



# **MONITOOL PROJECT**

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

## Report/Deliverable by

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## Disclaimer

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## Glossary

ASV: Anodic Stripping Voltammetry. In graphs refers to the mean concentration of a metal measured in spot samples collected to cover a determined exposure period.

CSV: Cathodic Stripping Voltammetry. In graphs refers to the mean concentration of a metal measured in spot samples collected to cover a determined exposure period.

DGT: Diffusive Gradients in Thin films. In graphs refers to the mean value of time-integrated concentrations of a metal measured by DGTs .

DOC: Dissolved Organic Carbon.

ICP-MS (or ICP): Inductively Coupled Plasma Mass Spectrometry. In graphs refers to the mean concentration of a metal measured in spot samples collect to cover a determined exposure period.

SPM: Suspended Particulate Matter.

Volt: Voltammetry. It refers to CSV or ASV.

WFD: EU Water Framework Directive (WFD, 2000/60/EC).



## Executive Summary

In this deliverable we evaluate the effect of seawater physico-chemical characteristics on the relationship between the concentration of metals obtained by means of Diffusive Gradients in Thin films (DGT) passive samplers and the mean concentrations measured in discrete water samples obtained by 'classical' spot sampling. The ratios were not significantly affected by the temperature, salinity, pH, oxygen, DOC, SPM or fouling giving a great confidence for all the techniques used. Within the EU Water Framework Directive this is a great advantage, since the simplicity of not needing to use corrections to minimize the effects of environmental variables could help in implementing DGTs within monitoring networks.

## 1. Introduction

The Monitool project studies the use of The Diffusive Gradients in Thin-films (DGTs) as an alternative or complementary system to 'classical' spot sampling. The DGT is the most extensively used sampler for *in situ* labile metal measurements (Davison and Zhang, 1994; Menegário et al., 2017). DGT samplers accumulate metals continuously during the deployment time, usually ranging from several days to weeks. This provides time-weighted average metal concentrations and enables the achievement of lower limits of quantification compared with low-volume water samples. In addition, DGT samplers only accumulate free metal ions and easily dissociable metal complexes, operationally known as DGT-labile concentration. These advantages might favour the inclusion of the DGT technique within monitoring programmes.

The relationships between metal content obtained by means of DGT to metal content measured in discrete water samples (i.e., spot sampling) have been explored at local scale and it was found to be affected or explained by environmental characteristics, such as the organic matter content in the water (e.g., Cindrić et al., 2020; Wallner-Kersanach et al., 2009). However, as far as we know, the relationship between both approaches on a broad geographic scale has not been evaluated at this time. Hence, this study evaluates whether differences in the physicochemical characteristics of seawater can affect the relationships between different methods of determining metals, covering estuaries and coasts of the Atlantic region from the Canary Islands to the Scottish Highlands & Islands, as well as the Mediterranean area. In the discrete water samples (spot sampling), ICP-MS was used to measure the total dissolved metal concentrations, moreover lead and cadmium labile fractions were determined by ASV and total dissolved nickel was also measured by Cathodic Stripping Voltammetry (CSV).

In this deliverable we study the relationship between the concentration of metals obtained by means of Diffusive Gradients in Thin films (DGT) passive samplers and the mean concentrations measured in discrete water samples obtained by 'classical' spot sampling.

## 1. Scope

The objective of this deliverable is to study the relationships between the different chemical forms of metals measured in waters by means of DGT and 'classic' spot sampling. This was investigated across a broad geographical scale, trying to evaluate whether differences in the physicochemical characteristics of seawater can affect the relationships between different methods of determining metals.

## 2. Material and Methods

### 2.1 Origin of data

At each sampling site three different ways were used to measure the metal content (Cd, Ni and Pb) in waters: i) Inductively Coupled Plasma-Mass Spectrometry for Diffusive Gradient in Thin films (DGTs), ii) Sea Fast Inductively Coupled Plasma-Mass Spectrometry (IPC-MS) for water spot sampling and, iii) voltammetry (Volt) for water spot sampling. Other metals (Co, Cu, Mn and Zn) were also measured but not by voltammetry. Among these last four metals, the Co will not be explored in this deliverable regarding environmental variables (it will be assessed with regard to DGT exposure time and fouling), since there is a poor relationship between the concentration obtained by DGT and the mean concentration obtained by spot sampling (ICP-MS).

Details of the laboratory and field methodologies are given in deliverables of WP5.

Some remarks:

- 1) The used data were produced within WP5. Only data obtained following the Monitool protocols have been considered.
- 2) At some sampling sites the DGTs were collected in two sampling dates. In those cases, the mean values of spot water samples were associated to each DGT deployment data and were calculated including only the water samples collected during the DGT exposure time. This implies that from the same sampling site and season there can be two data, e.g., one corresponding to DGTs from Day #0 to Day #2, and other to DGTs from Day #0 to Day #4 (Table 1). This implies that these data cannot be considered as independent data from a statistical point of view. Nevertheless, for the exploration of results, these data were considered as independent, and therefore, the statistical results should be taken into account carefully.
- 3) The voltammetry method was used for measuring three metals: Cd, Ni and Pb. Hence the determination of conditional labile Pb and Cd concentrations in filtered and acidified water samples was done by Anodic Stripping Voltammetry (ASV). For the determination of total Ni dissolved concentrations, Cathodic Stripping Voltammetry (CSV) was used after UV irradiation of water samples to guarantee the oxidation of organic matter. For Cd and Pb determination the samples were not UV-irradiated before the analysis. It should be noted that ASV is typically used for the measurement of labile metal species in water samples at natural pH, instead of in acidified water samples. Because the determination of ASV-labile concentrations at natural pH must be performed within a reasonable time after sample collection to minimize loss of metal species due to adsorption on to vessel walls, samples were acidified on site in this study. Immediate acidification of the water samples once filtered can, however, give information about the labile fraction at a lower pH than the natural one, in the presence of a still inert

- fraction that may comprise metals strongly bound to natural organic molecules or bound to colloids.
- 4) The total dissolved concentrations of Cd, Cu, Ni, Pb and Zn in the filtered and acidified water samples were determined by an online pre-concentration seaFAST system (Elemental Scientific, Nebraska, USA) coupled with an ICP-MS.
  - 5) The determination of trace elements in the DGTs by ICP-MS was done in the binding resin gel removed from the sampler and eluted in 1.22 mL of 1M HNO<sub>3</sub> acid solution for at least 24 hours. The resulting acid extracts were analysed by ICP-MS for the determination of Cd, Cu, Ni, Pb and Zn, after 5-time dilution with ultrapure water (Milli-Q, Millipore).
  - 6) The values below the quantification limit were considered as the half of the quantification limit. In those cases where the mean value of concentrations was below the quantification limit, the values were not included.
  - 7) The laboratories provided a list of possible anomalous results to the partners. Each partner, based in their experience and knowledge of the studies areas, checked the obtained data and decided which values should be removed or included for the statistical analysis.
  - 8) The relationships between the metal concentration analysis methodologies (ICP-MS in DGTs, ICP-MS on water spot sampling and voltammetry on water spot sampling) were explored based upon arithmetic mean values. Hence, for ICP-MS in DGTs, the mean value among replicates was used. For data based upon spot sampling, at each sampling site the mean value among replicates was calculated and the final mean value represented the mean value of all the calculated mean values at each sampling site, which was used as representative of the sampling period.
  - 9) In some water samples there is no available metal data from the three methods of analysis. In other words, it is possible that from a sampling site only results from one of two methods of analysis is available (e.g., due to problems in the transport to laboratories or problems in the sampling).
  - 10) Outliers were identified using linear modelling of the data. The objective was to identify outlier samples whose standardized residuals from the linear model were greater than 3 (values above 99.73% of the total values were rejected, assuming that their distribution follows a normal distribution). A detailed procedure is given in the Supplementary material of Rodríguez et al. (2021). Values identified as outliers were excluded.

**Table 1.** List of samples including the origin of the sample (partner and label-name), DGTs retrievals (two times in the same sampling site (at D2 and D4 or D3 and D5) marked with “X”) and the given label number.

Partner	Label (name)	Site with retrieval on two different dates	Label (number)
AZTI	DEBA_DS		1
AZTI	LEZO_DS		2
AZTI	MUSEO_DS_D2	X	3
AZTI	MUSEO_DS_D4	X	4
AZTI	PRACTICOS_DS		5
AZTI	DEBA_WS		6
AZTI	LEZO_WS		7
AZTI	MUSEO_WS_D3	X	8

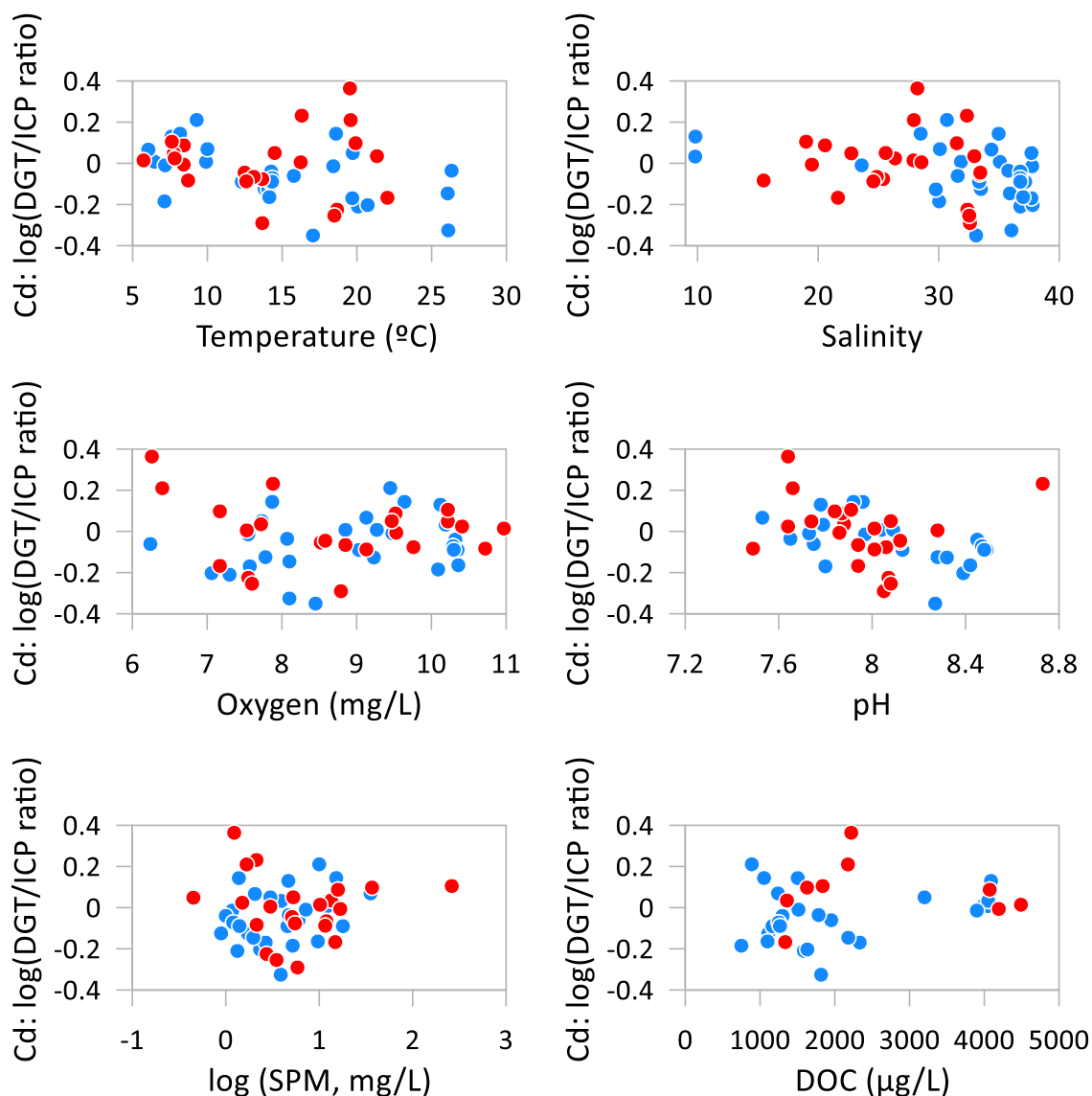
Partner	Label (name)	Site with retrieval on two different dates	Label (number)
AZTI	MUSEO_WS_D5	X	9
AZTI	PRACTICOS_WS		10
CEFAS	BELFAST_DS		11
CEFAS	FAL_DS_D2	X	12
CEFAS	FAL_DS_D4	X	13
CEFAS	LIVERPOOL_DS		14
CEFAS	X38A_DS		15
CEFAS	BELFAST_WS		16
CEFAS	FAL_WS_D2	X	17
CEFAS	FAL_WS_D4	X	18
CEFAS	LIVERPOOL_WS		19
CEFAS	X38A_WS		20
DCU	ABW_DS_D2	X	21
DCU	ABW_DS_D4	X	22
DCU	M69_DS		23
DCU	M70_DS		24
DCU	DUBLINBAYBUOY2_DS		25
DCU	DUBLINBAYBUOY4_DS		26
DCU	ABW_WS		27
DCU	M69_WS		28
DCU	M70_WS		29
DCU	DUBLINBAYBUOY2_WS	X	30
DCU	DUBLINBAYBUOY4_WS	X	31
IFREMER	FONTENELLE_DS		32
IFREMER	TERENEZ_DS		33
IFREMER	BESSIN_DS		34
IFREMER	LAZARET_EIL		35
IFREMER	SAINTNAZAIRE_DS_D2		36
IFREMER	SAINTNAZAIRE_DS_D4		37
IFREMER	SAUMONARD_DS		38
IFREMER	FONTENELLE_WS		39
IFREMER	ANTIFER_WS_BAF		40
IFREMER	BESSIN_WS		41
IFREMER	LECROISIC		42
IFREMER	SAINTNAZAIRE_WS_D2	X	43
IFREMER	SAINTNAZAIRE_WS_D4	X	44
IFREMER	SAUMONARD_WS		45
IFREMER	SAUMONARD_WS_BAF		46
IFREMER	SILLONDESANGLAIS_WS_BAF		47
IPMA	AVEIRO_DS		48
IPMA	PORTO_DS		49
IPMA	SESIMBRA_DS		50
IPMA	TAGUS_DS		51
IPMA	AVEIRO_WS_D3		52
IPMA	AVEIRO_WS_D5		53

