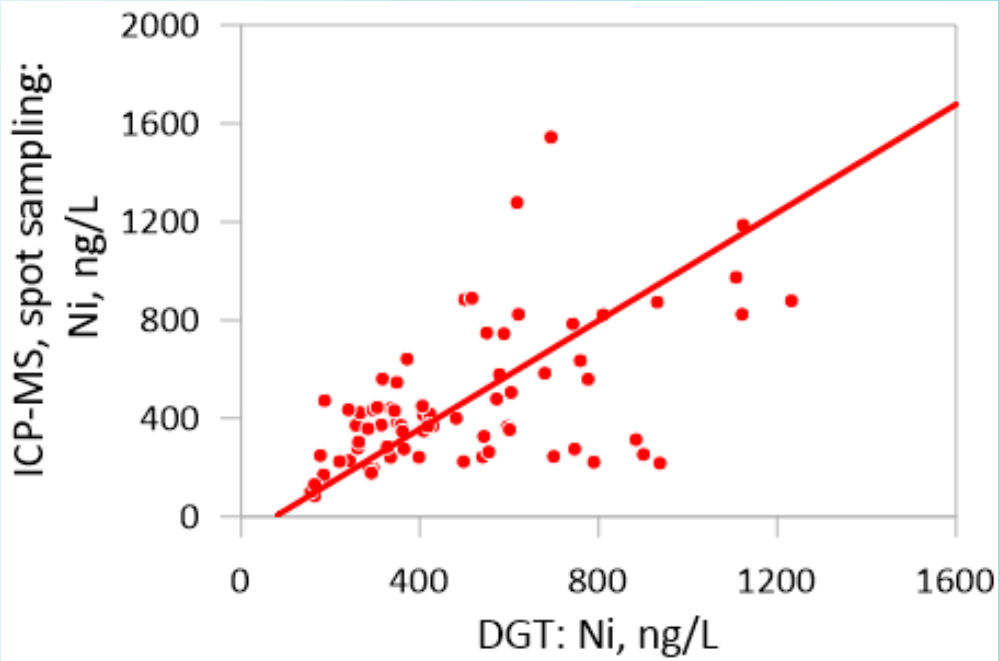
Equation Y = 0.9413407219 * X + 2.429713368
R-sq'd = 0.902628
P-Value = Less than 0.0001



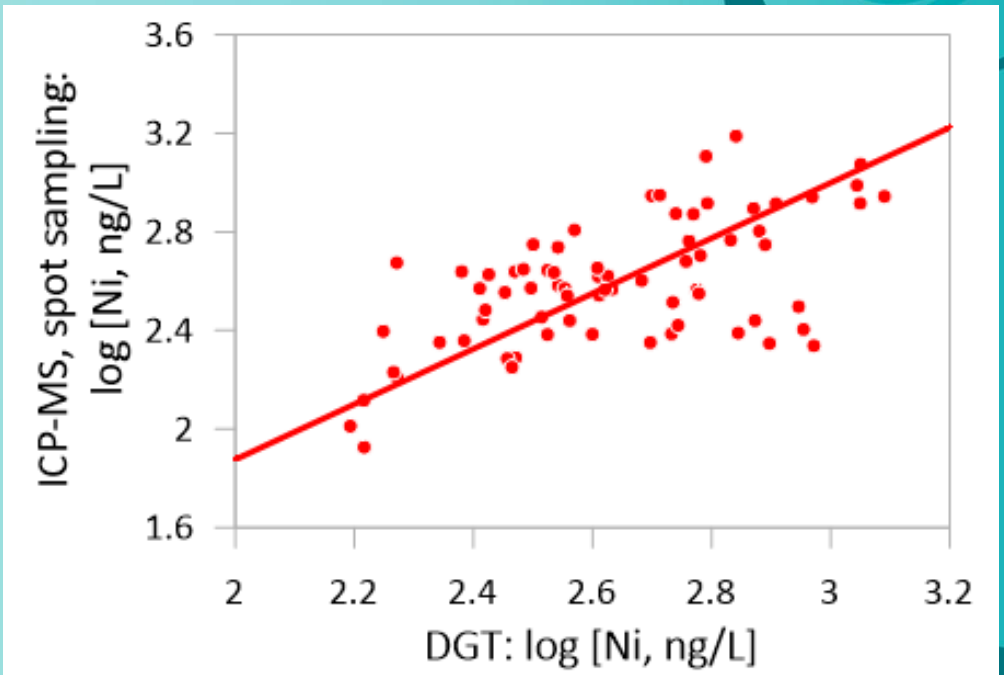
Equation Y = 0.7457457761 * X + 0.3606242077
R-sq'd = 0.795244
P-Value = Less than 0.0001

Nickel

WP4. Relationships among methods

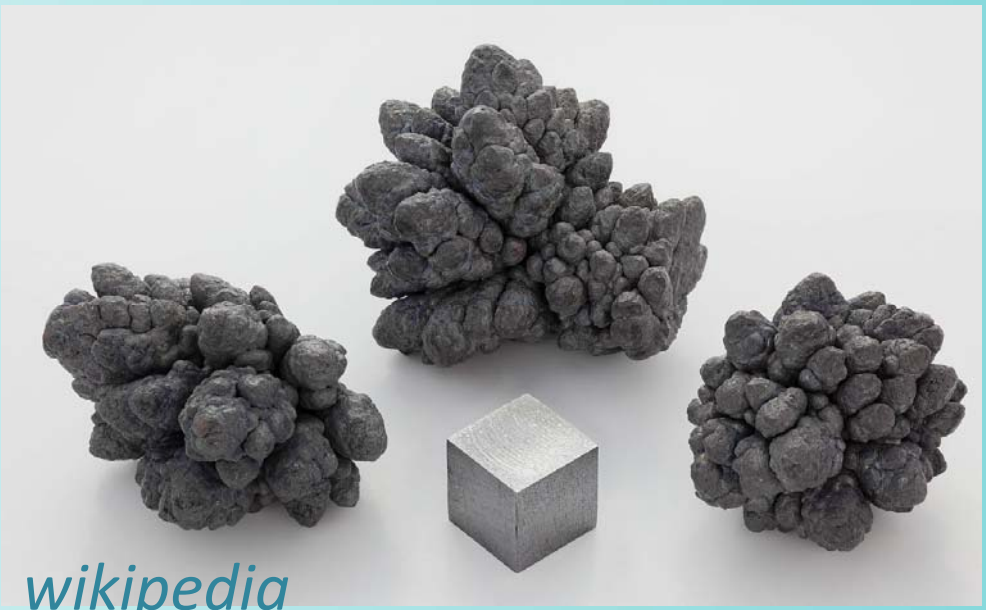


Equation Y = 1.10081161 * X - 82.94542108
R-sq'd = 0.529786
P-Value = Less than 0.0001



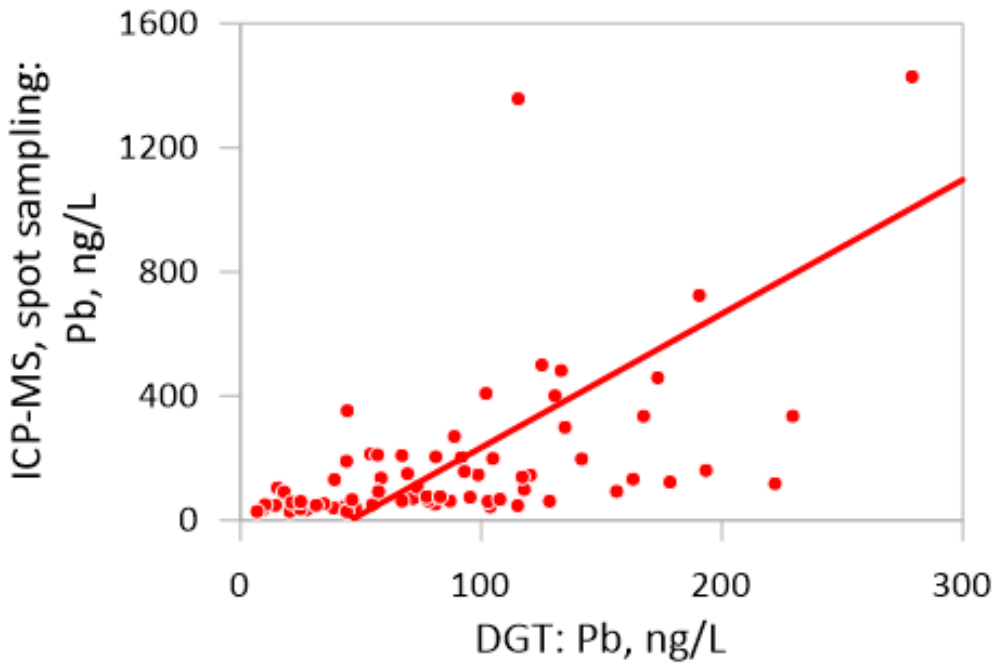
Equation Y = 1.122570614 * X - 0.3690151812
R-sq'd = 0.556486
P-Value = Less than 0.0001

Lead

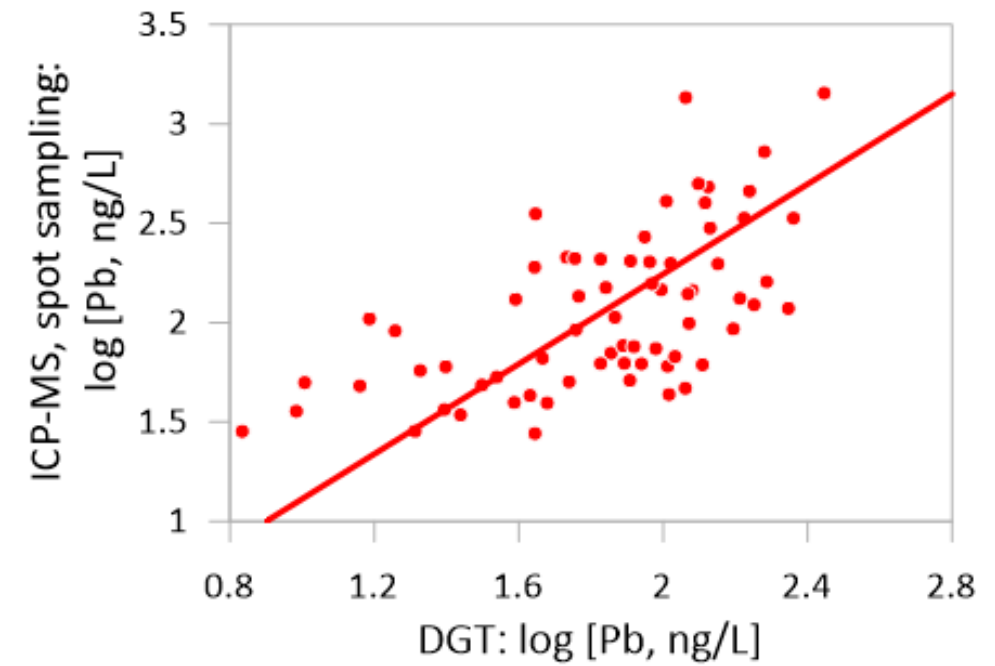


wikipedia

WP4. Relationships among methods



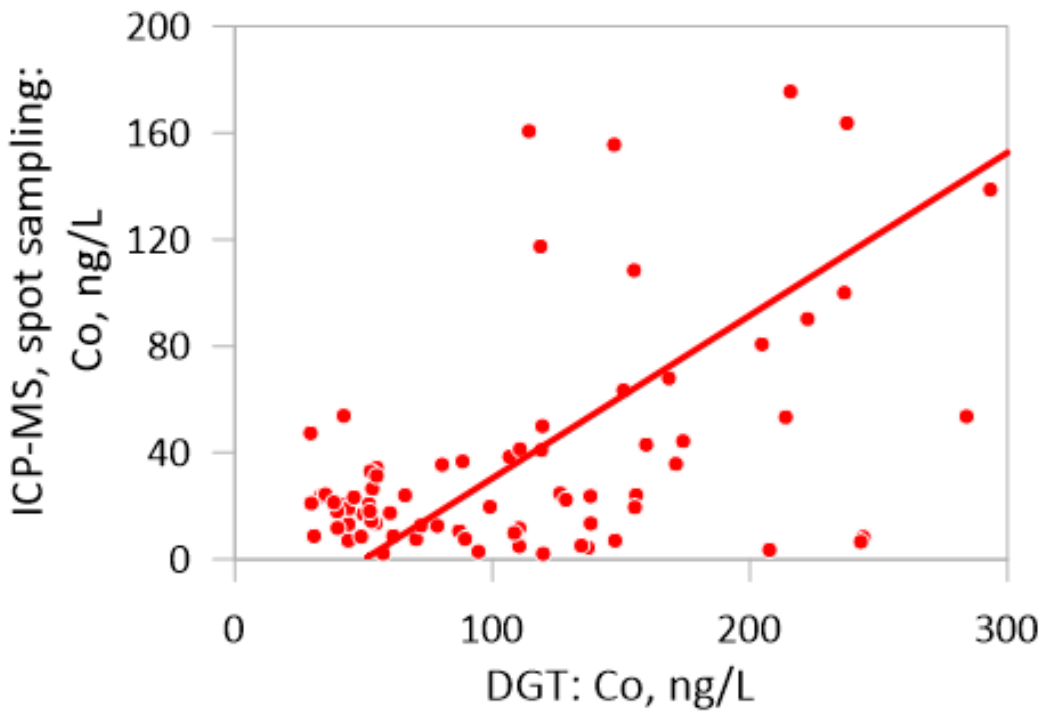
Equation Y = 4.31253146 * X - 197.0411321
R-sq'd = 0.521662
P-Value = Less than 0.0001