Partner	Label (name)	Site with retrieval on two different dates	Label (number)
IPMA	PORTO_WS		54
IPMA	SESIMBRA_WS_D2	X	55
IPMA	SESIMBRA_WS_D4	X	56
IPMA	TAGUS_WS_D2	X	57
IPMA	TAGUS_WS_D4	X	58
ITC	GANDO_DS		59
ITC	JINAMAR_DS		60
ITC	LUZ_DS_D2	X	61
ITC	LUZ_DS_D4	X	62
ITC	LUZ_WP4_2_D2	X	63
ITC	LUZ_WP4_2_D4	X	64
ITC	TALIARTE_DS		65
ITC	TALIARTE_WP4_2_D2	X	66
ITC	TALIARTE_WP4_2_D4	X	67
ITC	GANDO_WS		68
ITC	JINAMAR_WS		69
ITC	LUZ_WS_D3	X	70
ITC	LUZ_WS_D7	X	71
ITC	TALIARTE_WS		72
MSS-SEPA	BRAEHEAD_WS		73
MSS-SEPA	MONTROSE_WS		74
MSS-SEPA	NEWHAVEN_WS		75
UNICA	MOLODOGANA_DS		76
UNICA	MOLOINCHUSA_DS		77
UNICA	MOLORINASCITA_DS		78
UNICA	SANTELMO_DS_D2	X	79
UNICA	SANTELMO_DS_D5	X	80
UNICA	MOLODOGANA_WS		81
UNICA	MOLOINCHUSA_WS		82
UNICA	MOLORINASCITA_WS		83
UNICA	SANTELMO_WS_D3	X	84
UNICA	SANTELMO_WS_D5	X	85

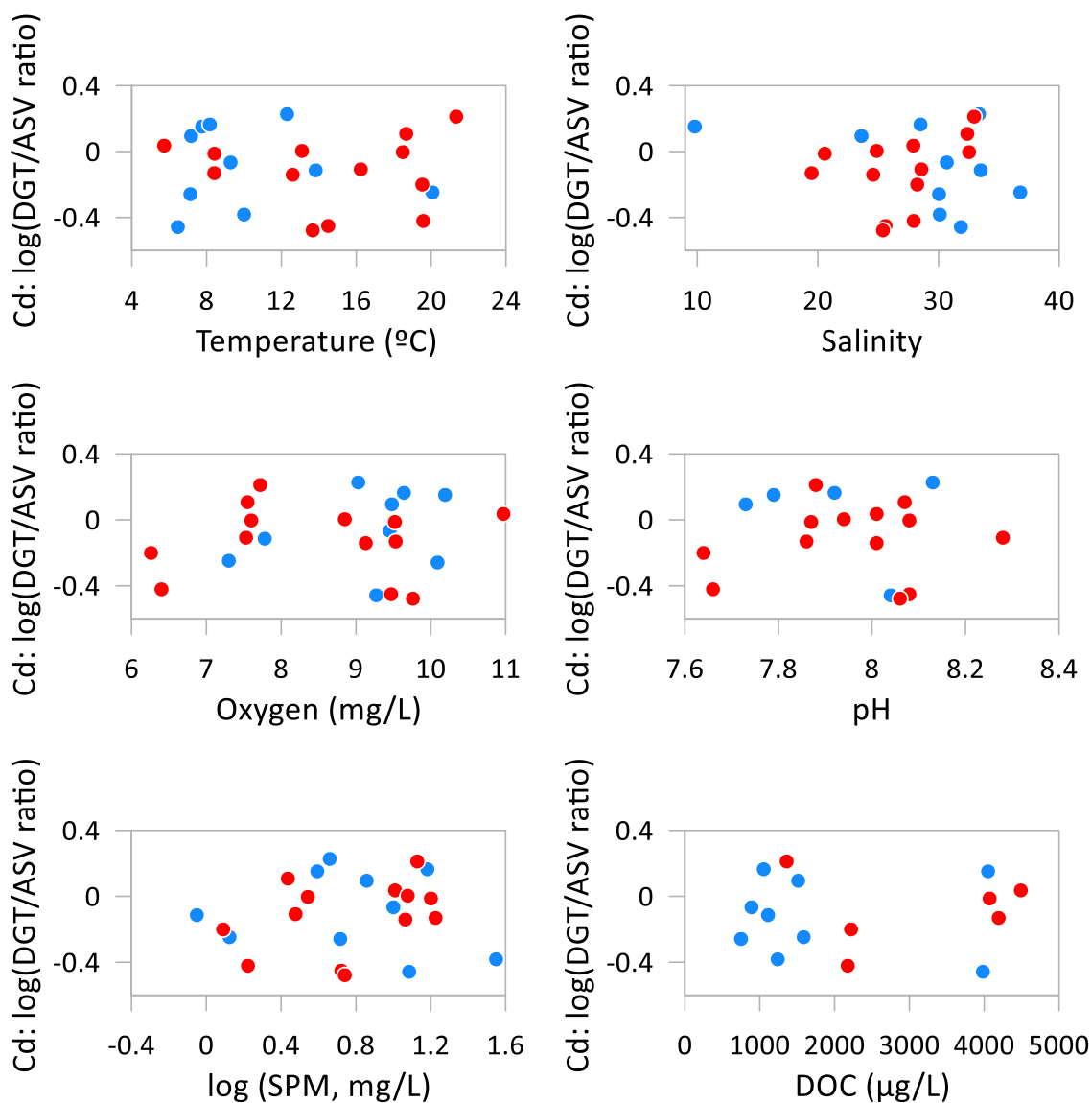
### 3. Cadmium

The exploration of the DGT/spot sampling ratio indicators vs environmental variables is shown in Figure 1 and Figure 2. For each of these figures, the mean value of the environmental variable measured in the water is shown on the X-axis, and on the Y-axis the logarithm of the ratio between the mean concentration obtained with DGT and the mean concentration obtained with spot sampling. No clear trends are found. In the case of DGT/ICP (spot sampling) ratio, it is significantly correlated to pH (Spearman rho = -0.46), but the relation is weak and very scattered.

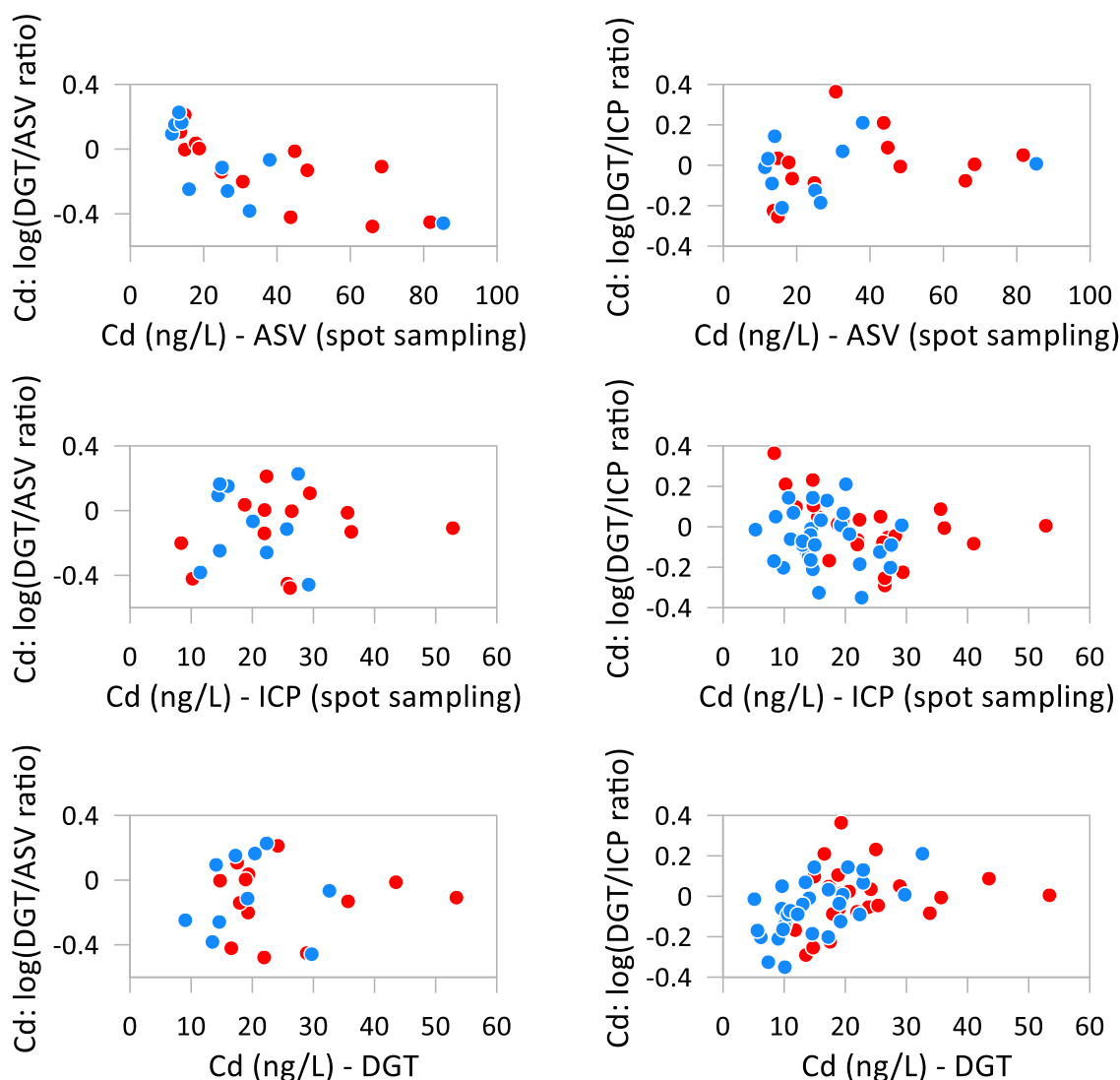
The DGT/Volt (spot sampling) ratio decreases clearly with the metal concentration in spot sampling measured by ASV (Figure 3). The DGT/ICP (spot sampling) ratio increases clearly with the metal concentration obtained by means of DGT (Figure 4).



**Figure 1.** Cd: DGT/ICP(spot sampling) ratio. Biplots of the ratio of the concentration of metal obtained with DGT to the mean concentration of metal obtained with spot sampling vs mean values of environmental variables measured in water. Key: DGT – concentration of a metal obtained by means of DGT passive sampler, ICP – mean concentration of a metal measured in spot samples using ICP-MS on filtered seawater, SPM - total suspended particulate material in seawater, DOC- dissolved organic carbon. The blue dots correspond to coastal areas and the red dots to estuaries.

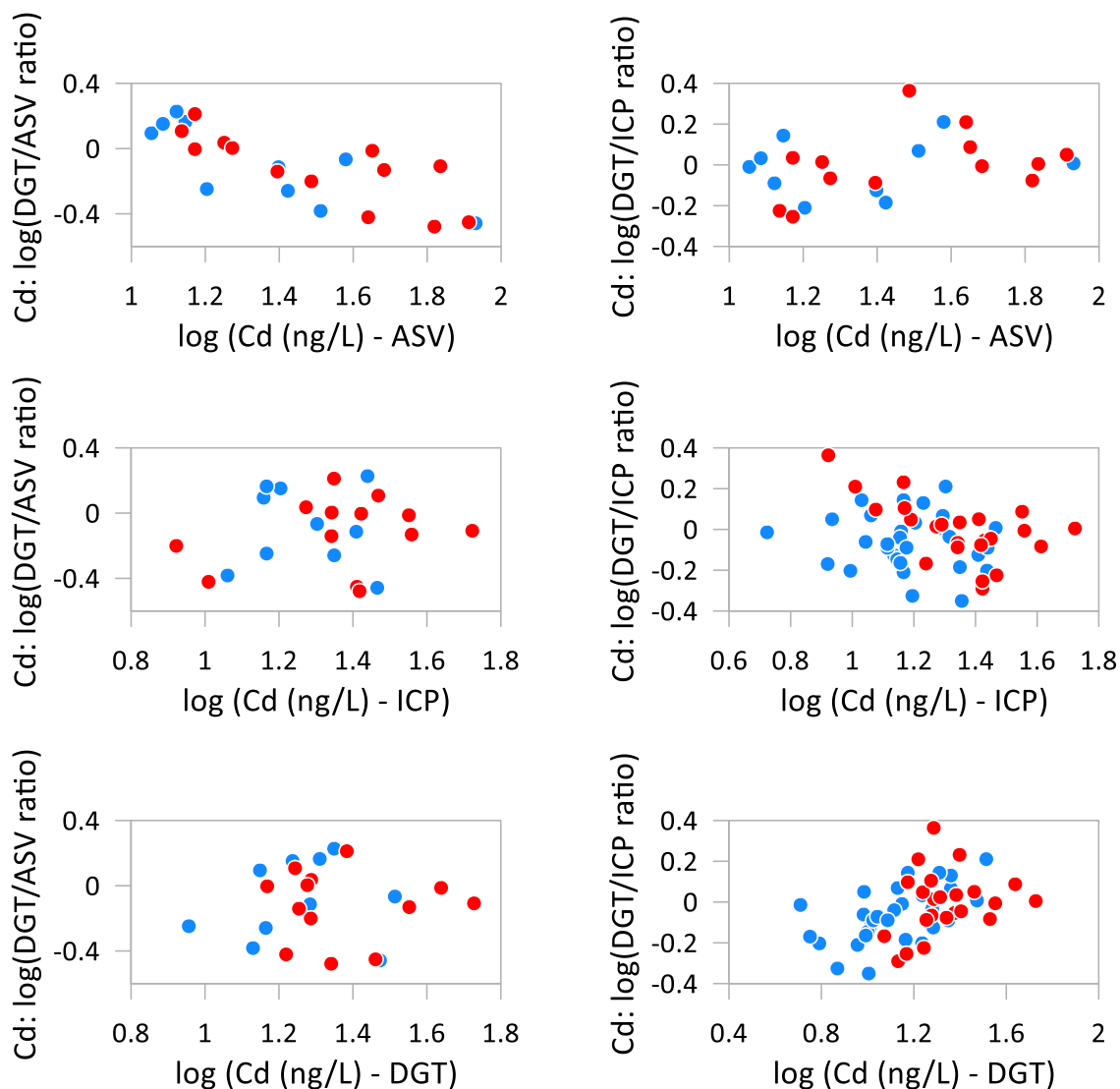


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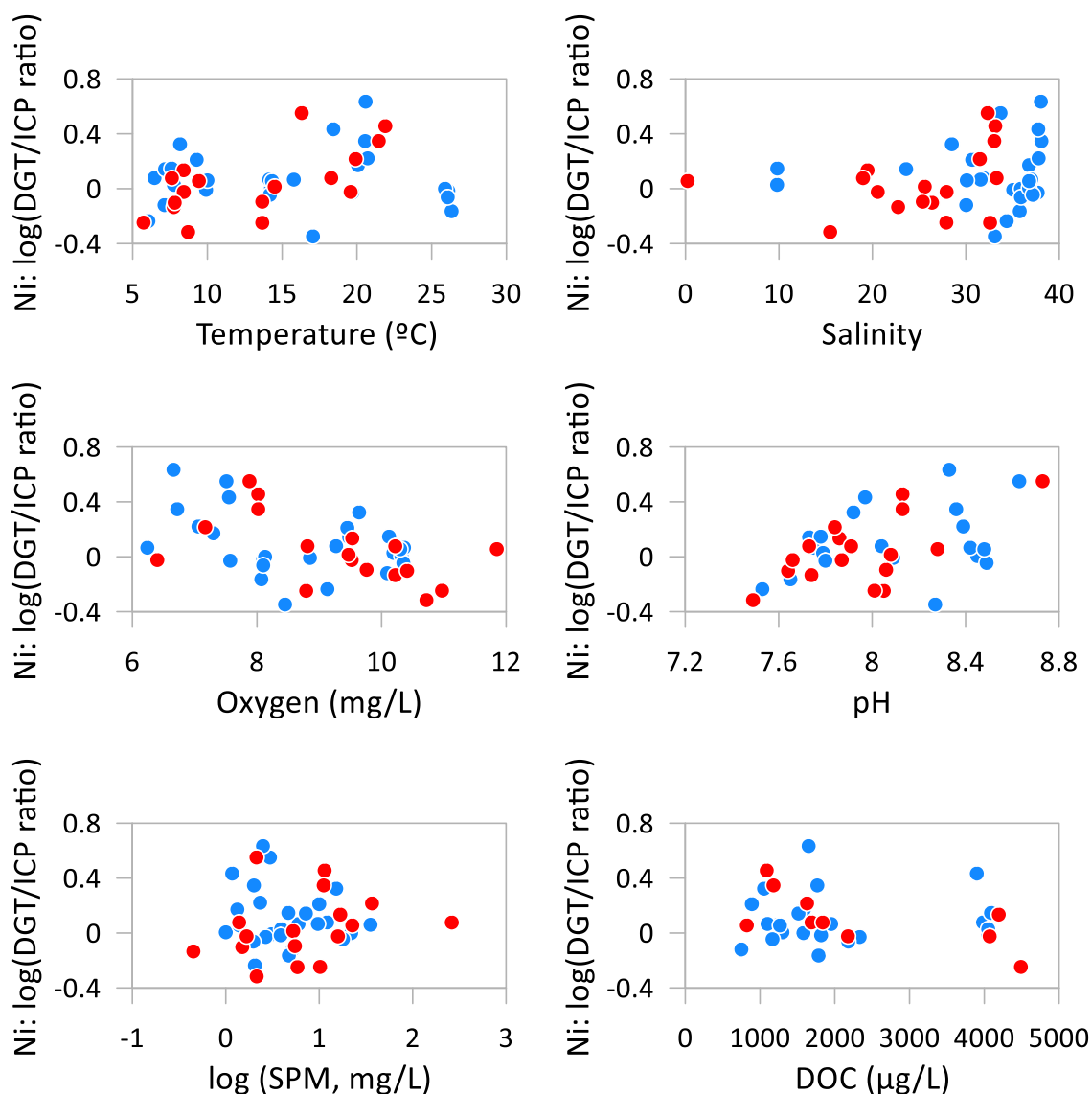


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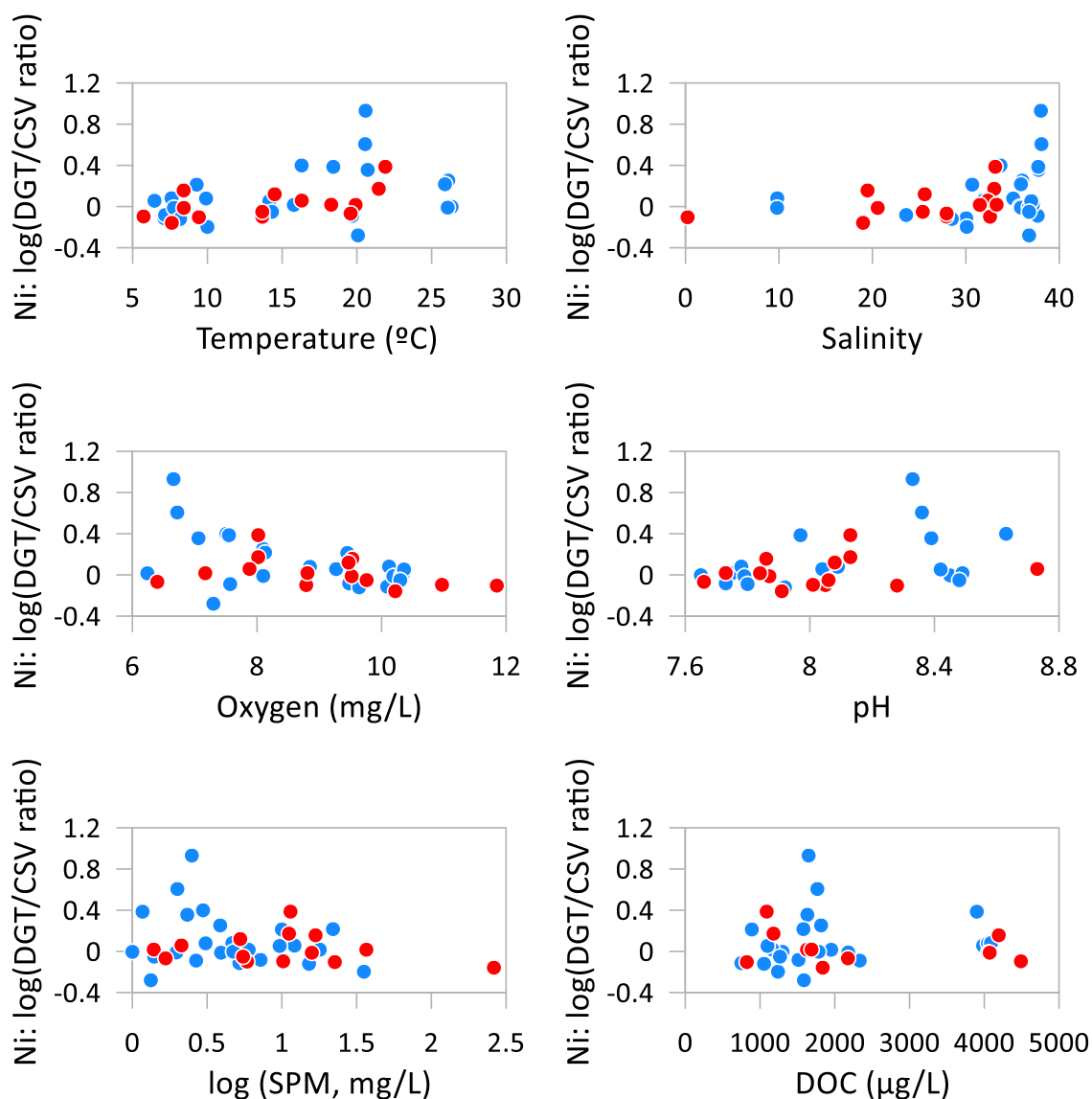
#### 4. Nickel

The exploration of the DGT/spot sampling ratio indicators vs environmental variables is shown in Figure 5 and Figure 6. No clear trends are found. In the case of DGT/ICP (spot sampling) ratio, this is significantly correlated to oxygen (Spearman rho = -0.44), but it is a weak and very scattered relation. In the case of DGT/Volt (spot sampling) ratio, there is a significant correlation with temperature (Spearman rho = 0.45), but the relation is weak and very scattered.