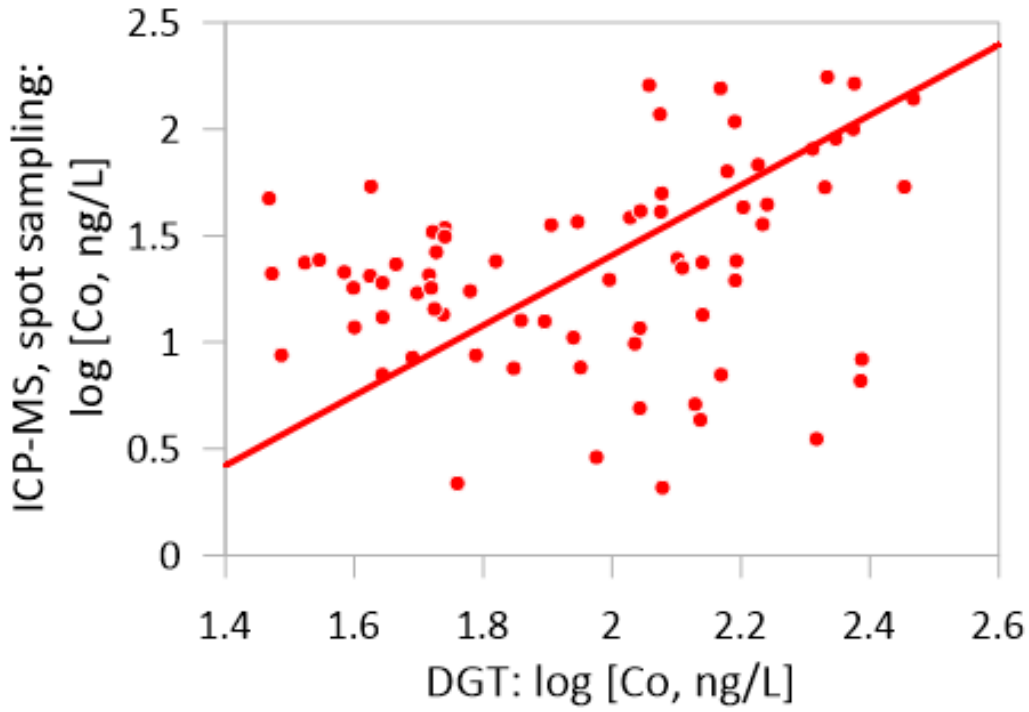
Equation Y = 1.132002399 * X - 0.01930857905
R-sq'd = 0.558358
P-Value = Less than 0.0001

Cobalt

WP4. Relationships among methods



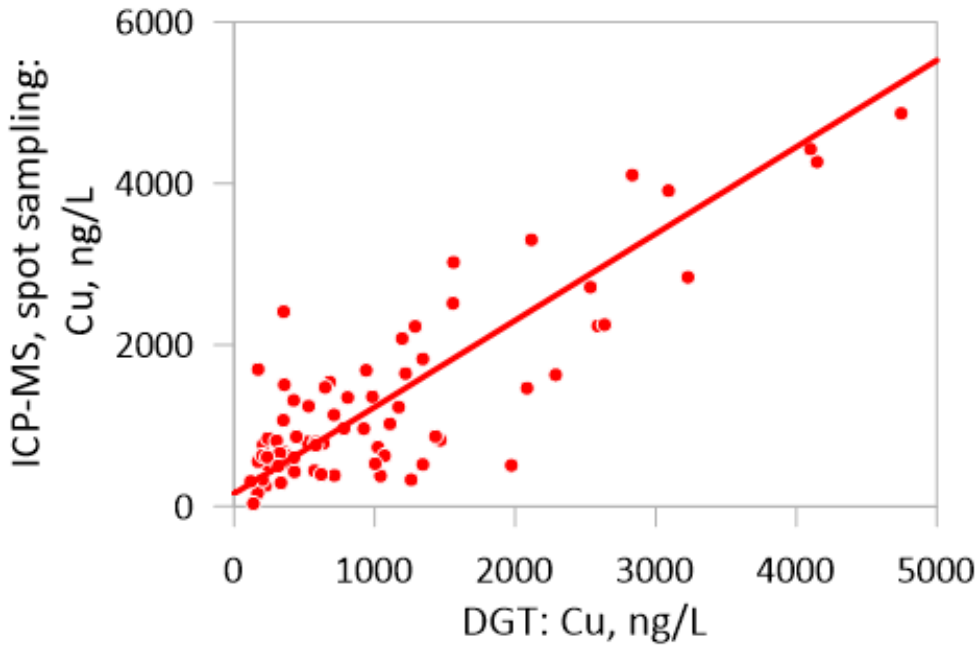
Equation Y = 0.6109370282 * X - 30.62247223
R-sq'd = 0.496098
P-Value = Less than 0.0001



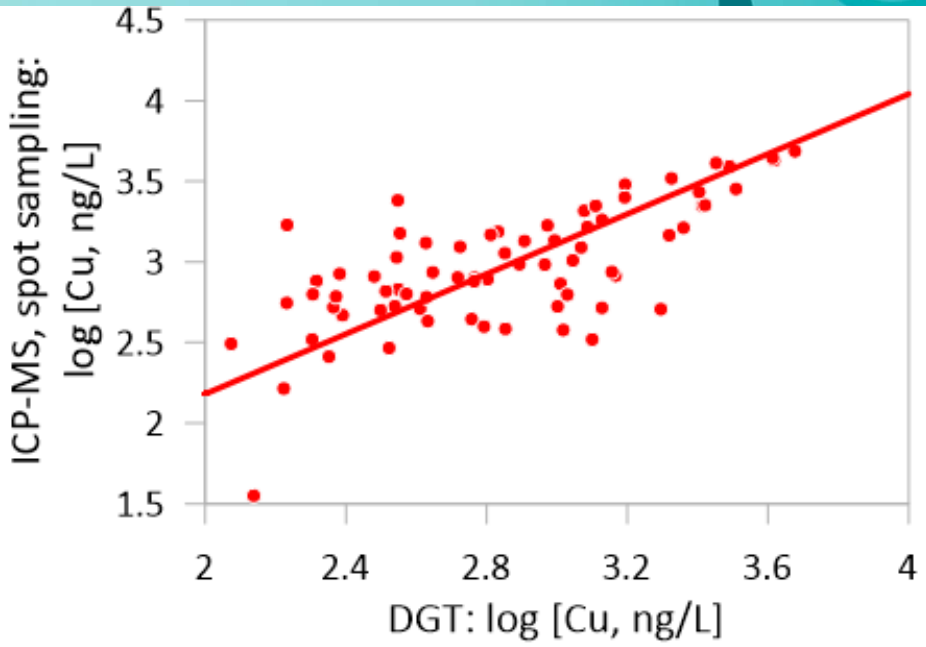
Equation Y = 1.643911752 * X - 1.879134839
R-sq'd = 0.414517
P-Value = 0.0110702217505928

Copper

WP4. Relationships among methods



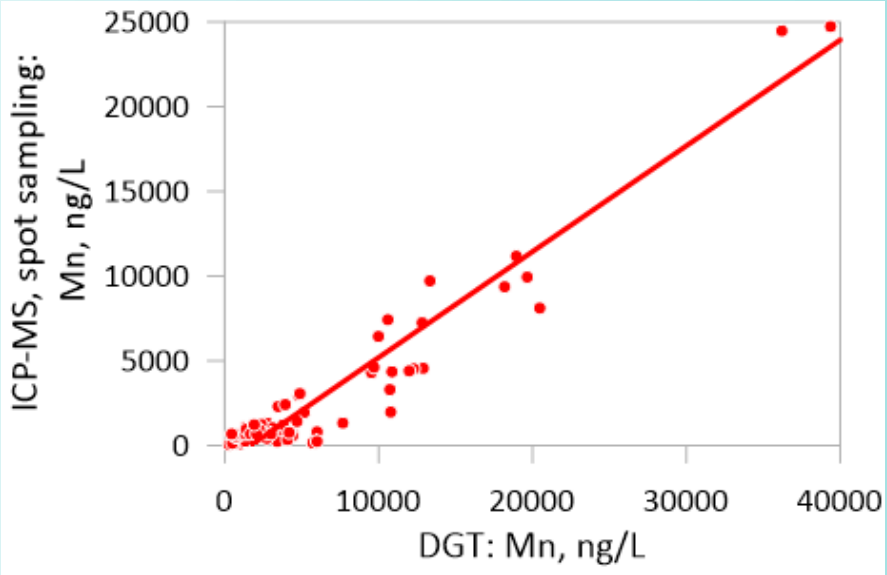
Equation Y = 1.073549595 * X + 157.4827267
R-sq'd = 0.758816
P-Value = Less than 0.0001



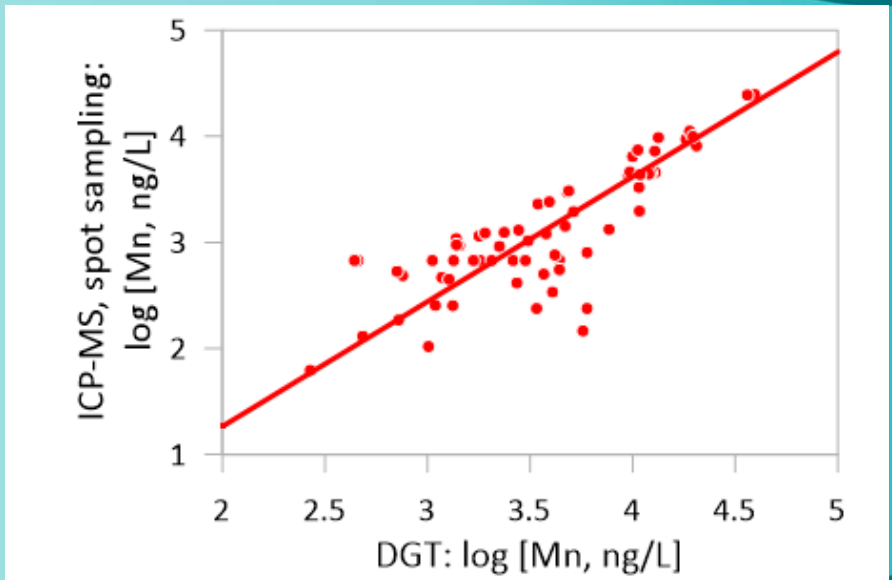
Equation Y = 0.9305188596 * X + 0.3201143484
R-sq'd = 0.621317
P-Value = Less than 0.0001

Manganese

WP4. Relationships among methods



Equation Y = 0.6246068198 * X - 1047.093151
R-sq'd = 0.920143
P-Value = Less than 0.0001



Equation Y = 1.176263723 * X - 1.086690433
R-sq'd = 0.733955
P-Value = Less than 0.0001

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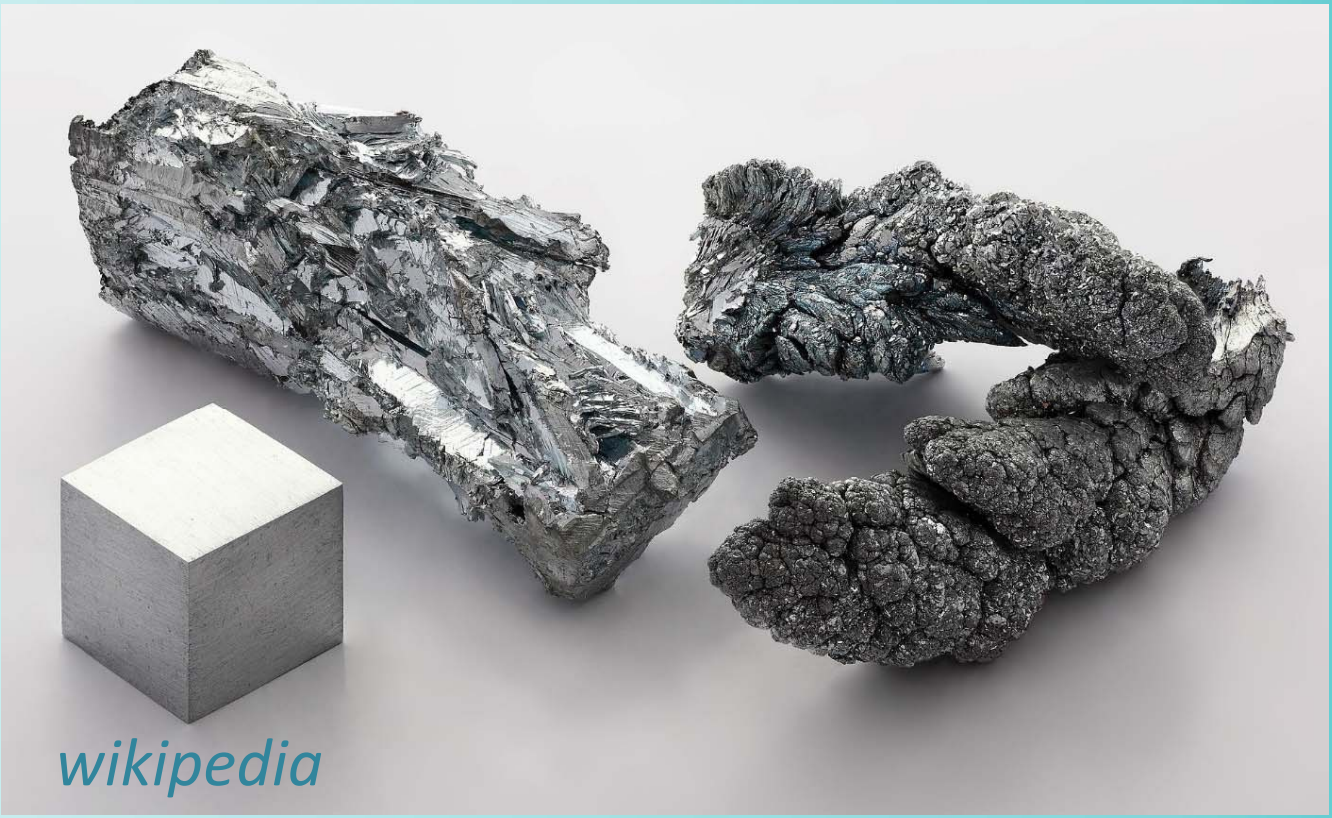
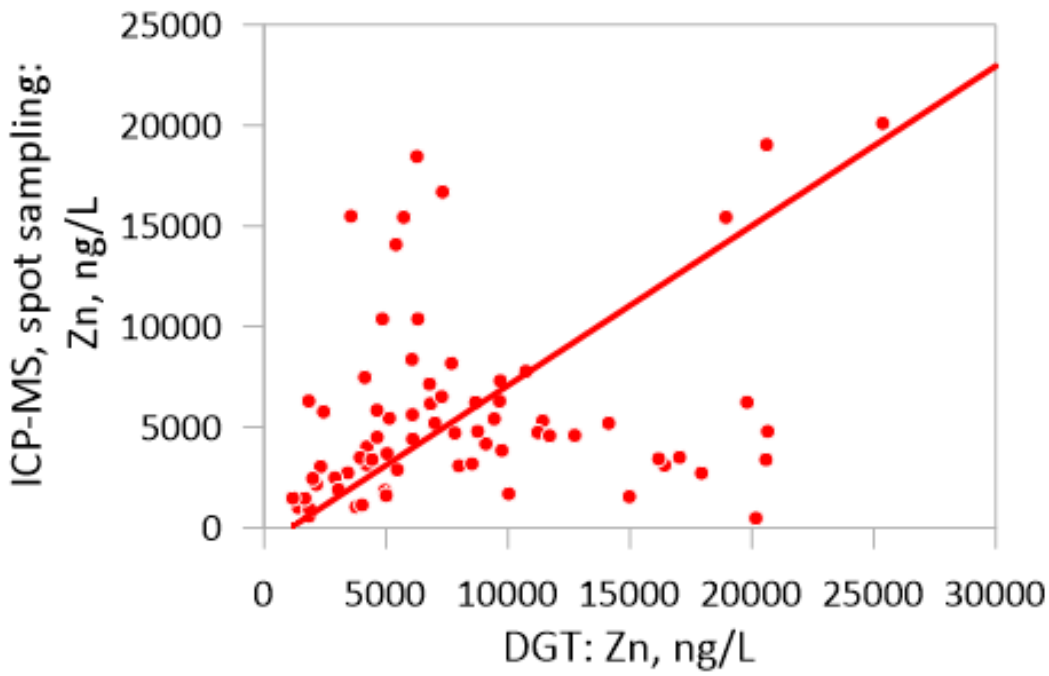
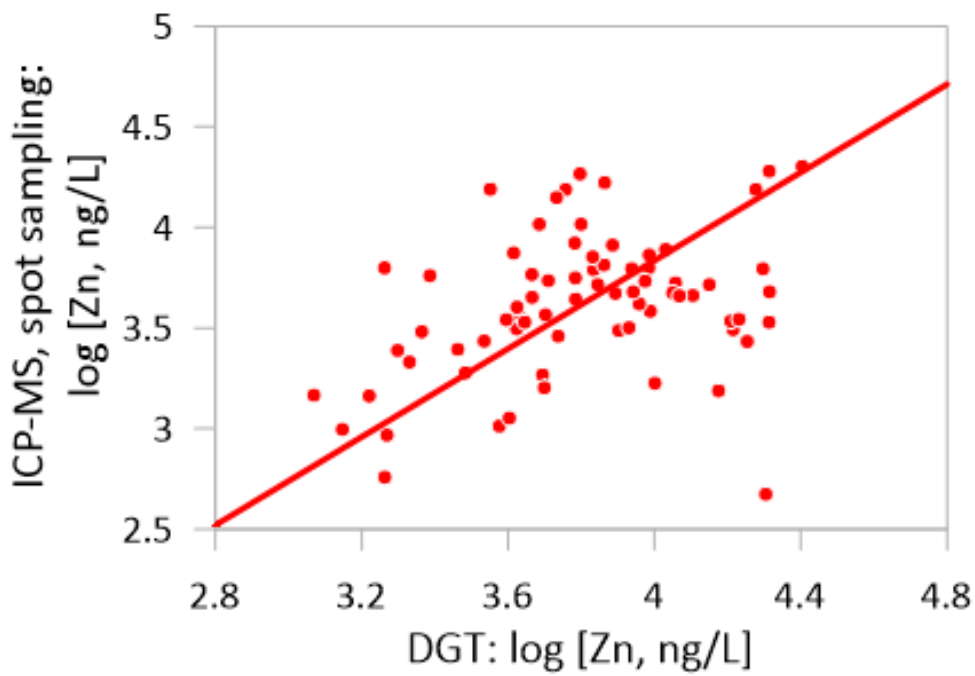
Zinc



WP4. Relationships among methods



Equation Y = 0.793884869 * X - 863.7856664
R-sq'd = 0.406561
P-Value = 0.0207946868409477



Equation Y = 1.095540387 * X - 0.5468783692
R-sq'd = 0.435844
P-Value = 0.00220304220964651

WP4. Relationships among methods

Main conclusions

Cd, Mn and Cu: there is a strong and direct log-log relationship between the concentration measured by DGT and the mean concentration measured by spot sampling (by ICP-MS). R^2 values: 0.61-0.80.

Ni and Pb: there is a medium-strength and direct log-log relationship between the concentration measured by DGT and the mean concentration measured by spot sampling (by ICP-MS). R^2 value: 0.56.

Co and Zn: there is a weak and direct log-log relationship between the concentration measured by DGT and the mean concentration measured by spot sampling (by ICP-MS). R^2 values: 0.41-0.44.

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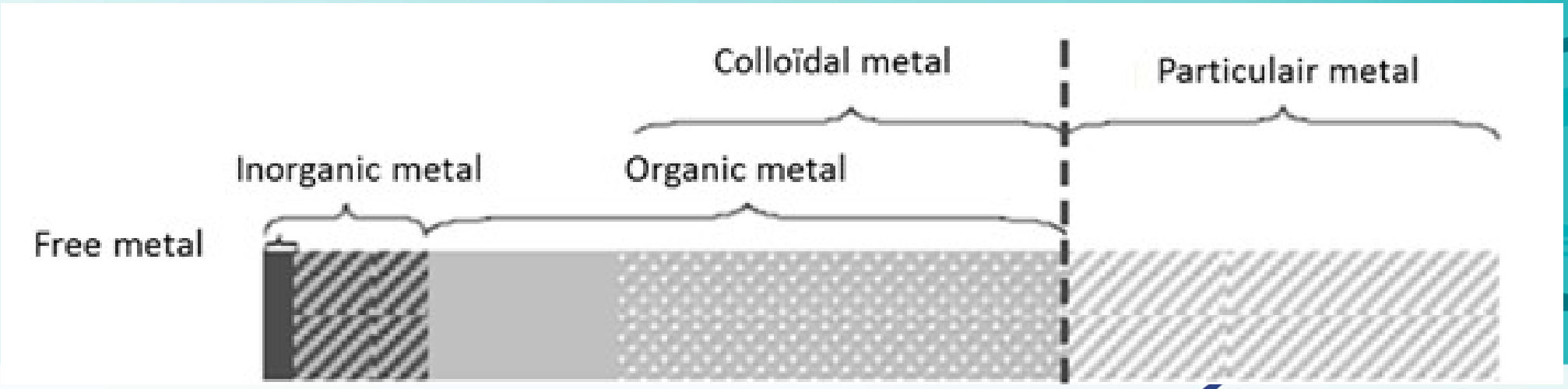
WP4. Influence of water physicochemical parameters in DGT trace metals sequestration. (WP nr. 4, action nr. 3)

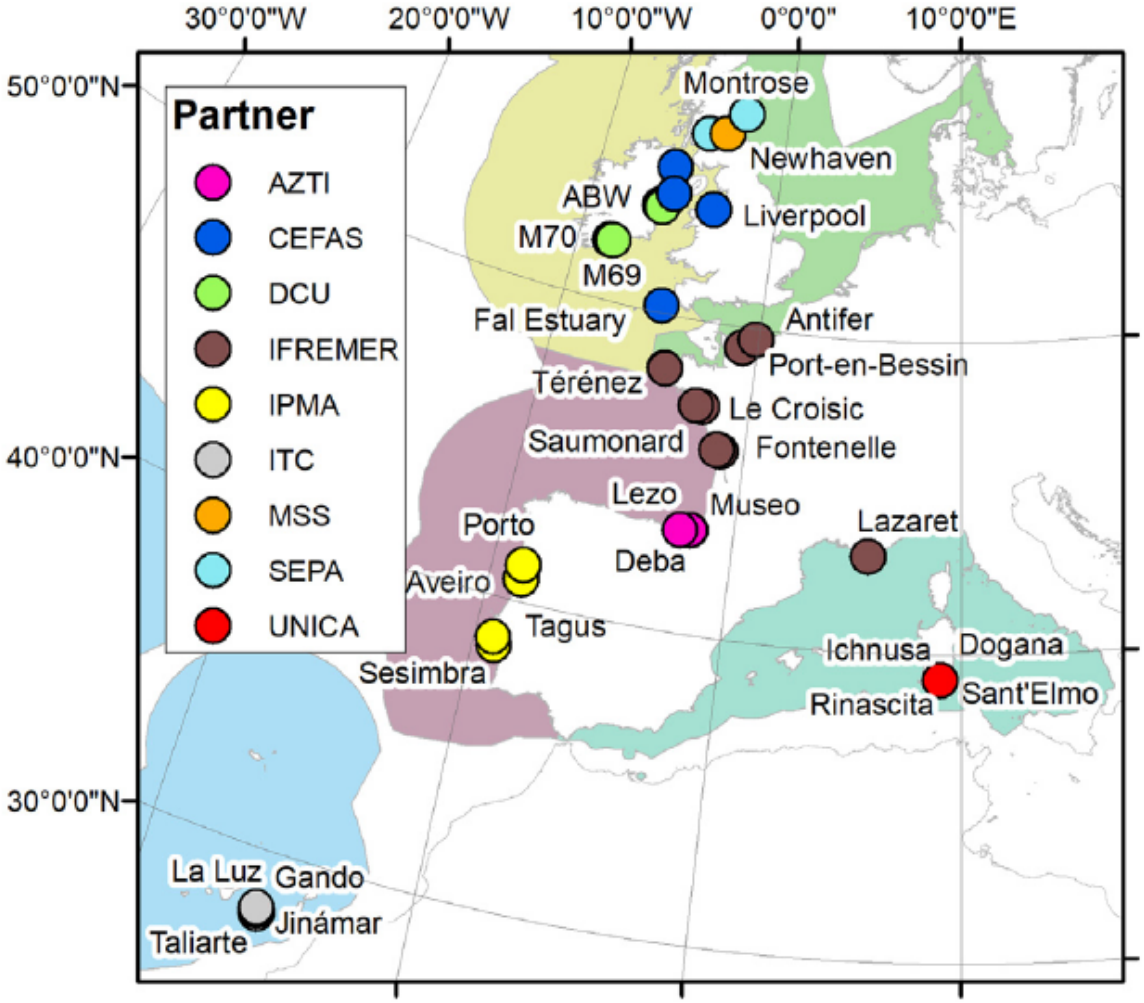
WP4. Influence of physicochemical parameters