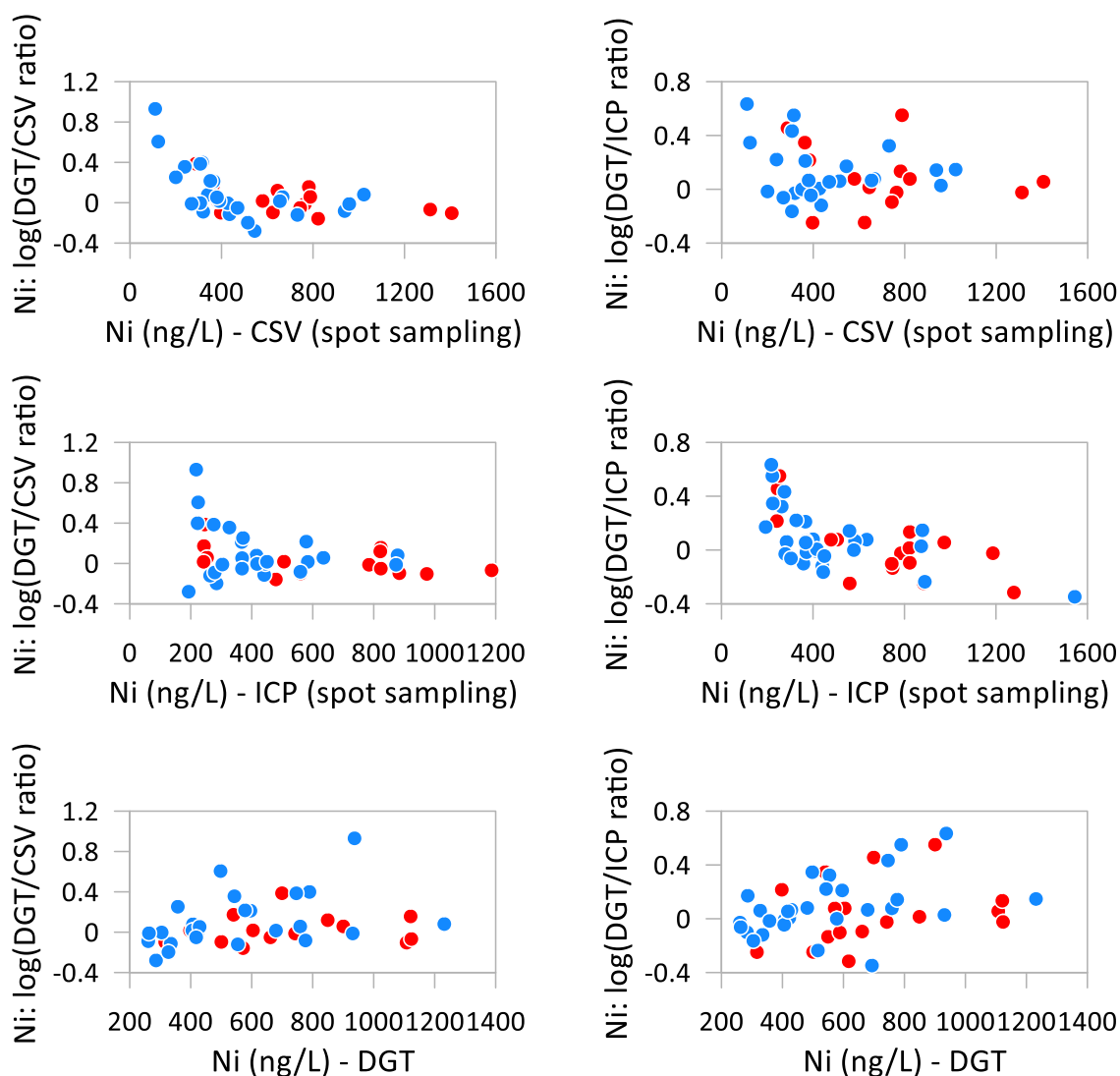
The DGT/Volt (spot sampling) ratio decreases clearly with the metal concentration in spot sampling measured by CSV (Figure 7 and Figure 8). The DGT/IPC (spot sampling) ratio decreases clearly with the mean metal concentration in spot samples (Figure 7 and Figure 8).



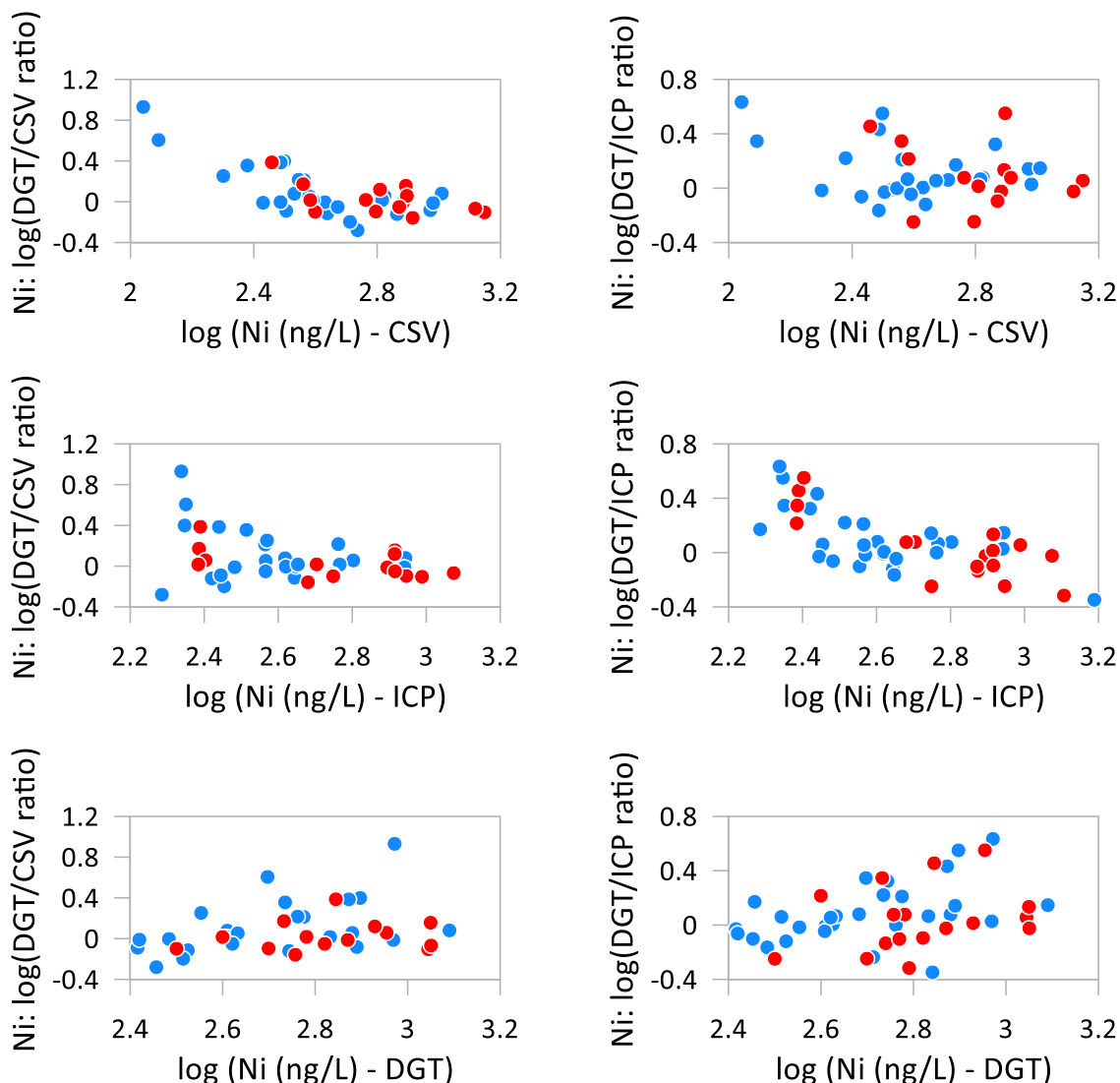
**Figure 5.** Ni: DGT/IPC ratio. Biplots of the ratio of the concentration of metal obtained with DGT to the mean concentration of metal obtained with spot sampling vs mean values of environmental variables measured in water. Key: DGT – concentration of a metal obtained by means of DGT passive sampler, IPC – mean concentration of a metal measured in spot samples using ICP-MS on filtered seawater, SPM - total suspended particulate material in seawater, DOC- dissolved organic carbon. The blue dots correspond to coastal areas and the red dots to estuaries.



**Figure 6.** Ni: DGT/CSV ratio. Biplots of the ratio of the concentration of metal obtained with DGT to the mean concentration of metal obtained with spot sampling vs mean values of environmental variables measured in water. Key: DGT – concentration of a metal obtained by means of DGT passive sampler, CSV – mean concentration of a metal measured in spot samples using cathodic stripping voltammetry on filtered seawater, SPM - total suspended particulate material in seawater, DOC- dissolved organic carbon. The blue dots correspond to coastal areas and the red dots to estuaries.



**Figure 7.** Ni: Biplots of the ratio of the concentration of metal obtained with DGT to the mean concentration of metal obtained with spot sampling vs mean values of concentrations of metals. Key: DGT – concentration of a metal measured by means of DGT passive sampler, ICP – mean concentration of a metal measured by spot sampling using ICP-MS on filtered seawater, CSV – mean concentration of a metal measured in spot samples using cathodic stripping voltammetry on filtered seawater. The blue dots correspond to coastal areas and the red dots to estuaries.

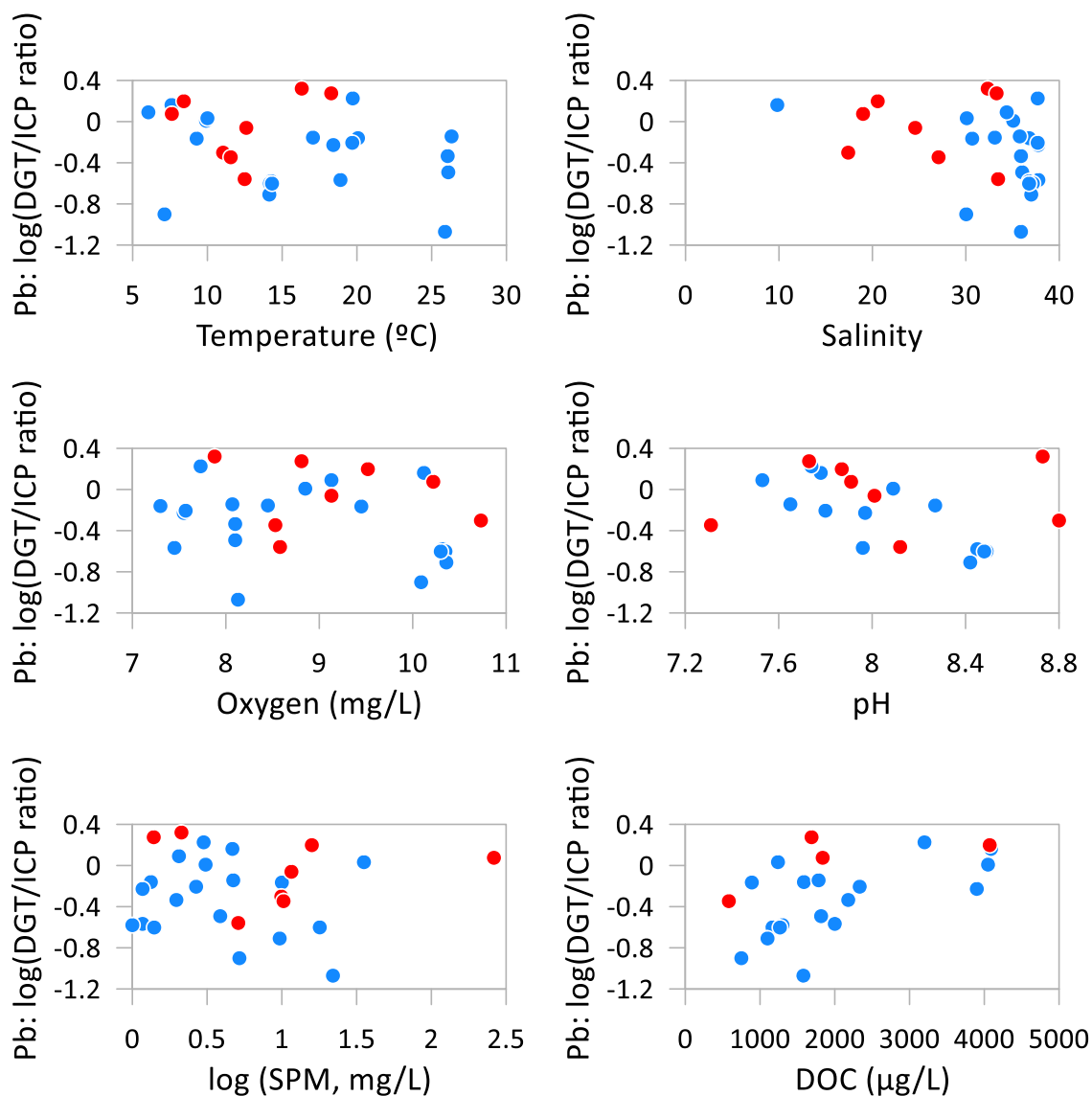


**Figure 8.** Ni: Biplots of the ratio of the concentration of metal obtained by means of DGT to the mean concentration of metal obtained by spot sampling vs mean values of concentrations of metals (log-transformed). Key: DGT – concentration of a metal measured by means of DGT passive sampler, ICP – mean concentration of a metal measured in spot samples using ICP-MS on filtered seawater, CSV – mean concentration of a metal measured by spot sampling using cathodic stripping voltammetry on filtered seawater. The blue dots correspond to coastal areas and the red dots to estuaries.

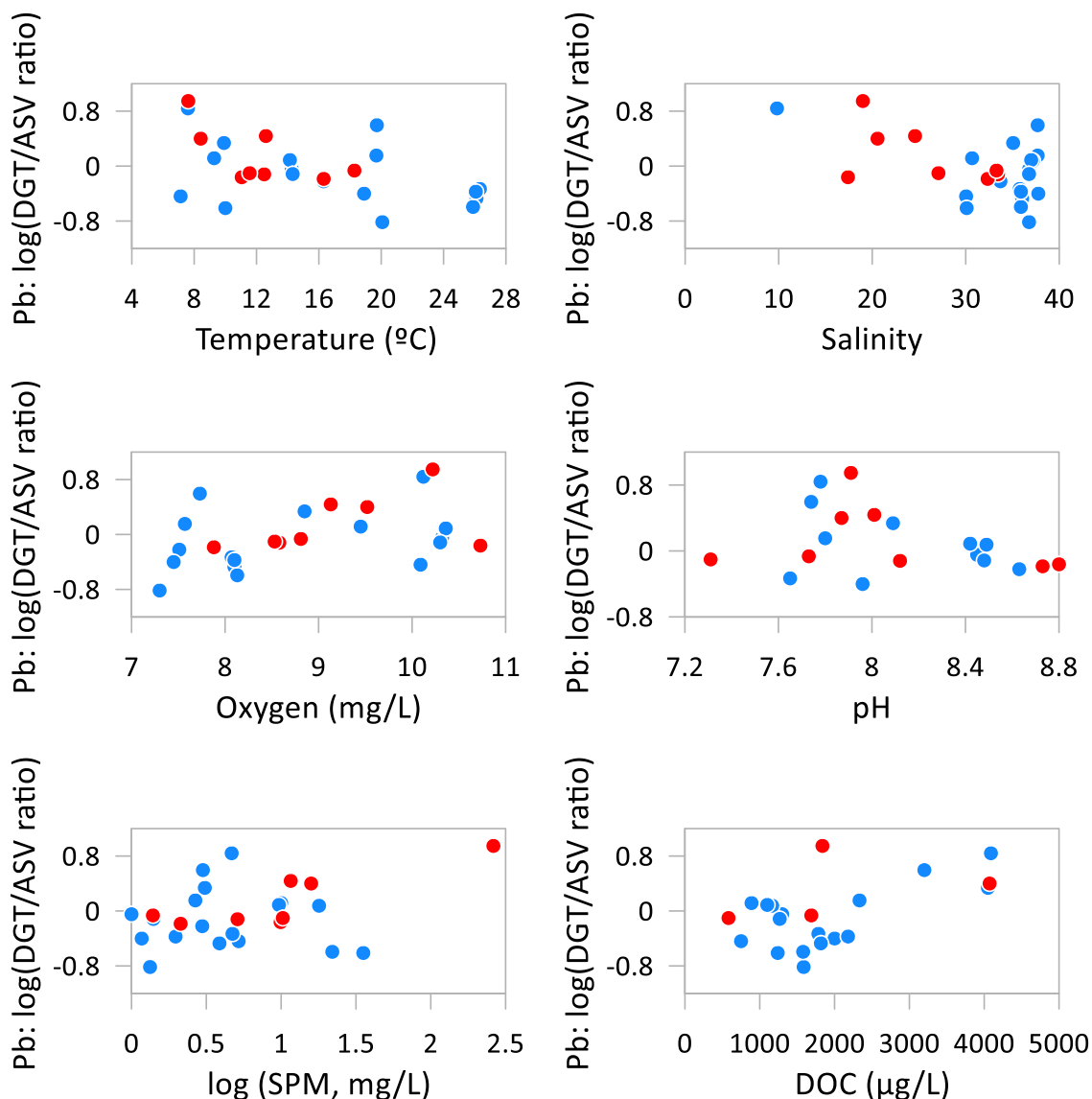
## 5. Lead

The exploration of the DGT/ICP-MS (spot sampling) ratio indicators vs environmental variables is shown in Figure 9 and Figure 10. No clear trends are found.

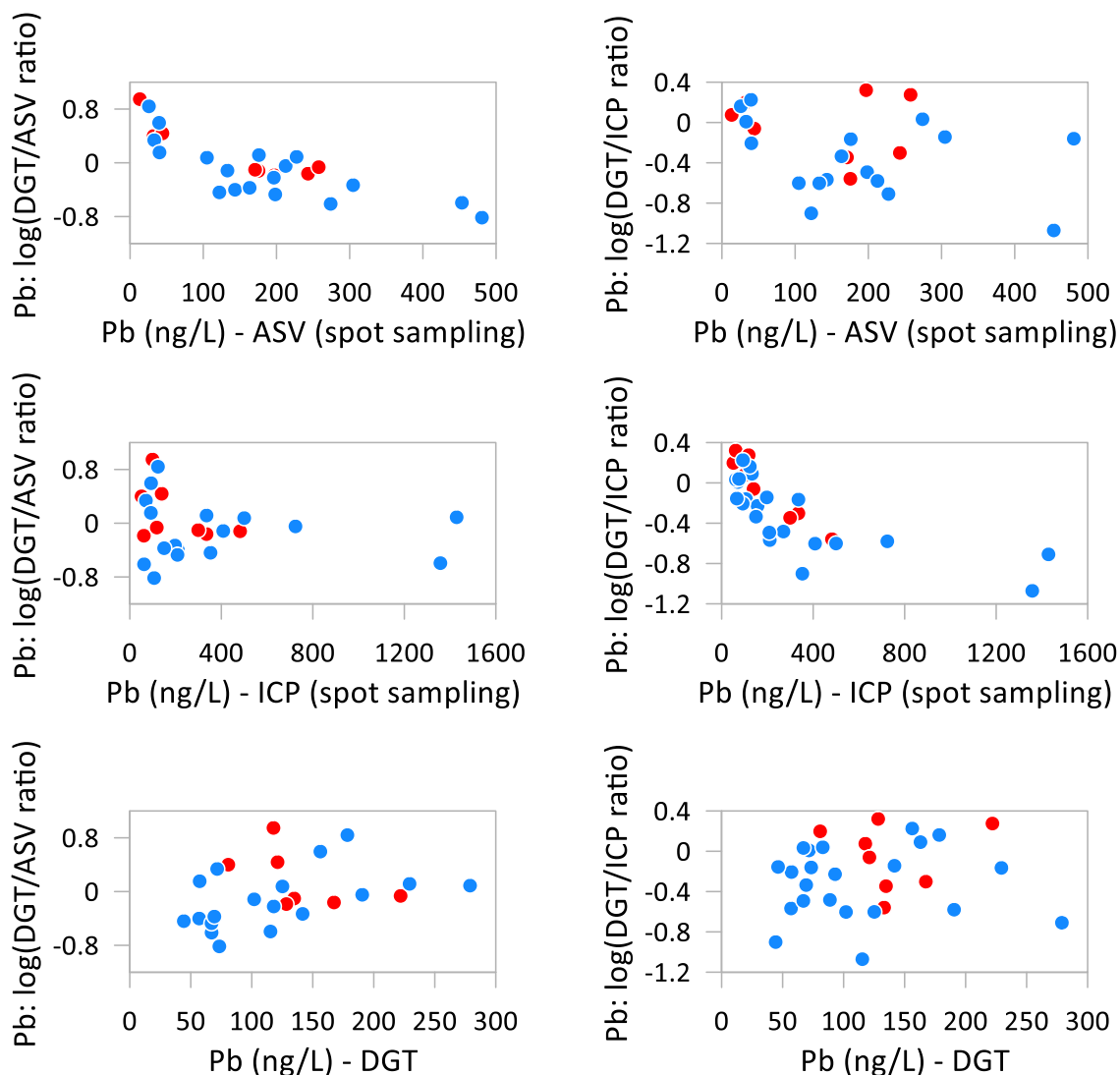
The DGT/Volt (spot sampling) ratio decreases clearly with the metal concentration in spot samples measured by ASV (Figure 11 and Figure 12). The DGT/IPC-MS (spot sampling) ratio decreases clearly with the mean metal concentration in spot samples (Figure 11 and Figure 12).



**Figure 9.** Pb: DGT/ICP ratio. Biplots of the ratio of the concentration of metal obtained with DGT to the mean concentration of metal obtained with spot sampling vs mean values of environmental variables measured in water. Key: DGT – concentration of a metal obtained by means of DGT passive sampler, ICP – mean concentration of a metal measured in spot samples using ICP-MS on filtered seawater, SPM - total suspended particulate material in seawater, DOC- dissolved organic carbon. The blue dots correspond to coastal areas and the red dots to estuaries.

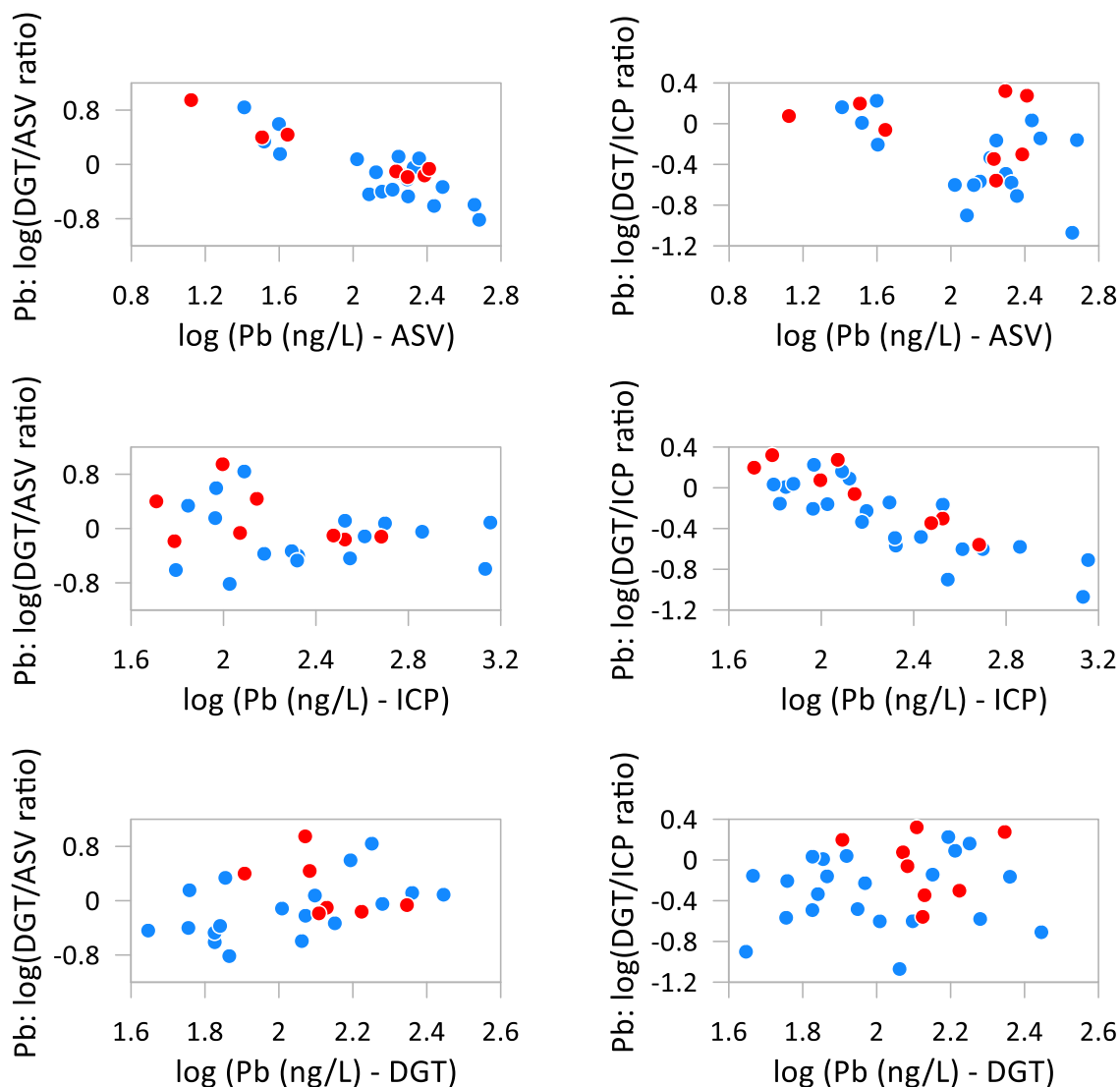


**Figure 10.** Pb: DGT/ASV ratio. Biplots of the ratio of the concentration of metal obtained by means of DGT to the mean concentration of metal obtained by spot sampling vs mean values of environmental variables measured in water. Key: DGT – concentration of a metal obtained by means of DGT passive sampler, ASV – mean concentration of a metal measured in spot samples using anodic stripping voltammetry on filtered seawater, SPM - total suspended particulate material in seawater, DOC- dissolved organic carbon. The blue dots correspond to coastal areas and the red dots to estuaries.



**Figure 11.** Pb: Biplots of the ratio of the concentration of metal obtained by means of DGT to the mean concentration of metal obtained by spot sampling vs mean values of concentrations of metals. Key: DGT – concentration of a metal obtained by means of DGT passive sampler, ICP – mean concentration of a metal measured in spot samples using ICP-MS on filtered seawater, ASV – mean concentration of a metal measured in spot samples using anodic stripping voltammetry on filtered seawater. The blue dots correspond to coastal areas and the red dots to estuaries.