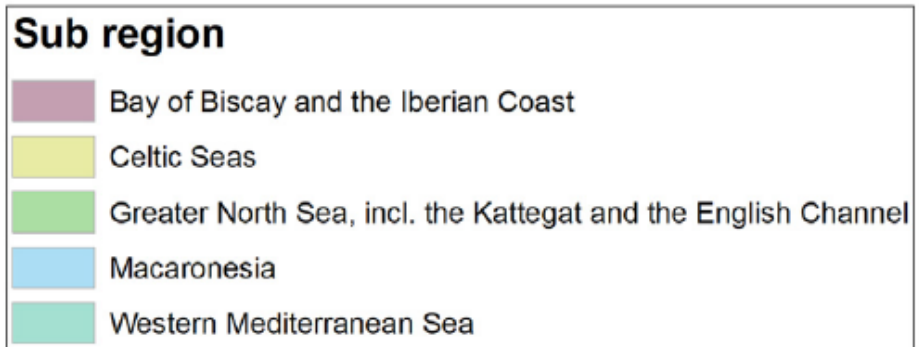
Previous research with DGT had found that **at the local scale** the variability in **the ratio of the DGT labile fraction to the total dissolved fraction** may depend on the characteristics of the environment.

E.g., for some metals, the dissolved organic carbon (DOC) can affect this ratio.



WP4. Influence of physicochemical parameters





In the Monitool project we have investigated this issue, but on a **broad geographic scale** (not at the local level).

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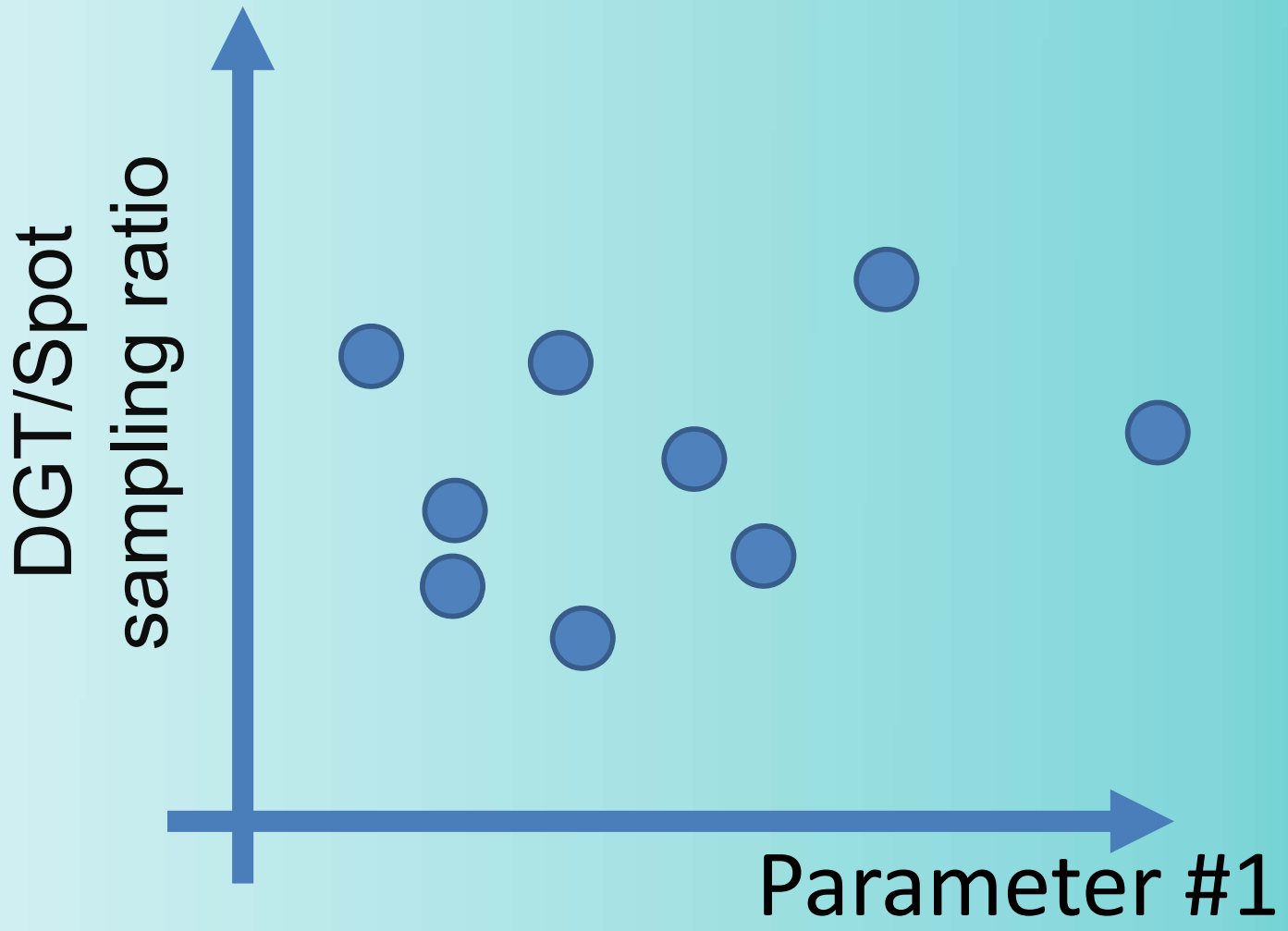
WP4. Influence of physicochemical parameters

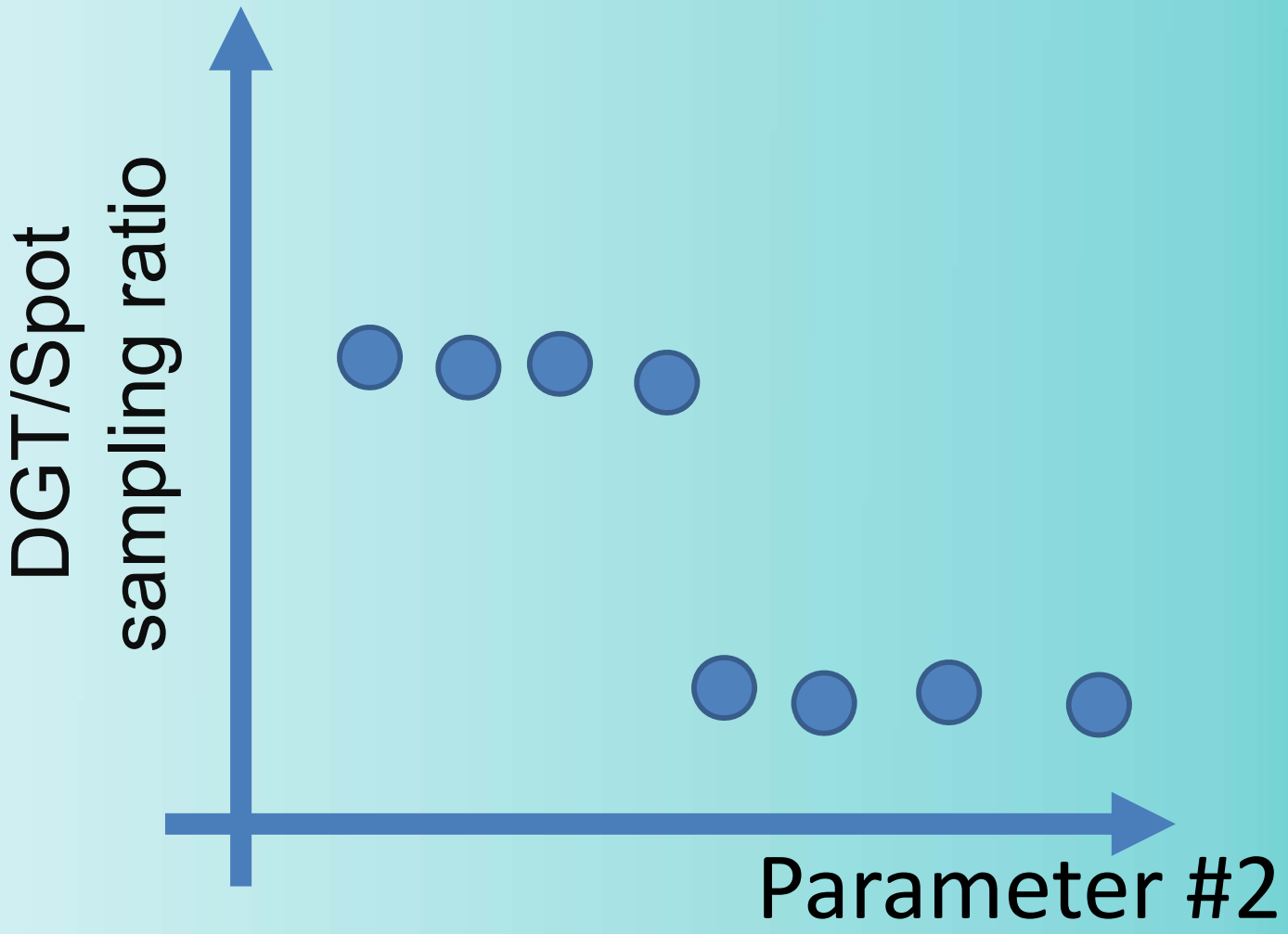
We have explored this variables/factors:

- Temperature
- Salinity
- Oxygen
- pH
- Suspended Particulate Matter (SPM)
- Dissolved organic carbon (DOC)
- Fouling
- Coastal sites/Estuaries

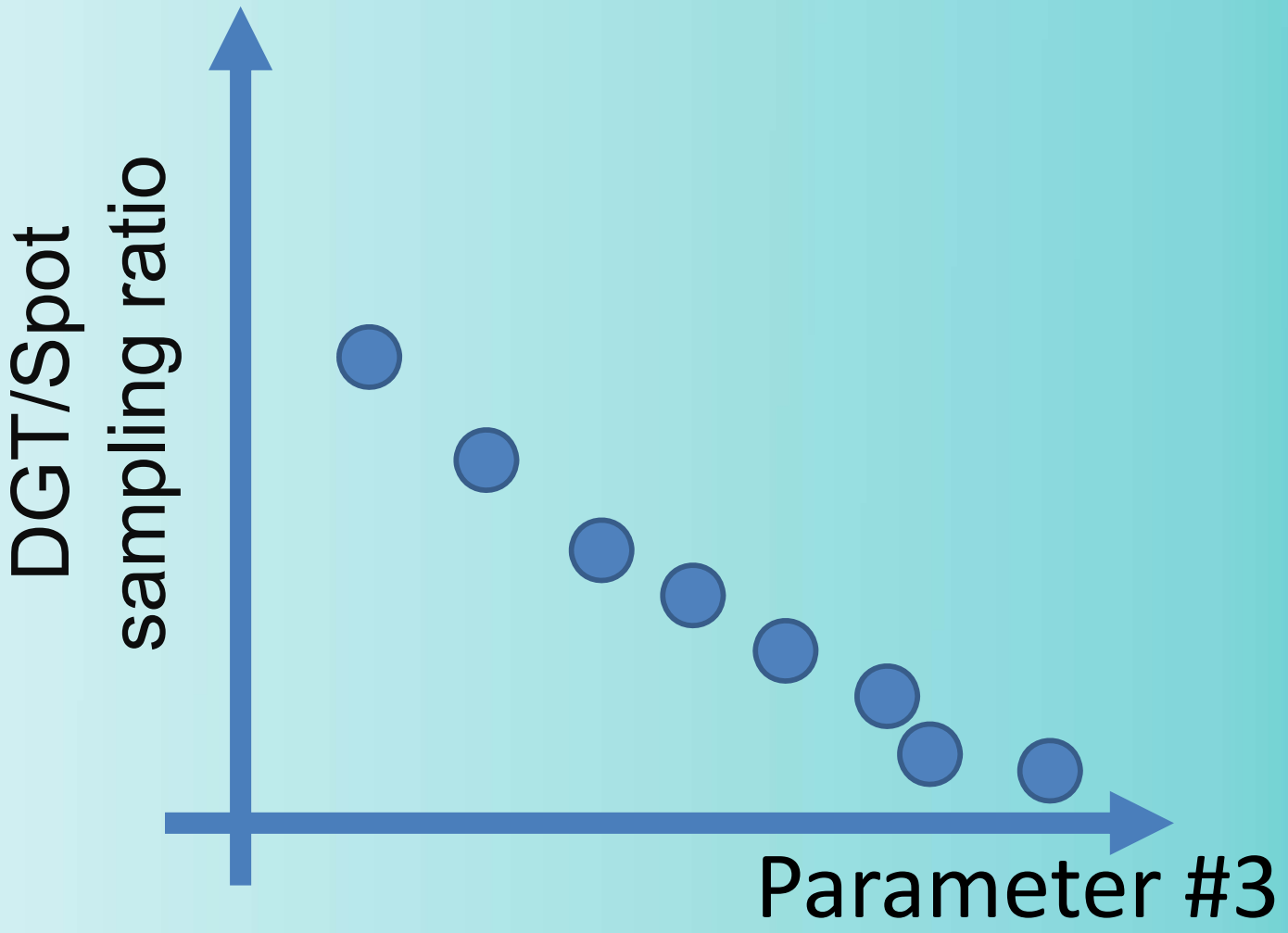
WP4. Influence of physicochemical parameters