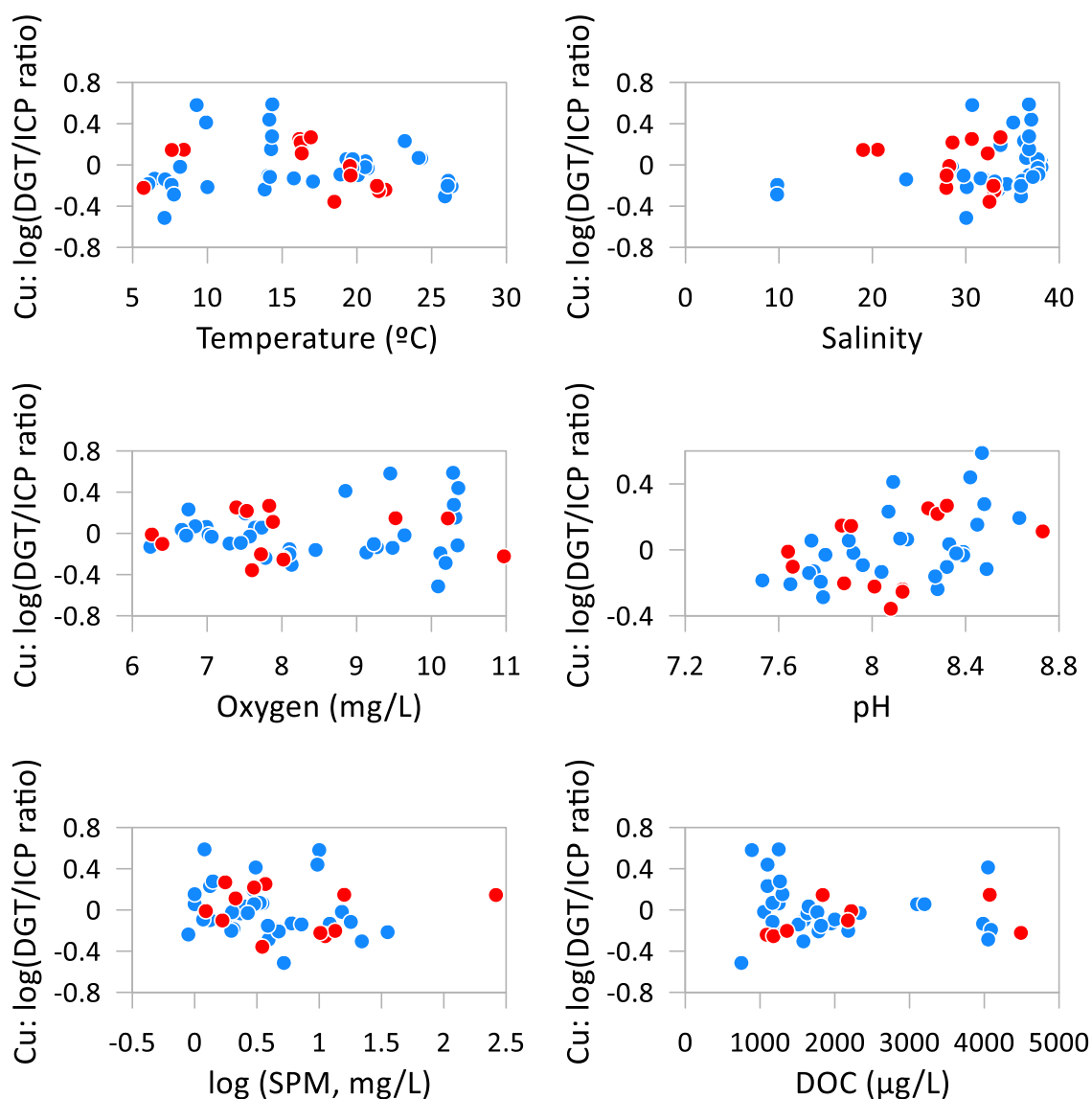


**Figure 12.** Pb: Biplots of the ratio of the concentration of metal obtained by means of DGT to the mean concentration of metal obtained by spot sampling vs mean values of concentrations of metals (log-transformed). Key: DGT – concentration of a metal obtained by means of DGT passive sampler, ICP – mean concentration of a metal measured in spot samples using ICP-MS on filtered seawater, ASV – mean concentration of a metal measured in spot samples using anodic stripping voltammetry on filtered seawater. The blue dots correspond to coastal areas and the red dots to estuaries.

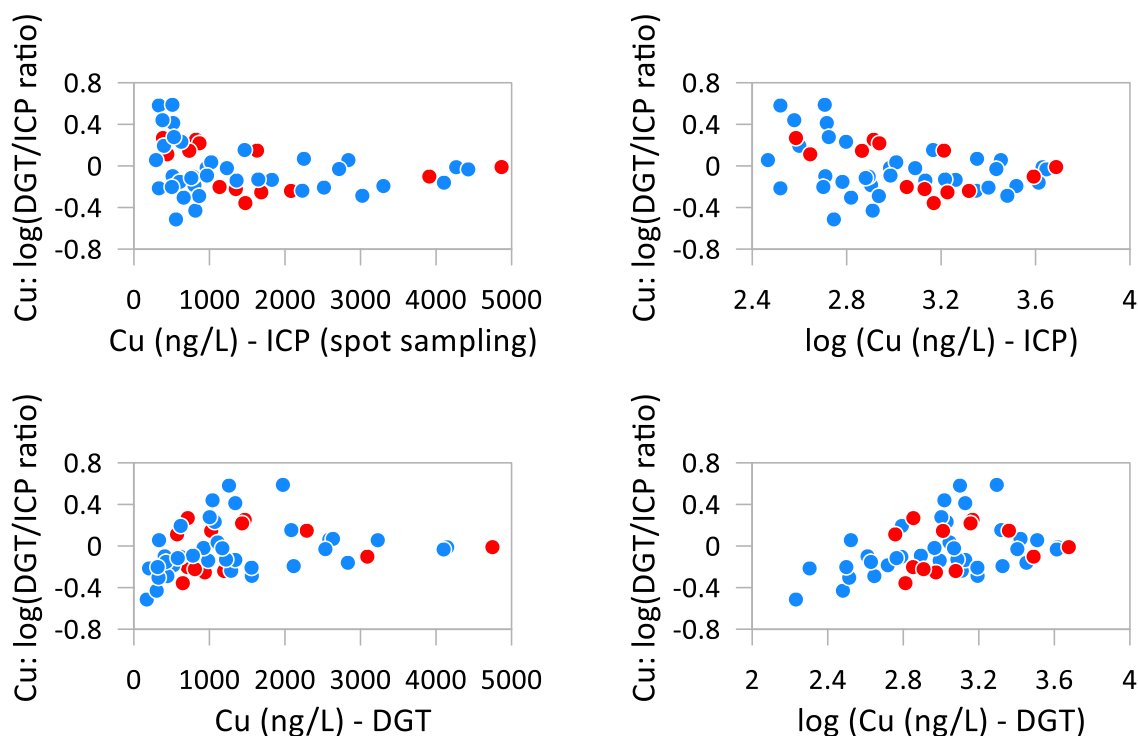
## 6. Cooper

The exploration of the DGT/ICP (spot sampling) ratio indicators vs environmental variables is shown in Figure 13. No clear trends are found.

The DGT/ICP (spot sampling) ratio is not related to the metal concentration obtained by spot sampling nor by DGT (Figure 14).



**Figure 13.** Cu: DGT/ICP ratio. Biplots of the ratio of the concentration of metal obtained by means of DGT to the mean concentration of metal obtained by spot sampling vs mean values of environmental variables measured in water. Key: DGT – concentration of a metal obtained by means of DGT passive sampler, ICP – mean concentration of a metal measured in spot samples using ICP-MS on filtered seawater, SPM - total suspended particulate material in seawater, DOC- dissolved organic carbon. The blue dots correspond to coastal areas and the red dots to estuaries.

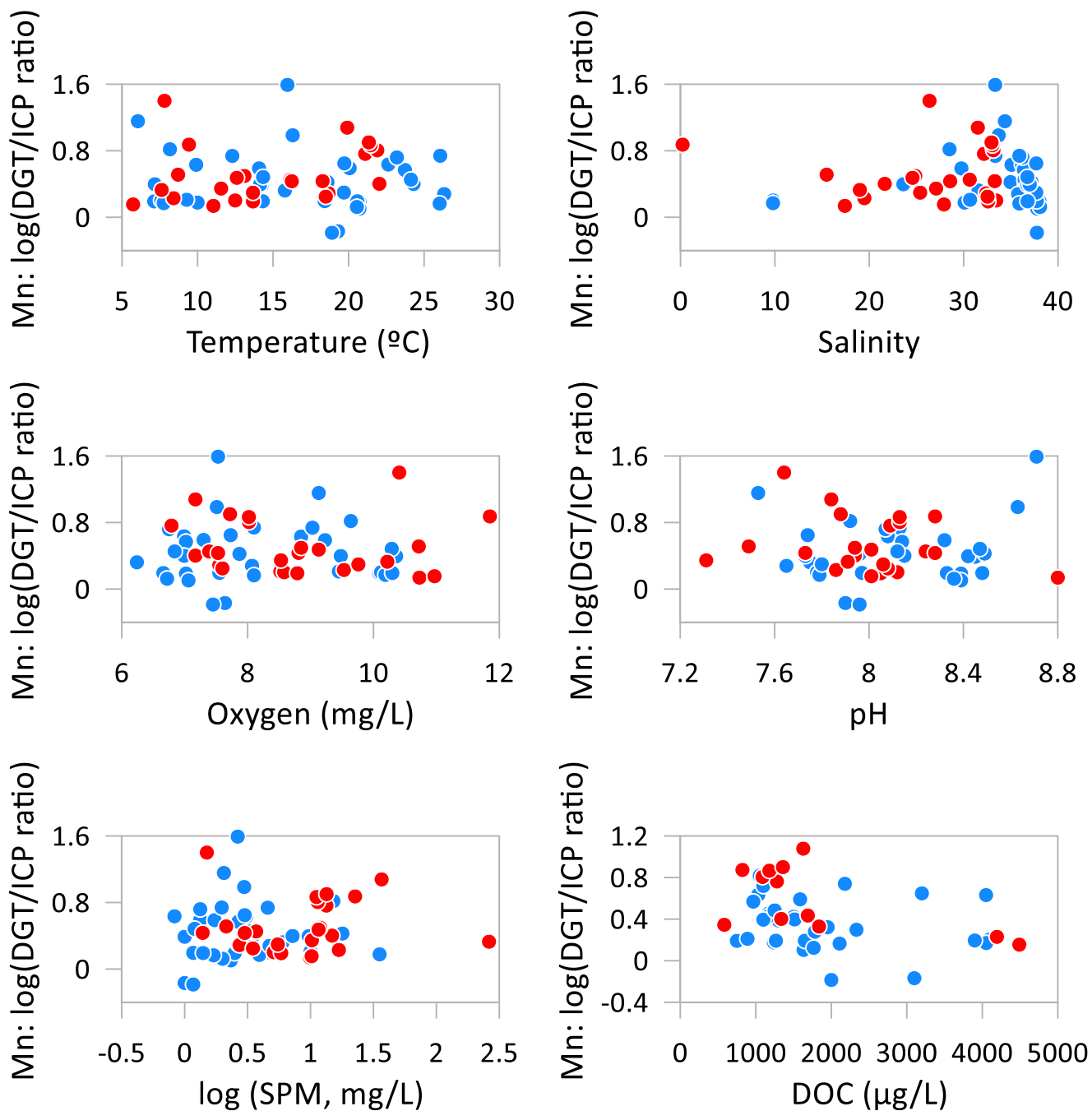


**Figure 14.** Cu: Biplots of the ratio of the concentration of metal obtained by means of DGT to the mean concentration of metal obtained by spot sampling vs mean values of concentrations of metals (left: not transformed, right: log-transformed). Key: DGT – concentration of a metal obtained by means of DGT passive sampler, ICP – mean concentration of a metal measured in spot samples using ICP-MS on filtered seawater. The blue dots correspond to coastal areas and the red dots to estuaries.