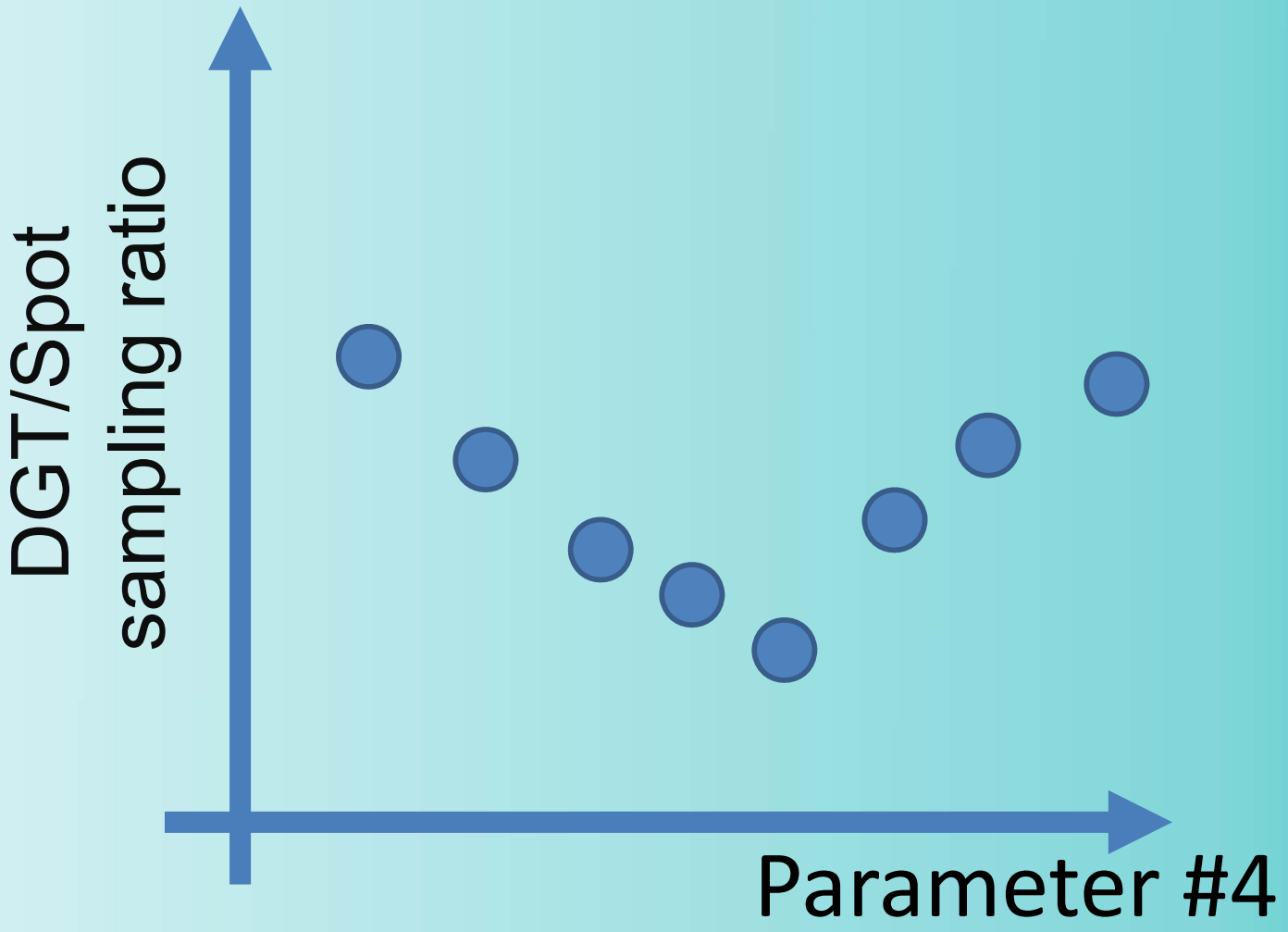
WP4. Influence of physicochemicalparameters



WP4. Influence of physicochemicalparameters



WP4. Influence of physicochemicalparameters



WP4. Influence of physicochemicalparameters

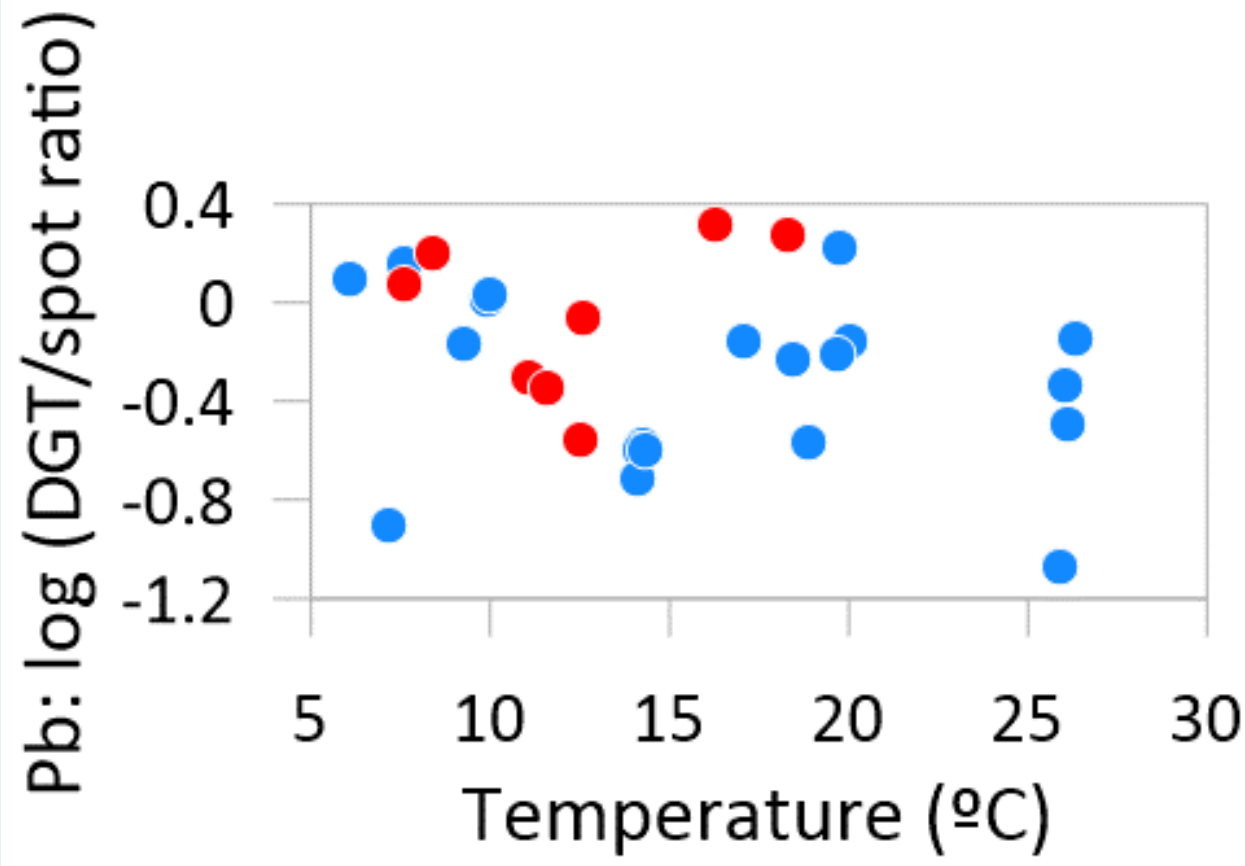
DGT/Spot sampling ratio

The ratio is log transformed (the double=middle in size)

The parameter is log-transformed in some cases

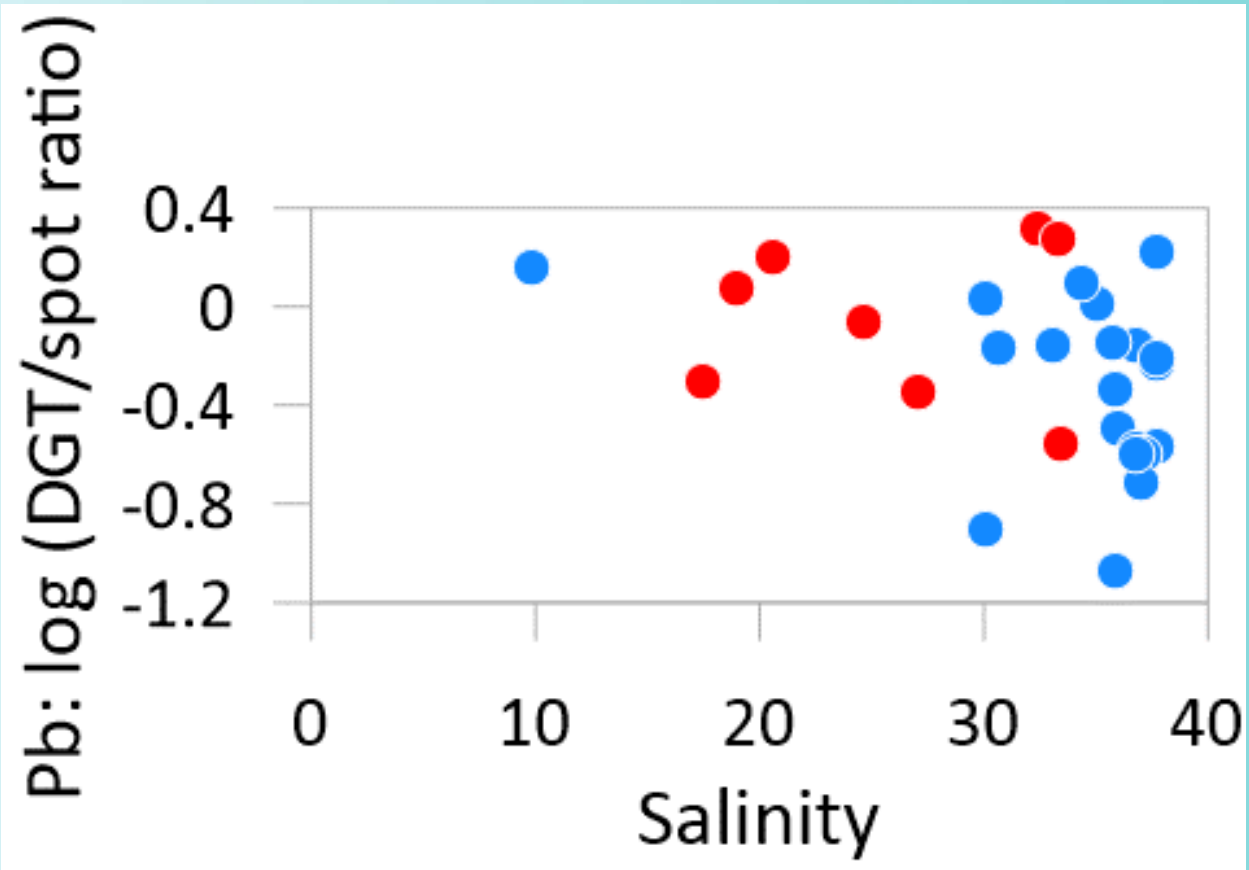
Parameter #

WP4. Influence of physicochemicalparameters

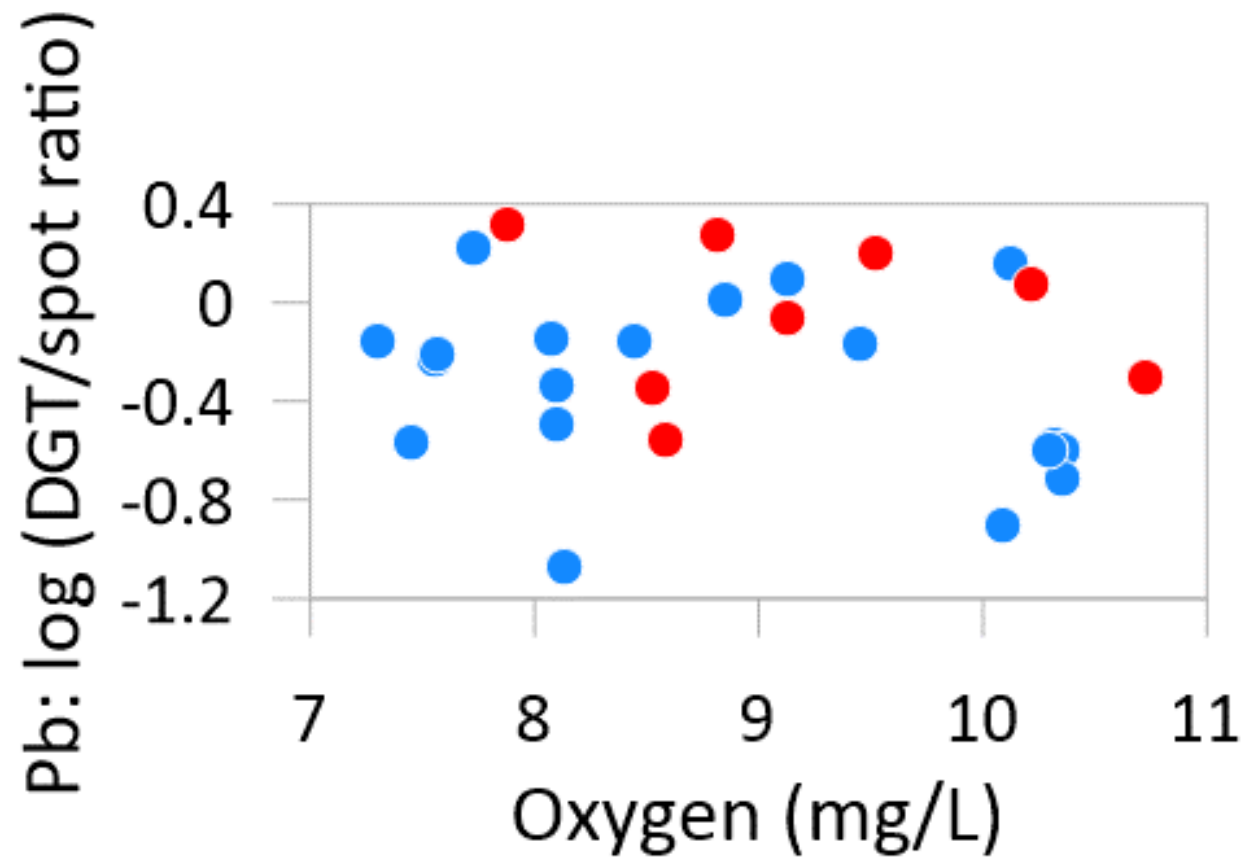


The blue dots correspond to coastal areas and the red dots to estuaries.

WP4. Influence of physicochemicalparameters



WP4. Influence of physicochemicalparameters



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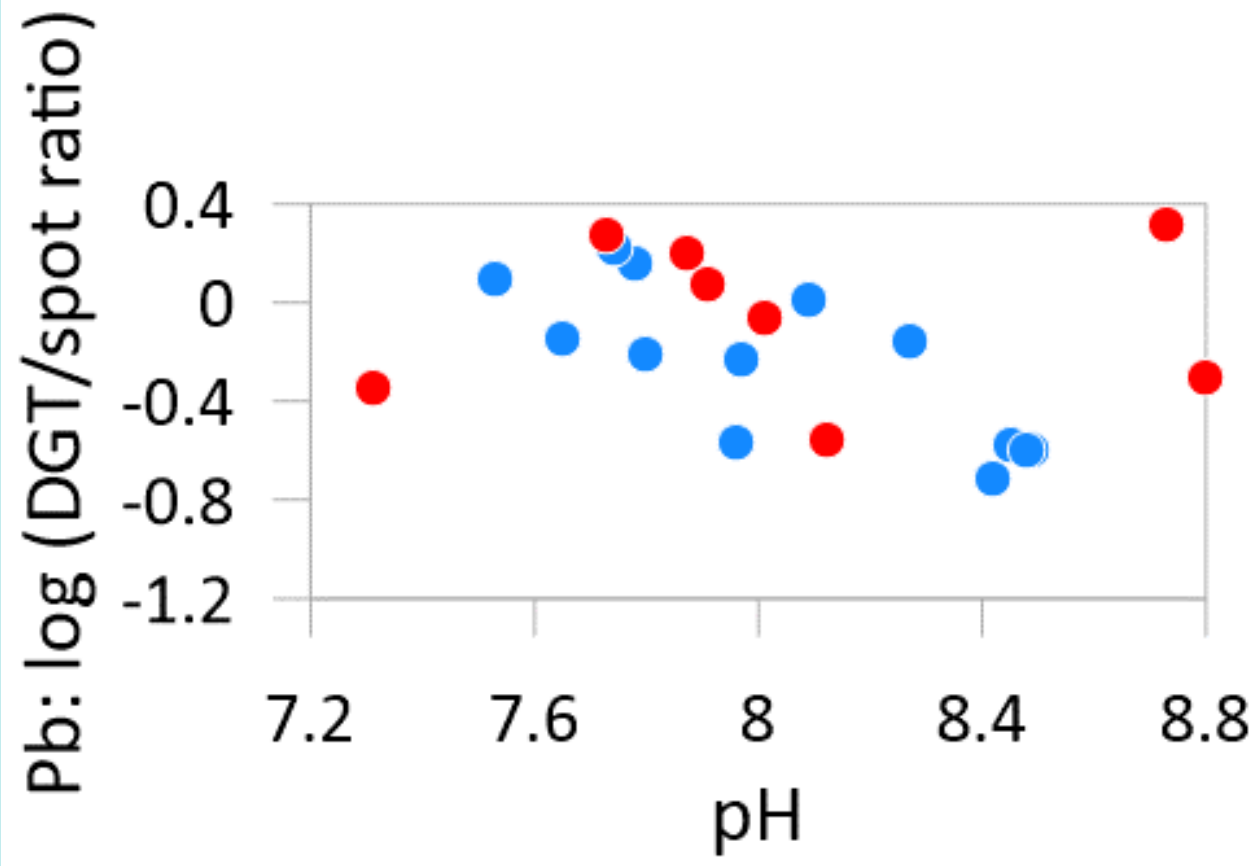
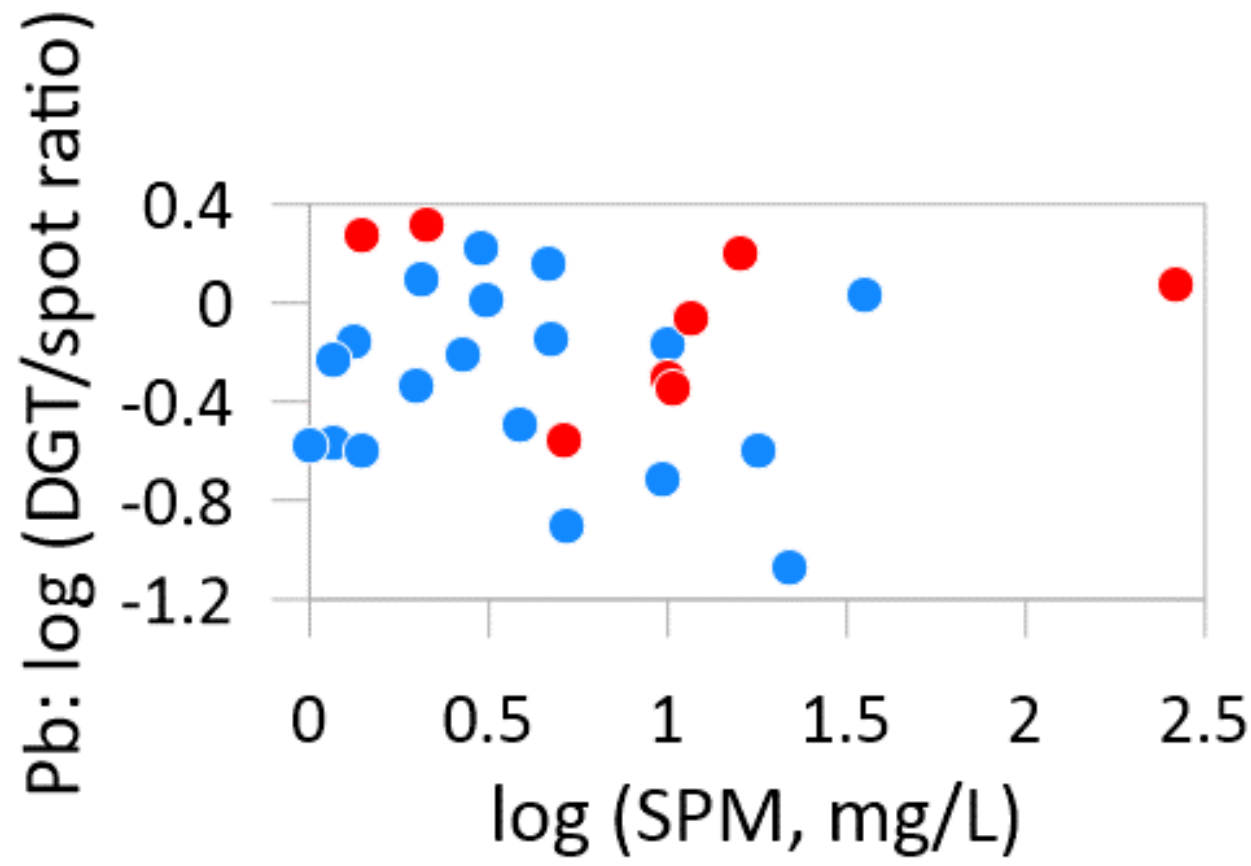


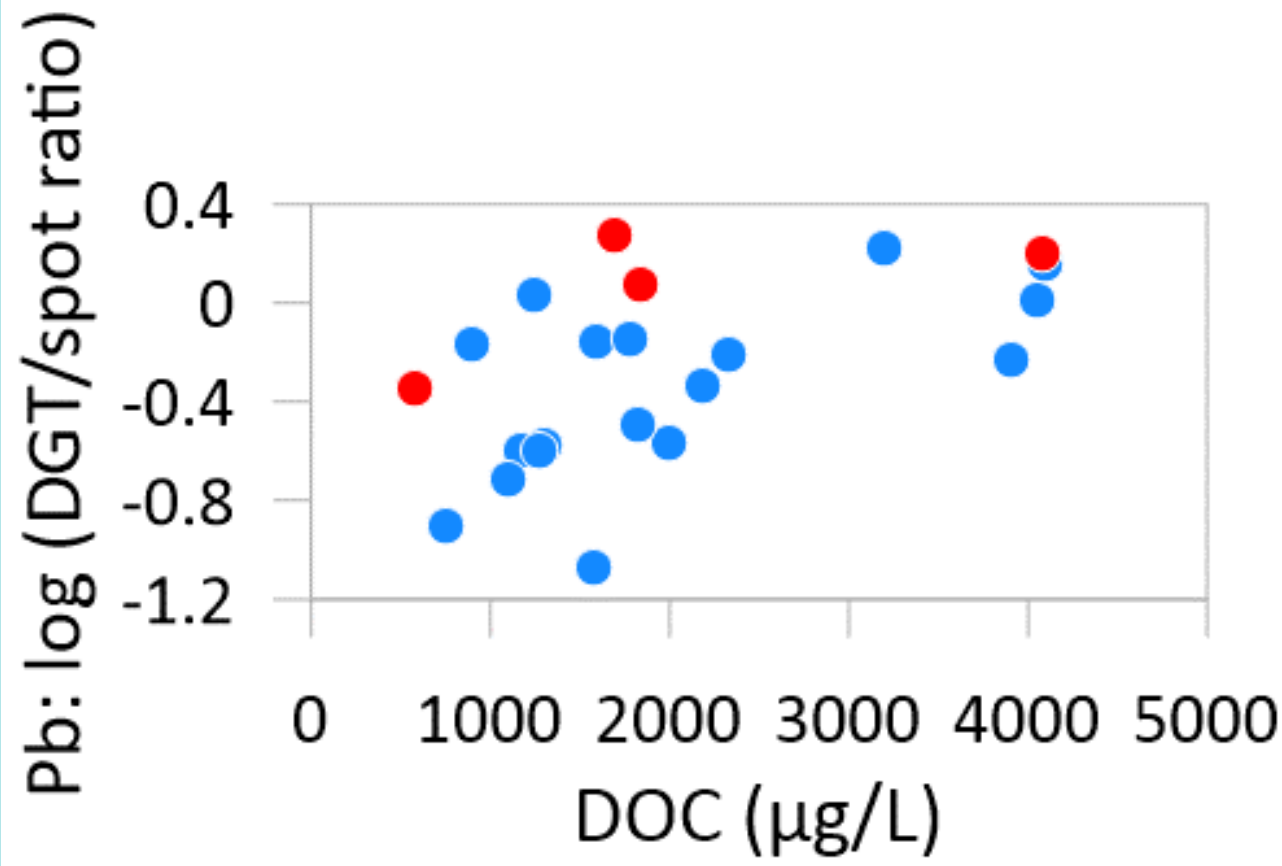
WP4. Influence of physicochemicalparameters