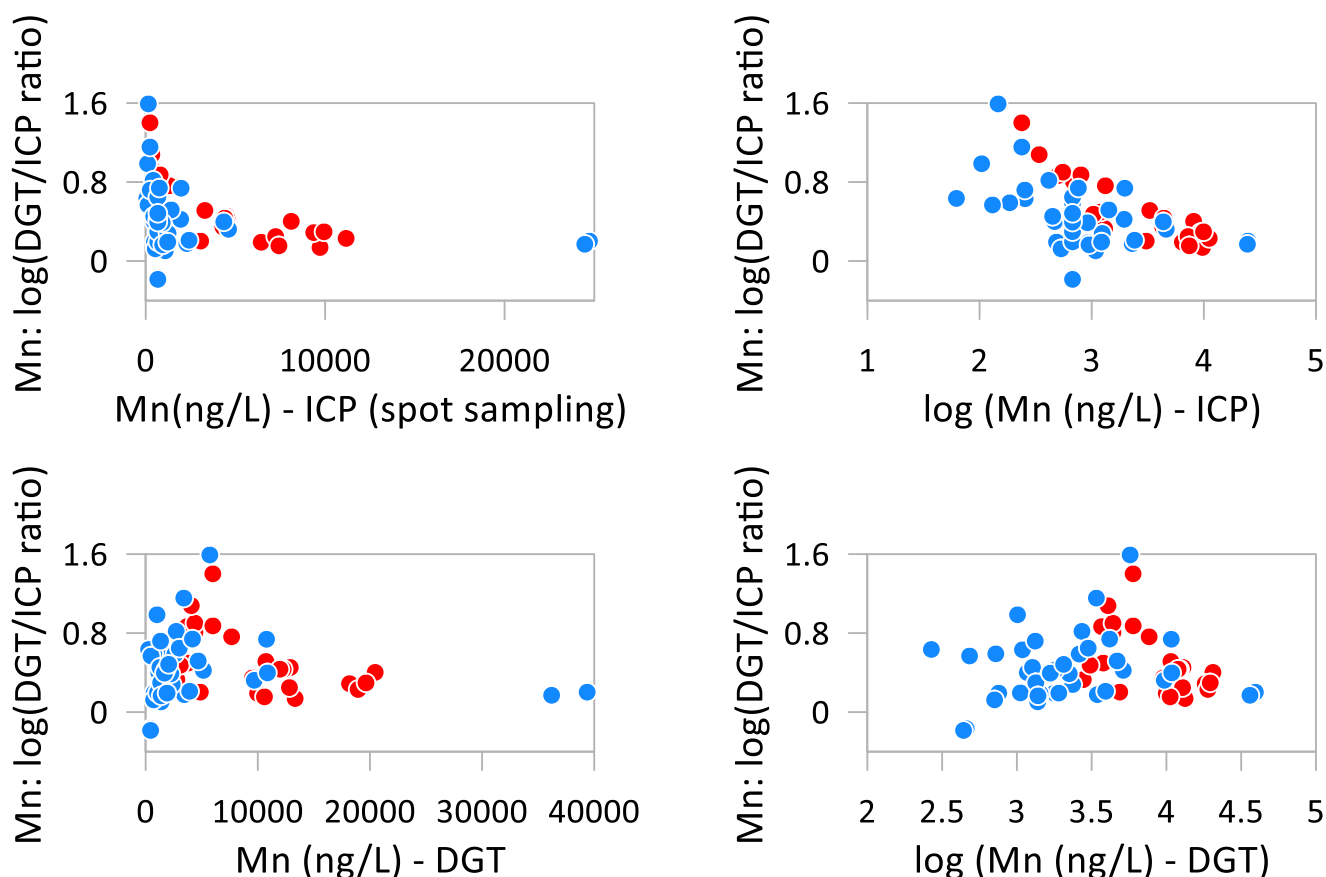
## 7. Manganese

The exploration of the DGT/ICP (spot sampling) ratio indicators vs environmental variables is shown in Figure 15. No clear trends are found.

The DGT/ICP (spot sampling) ratio is not related to the metal concentration obtained by spot sampling nor by DGT (Figure 16).



**Figure 15.** Mn: DGT/ICP ratio. Biplots of the ratio of the concentration of metal obtained with DGT to the mean concentration of metal obtained with spot sampling vs mean values of environmental variables measured in water. Key: DGT – concentration of a metal obtained by means of DGT passive sampler, ICP – mean concentration of a metal measured in spot samples using ICP-MS on filtered seawater, SPM - total suspended particulate material in seawater, DOC- dissolved organic carbon. The blue dots correspond to coastal areas and the red dots to estuaries.

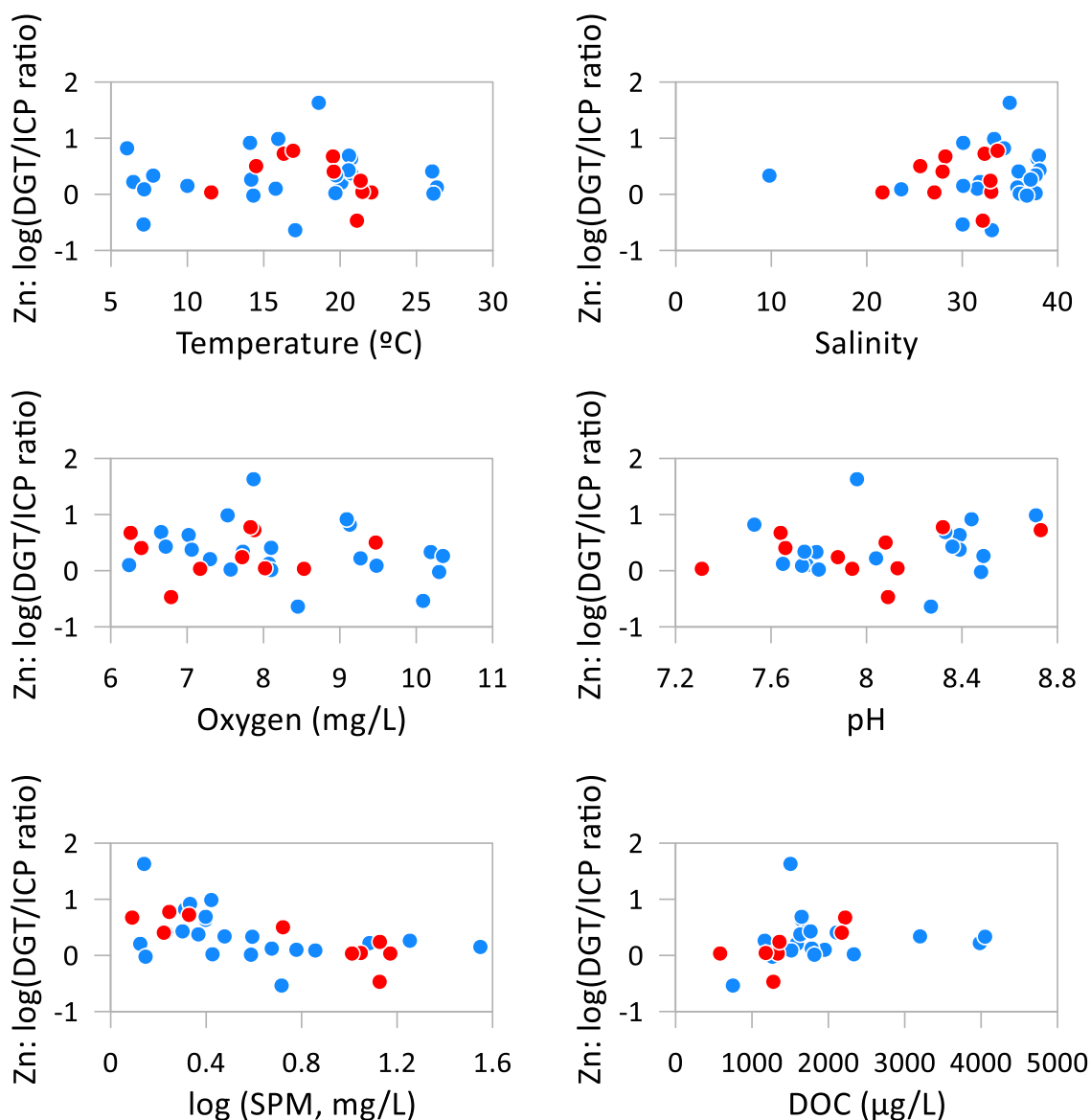


**Figure 16.** Mn: Biplots of the ratio of the concentration of metal obtained by means of DGT to the mean concentration of metal obtained by spot sampling vs mean values of concentrations of metals (left: not transformed, right: log-transformed). Key: DGT – concentration of a metal obtained by means of DGT passive sampler, ICP – mean concentration of a metal measured in spot samples using ICP-MS on filtered seawater. The blue dots correspond to coastal areas and the red dots to estuaries.

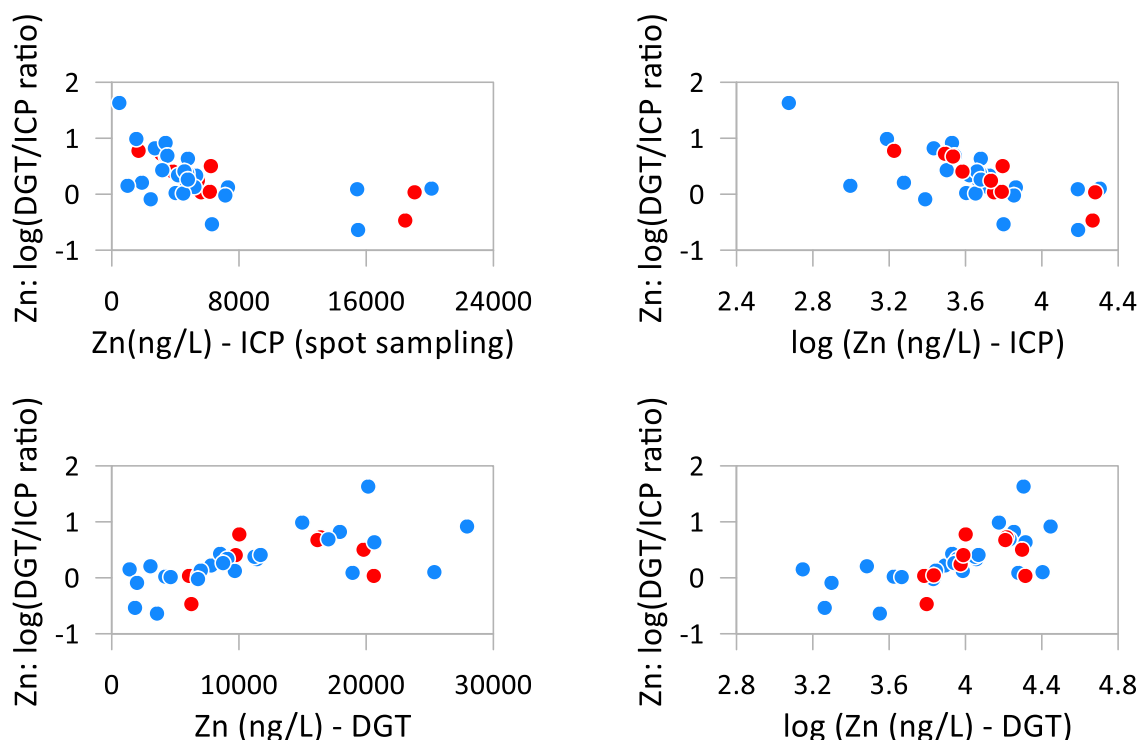
## 8. Zinc

The exploration of the DGT/spot sampling ratio indicators vs environmental variables is shown in Figure 17. No clear trends are found for most of the cases. However, the ratio is significantly correlated with SPM (Suspended Particulate Matter) (Spearman rho = -0.53), but the relation is weak and very scattered.

The DGT/spot sampling ratio decreases with the metal concentration in spot sampling measured by ICP-MS and increases with the metal concentration in DGT (Figure 18).



**Figure 17.** Zn: DGT/ICP ratio. Biplots of the ratio of the concentration of metal obtained with DGT to the mean concentration of metal obtained with spot sampling vs mean values of environmental variables measured in water. Key: DGT – concentration of a metal obtained by means of DGT passive sampler, ICP – mean concentration of a metal measured in spot samples using ICP-MS on filtered seawater, SPM - total suspended particulate material in seawater, DOC- dissolved organic carbon. The blue dots correspond to coastal areas and the red dots to estuaries.



**Figure 18.** Zn: Biplots of the ratio of the concentration of metal obtained by means of DGT to the mean concentration of metal obtained by spot sampling vs mean values of concentrations of metals (left: not transformed, right: log-transformed). Key: DGT – concentration of a metal obtained by means of DGT passive sampler, ICP – mean concentration of a metal measured in spot samples using ICP-MS on filtered seawater. The blue dots correspond to coastal areas and the red dots to estuaries.