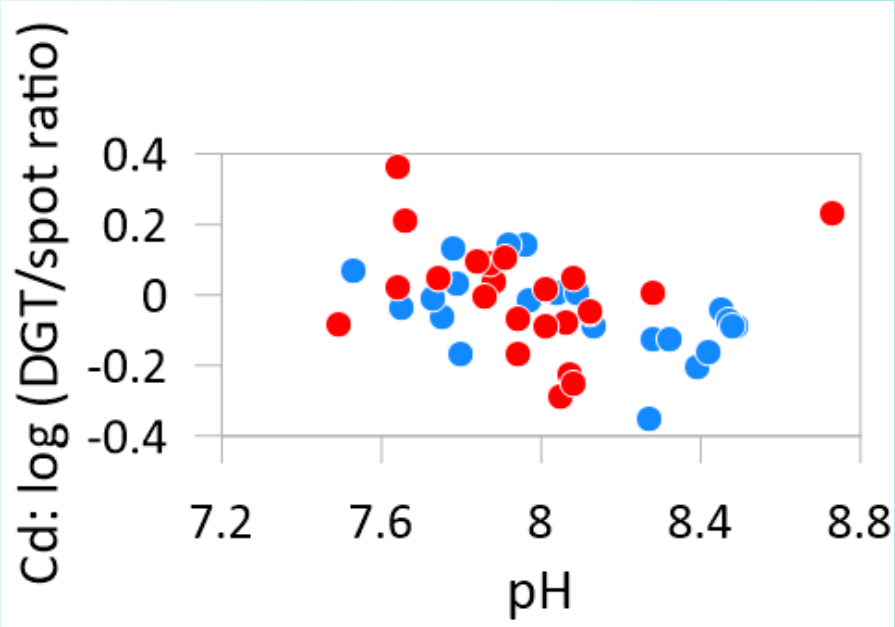
SPM = Suspended Particulate Matter

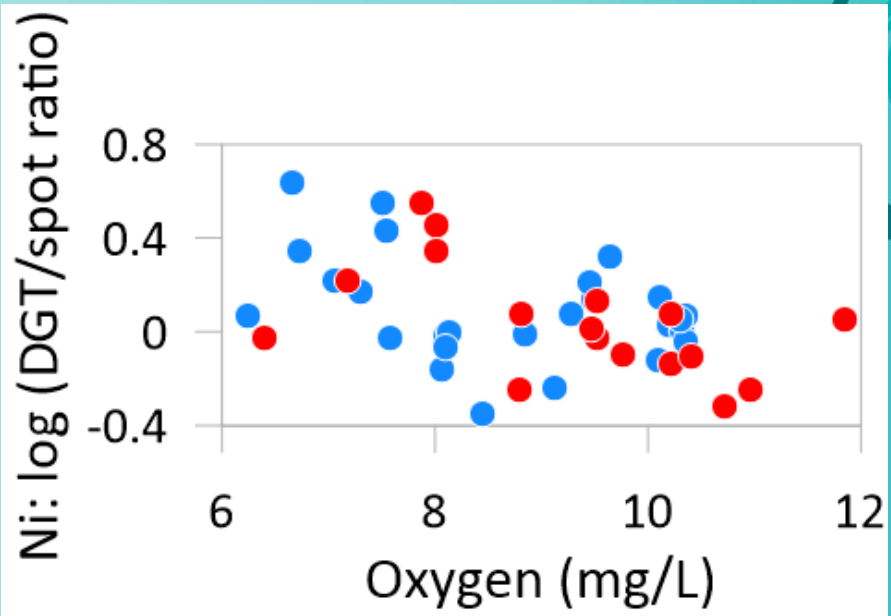
WP4. Influence of physicochemicalparameters

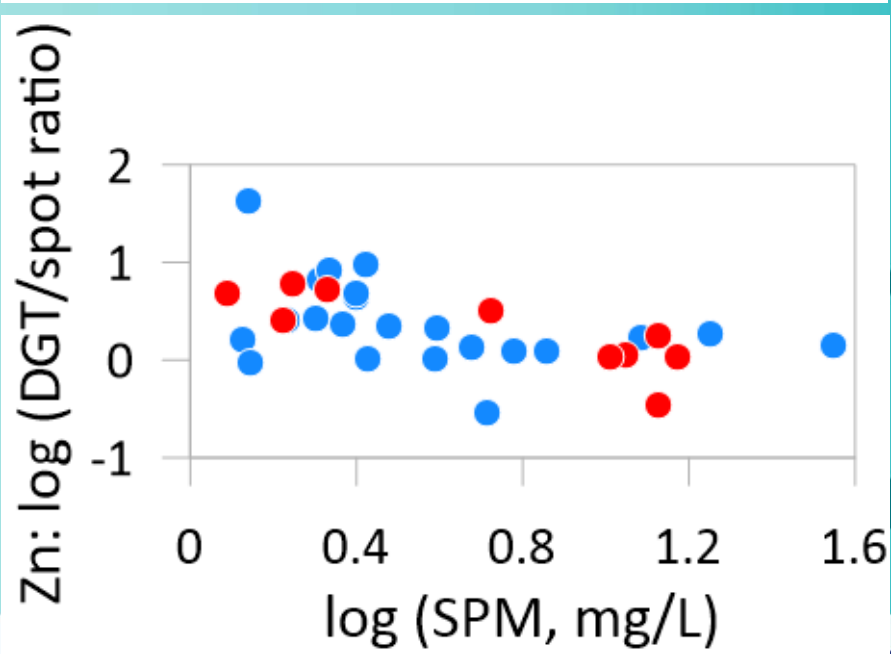
A direct relationship with Dissolved Organic Carbon (DOC) is found, but it is not statistically significant.



WP4. Influence of physicochemicalparameters







There were a few significant relationships, however, they are very scattered.

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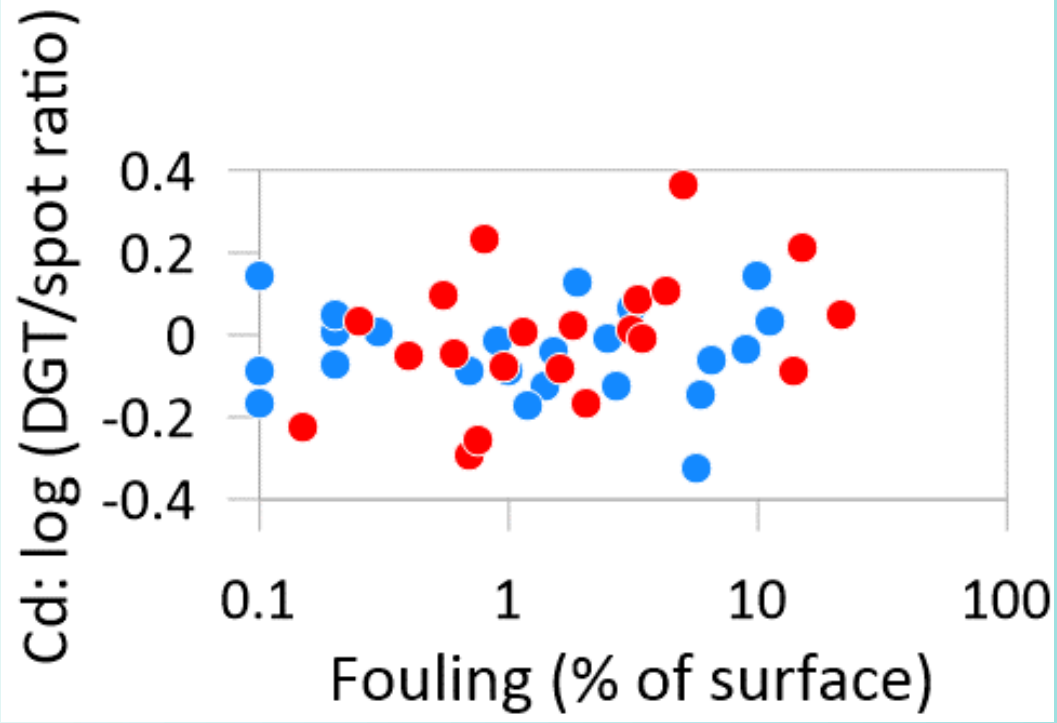
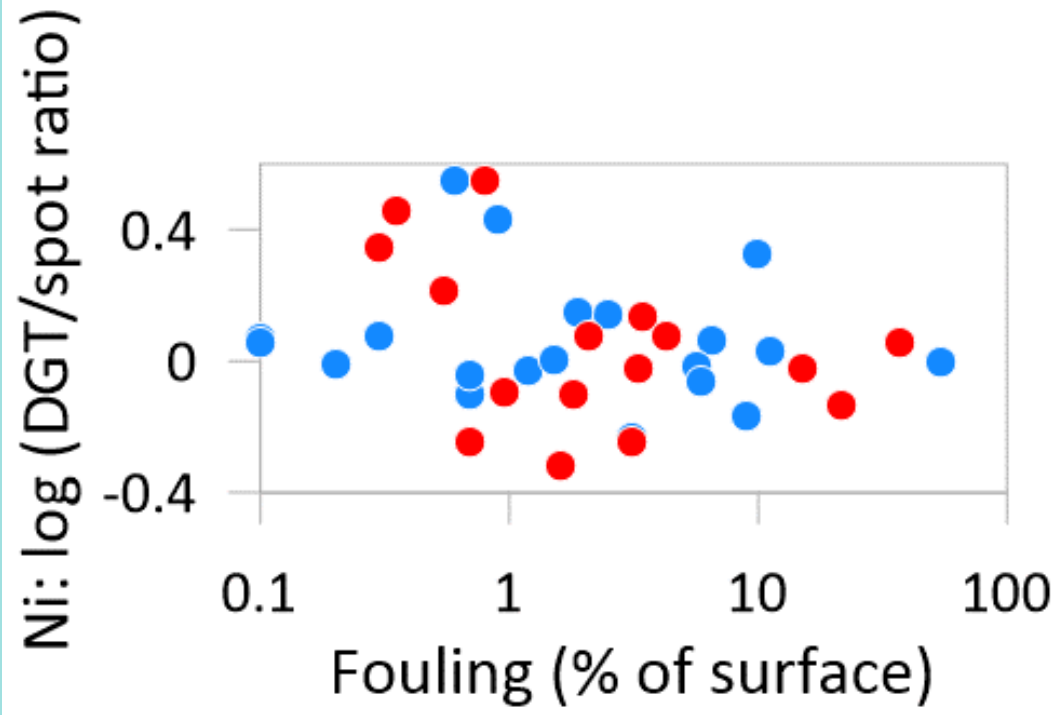
WP4. Influence of physicochemicalparameters

What about fouling (the accumulation of unwanted material on DGT)?

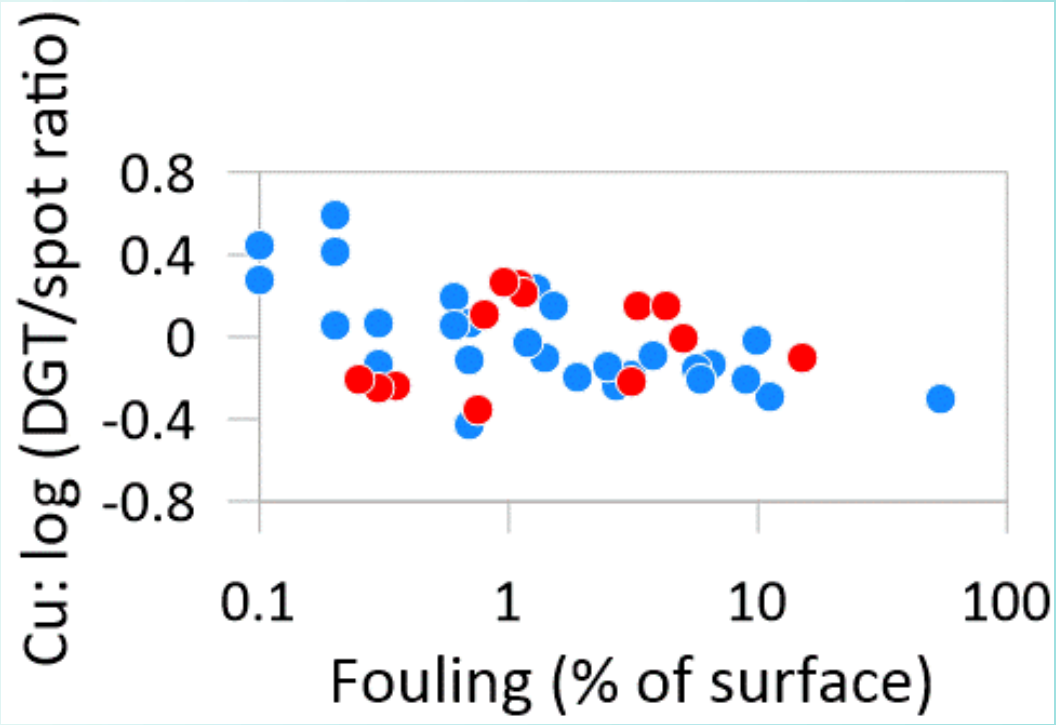
WP4. Influence of physicochemicalparameters

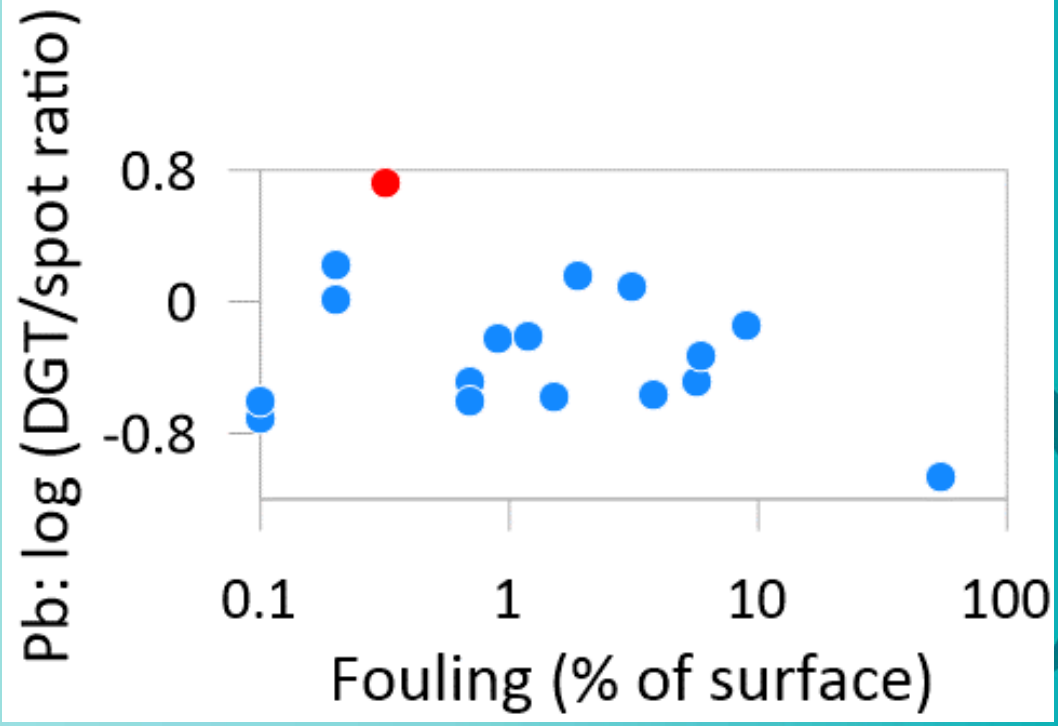




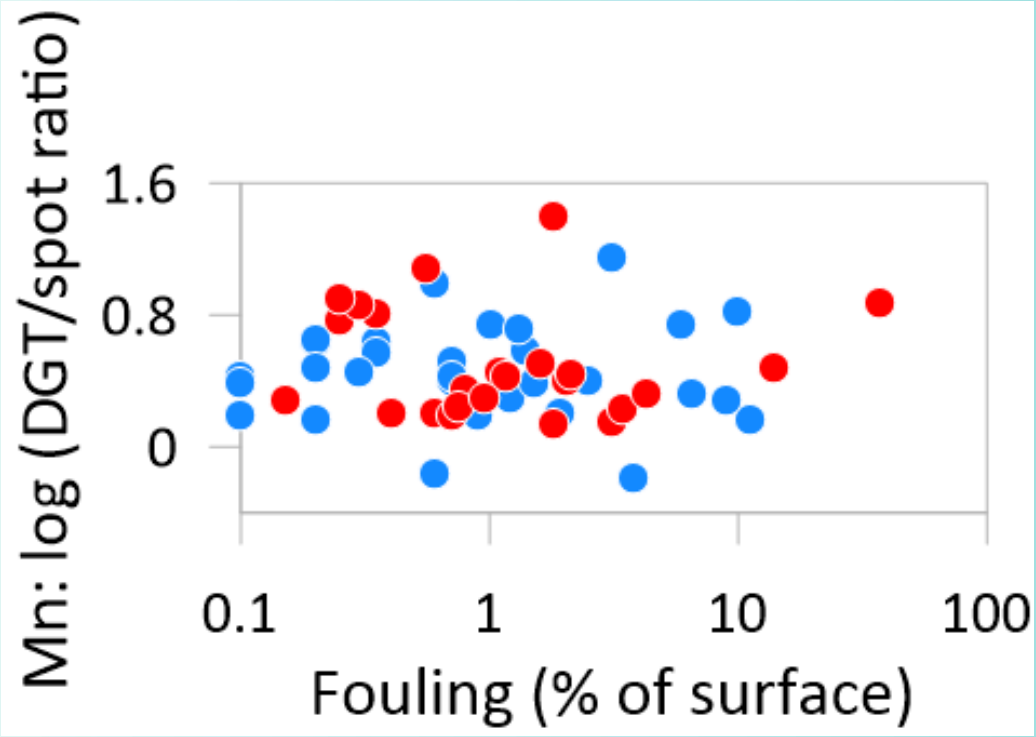
WP4. Influence of physicochemicalparameters

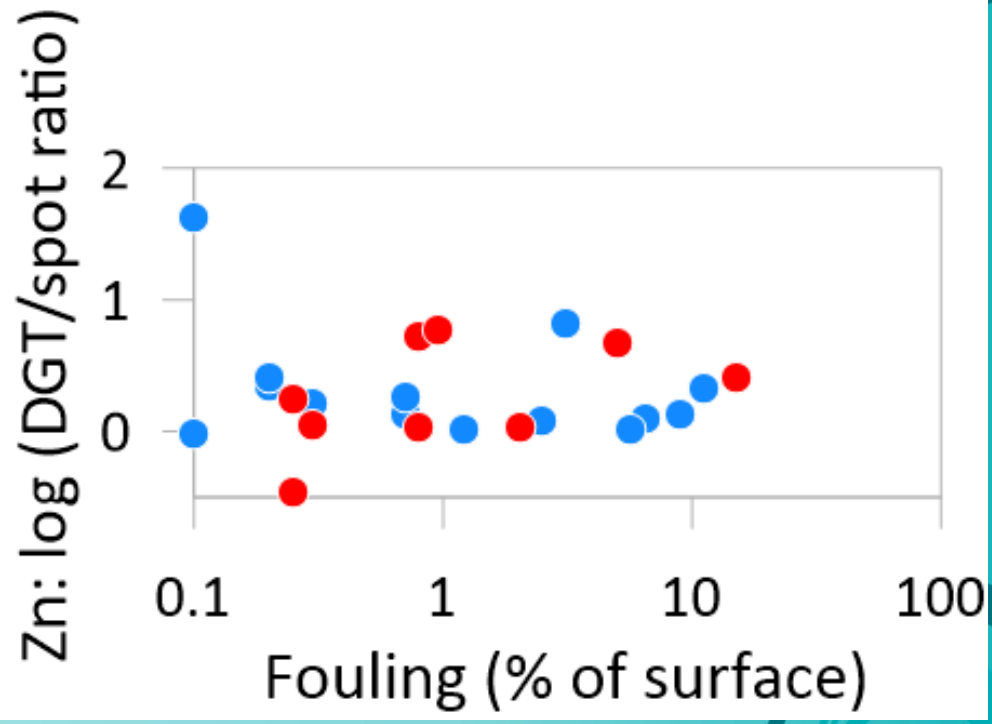
Cu -> the relationship is significant





WP4. Influence of physicochemicalparameters



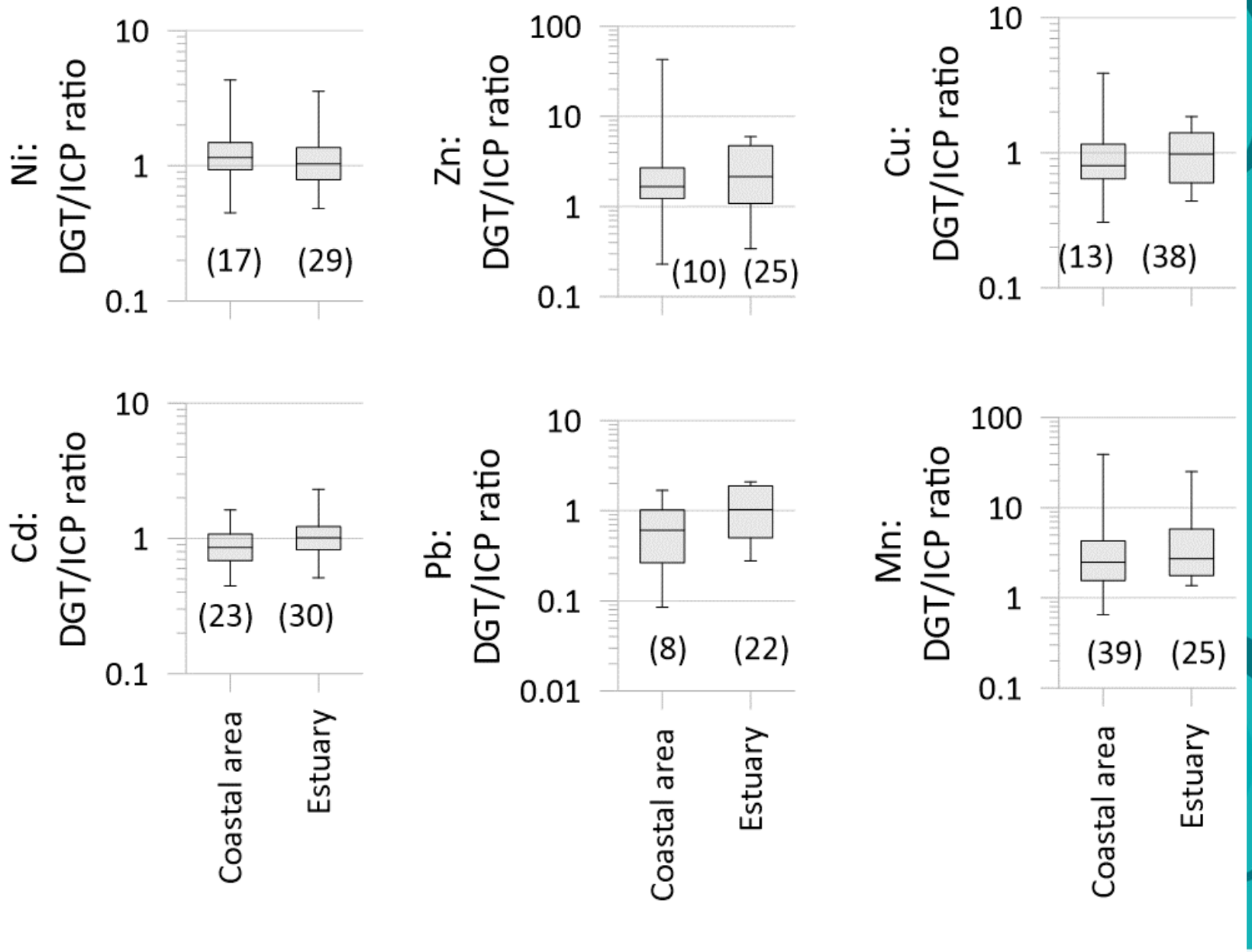


WP4. Influence of physicochemicalparameters

What about coastal sites/estuaries?

WP4. Influence of physicochemical parameters

No significant differences in median values were found



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WP4. Influence of physicochemicalparameters

Main conclusion:

In general, the DGT/spot ratios were not explained by the temperature, salinity, pH, oxygen, DOC, SPM, fouling or estuary/coastal factor (some relationships were statistically significant but very scattered).

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Assessing variability in the ratio of metal concentrations measured by DGT-type passive samplers and spot sampling in European seawaters

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