## 9. Other factors

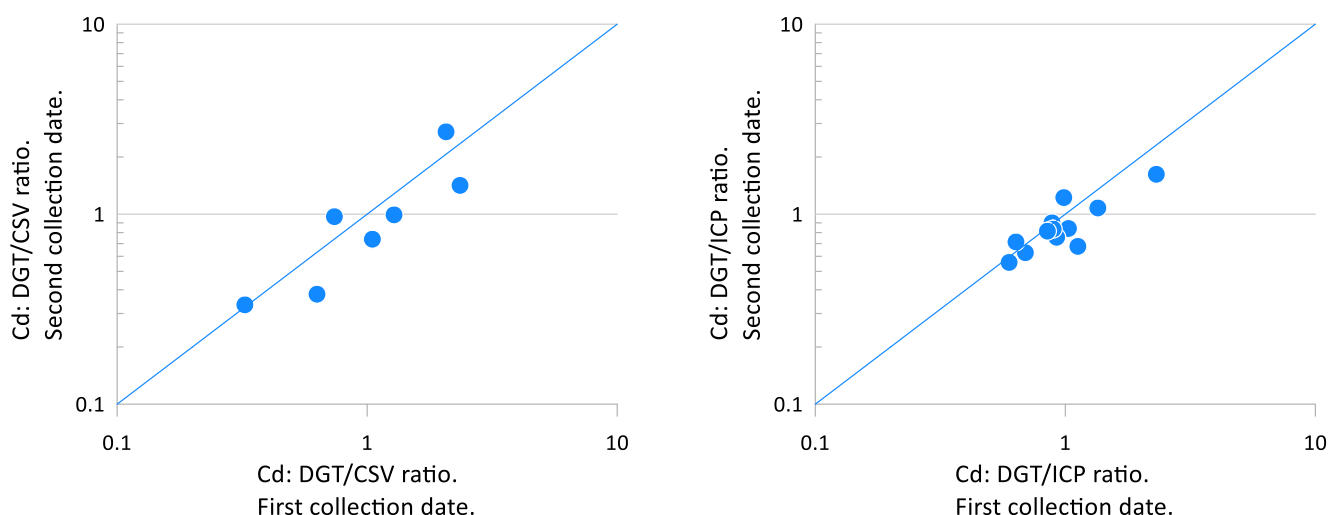
This section explores the possible influence of other factors that could explain or affect the relationship among the mean metal values obtained by the different sampling methods.

### 9.1 Time of exposure

This section explores whether there is an influence of the exposure time of the DGTs on the observed ratio between the concentrations obtained by different methods. For this purpose, the ratios between methods were compared at those sites where there were two different exposure times of the DGTs. Typically, the shortest exposure time was two days, and the longest exposure time was four days (although there were exceptions).

Figure 19 shows on the x-axis the ratio between the mean Cd concentration obtained by means of DGT and the mean concentration obtained by the classical spot sampling method on the first retrieval date. Similarly, on the y-axis this ratio is plotted for the second retrieval date at the same site and time of the year. On the left it can be seen that the DGT/spot sampling (voltammetry) ratios are remarkably close to the theoretical 1:1 ratio (that is, the values are very similar on the first and second sampling

dates). Therefore, in this case there seems to be no clear influence of exposure time. Similarly, on the right side, the DGT/spot sampling ratios (ICP-MS) are shown, where no significant differences with respect to the theoretical 1:1 ratio are observed.



**Figure 19.** Cd: DGT/(spot sampling) ratios. Biplots of the ratio of the concentration of metal obtained by means of DGT to the mean concentration of metal obtained by spot sampling at two sampling dates. Key: DGT – concentration of a metal obtained by means of DGT passive sampler, CSV – mean concentration of a metal measured in spot samples using cathodic stripping voltammetry on filtered seawater, ICP – mean concentration of a metal measured in spot samples using ICP-MS on filtered seawater. The blue diagonal line represents a hypothetical 1:1 ratio.

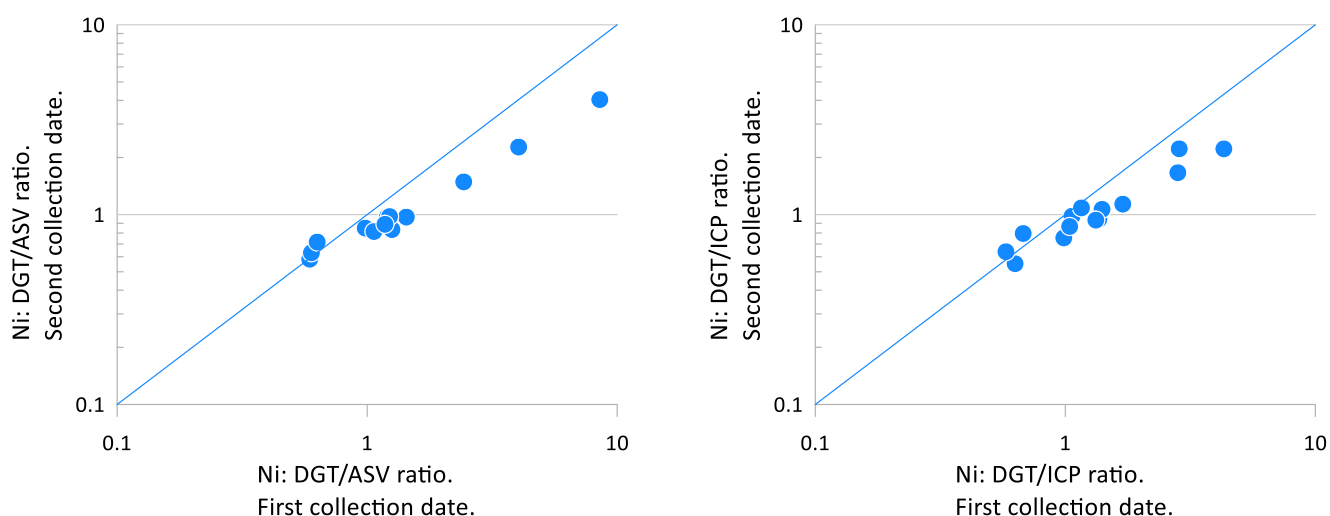
For Ni the situation is slightly different than Cd (Figure 20). It can be observed that at low ratios the values measured on both dates are similar. However, at higher ratios, the value obtained on the second date is lower than the value obtained in the first date (not when the DGT/spot sampling ratios are low, *i.e.* less than 1 in the first retrieval date).

In the case of Pb (Figure 21) the situation is similar to Ni: when the ratio at the first date is lower than 0.3, it is generally lower at the second date (with some exceptions).

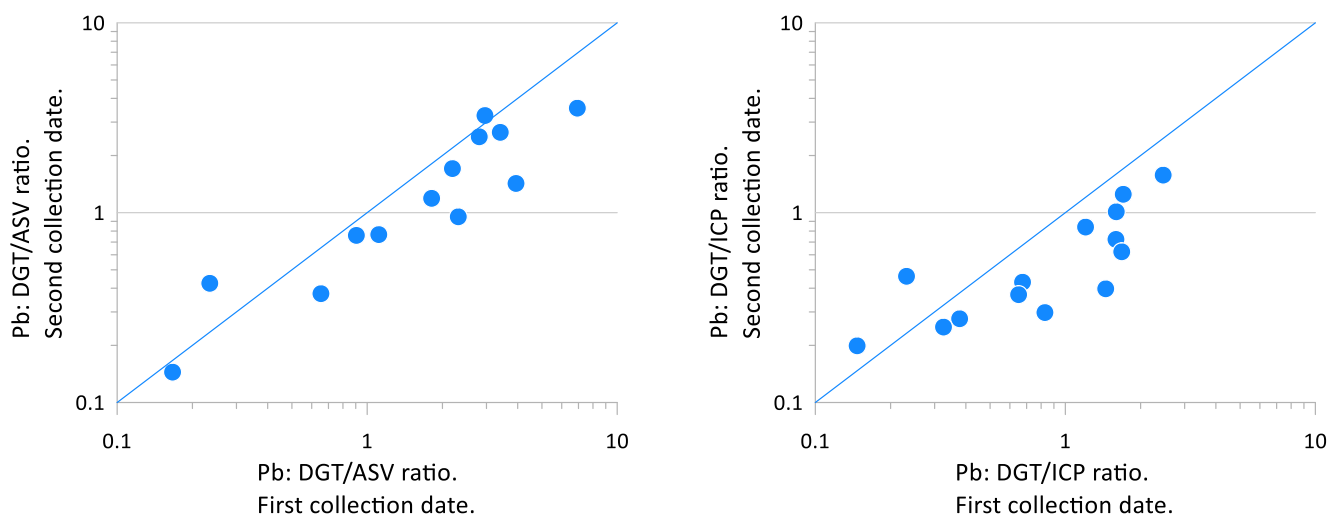
In the case of Cu and Mn (Figure 22) the situation is similar to Cd: it can be seen that the values are distributed on both sides of the hypothetical 1:1 line.

In the case of Co and Zn (Figure 22) it is observed that the ratio values are generally lower on the second date than on the first date.

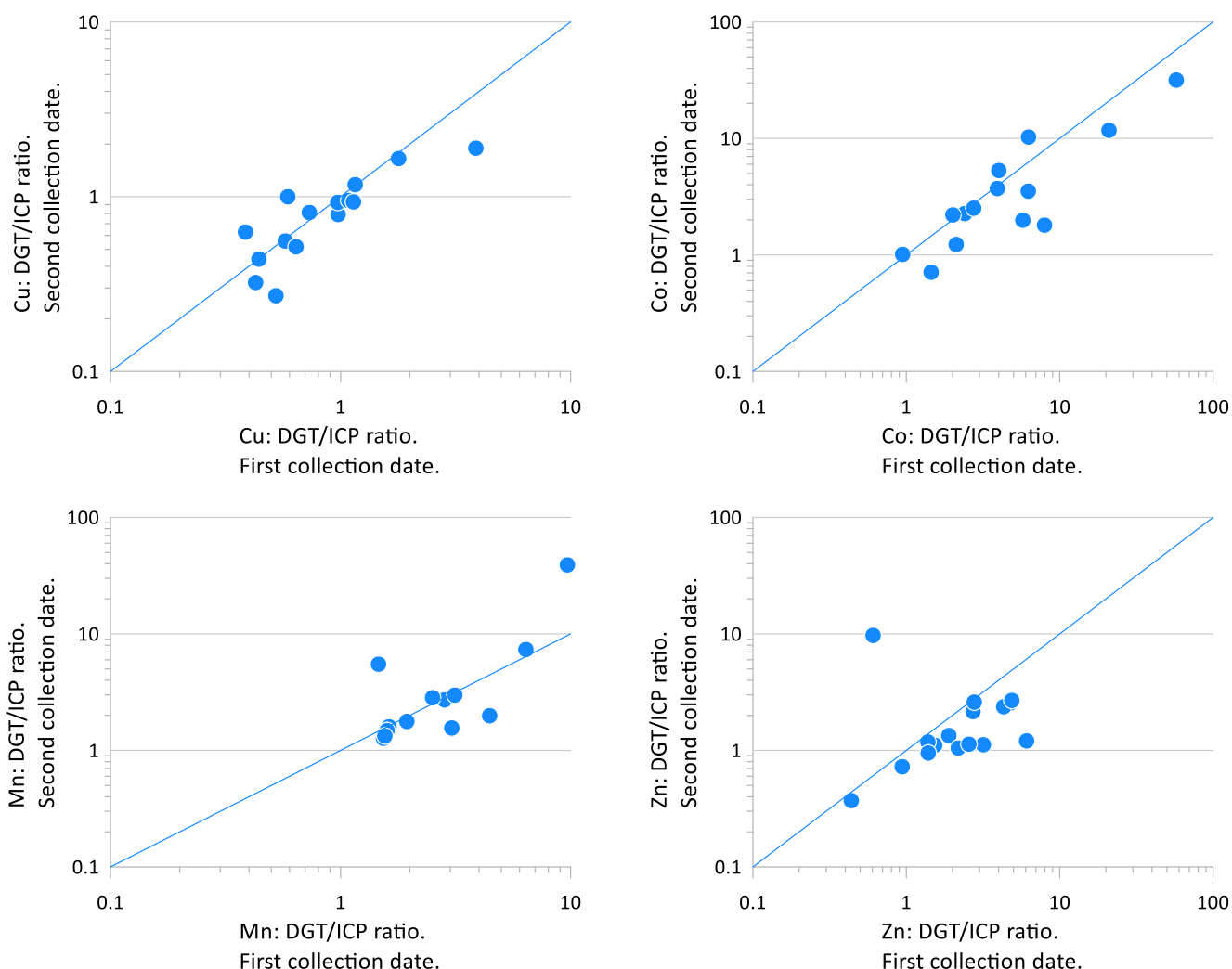




**Figure 20.** Ni: DGT/(spot sampling) ratios. Biplots of the ratio of the concentration of metal obtained by means of DGT to the mean concentration of metal obtained by spot sampling at two sampling dates. Key: DGT – concentration of a metal obtained by means of DGT passive sampler, CSV – mean concentration of a metal measured in spot samples using cathodic stripping voltammetry on filtered seawater, ICP – mean concentration of a metal measured in spot samples using ICP-MS on filtered seawater. The blue diagonal line represents a hypothetical 1:1 ratio.



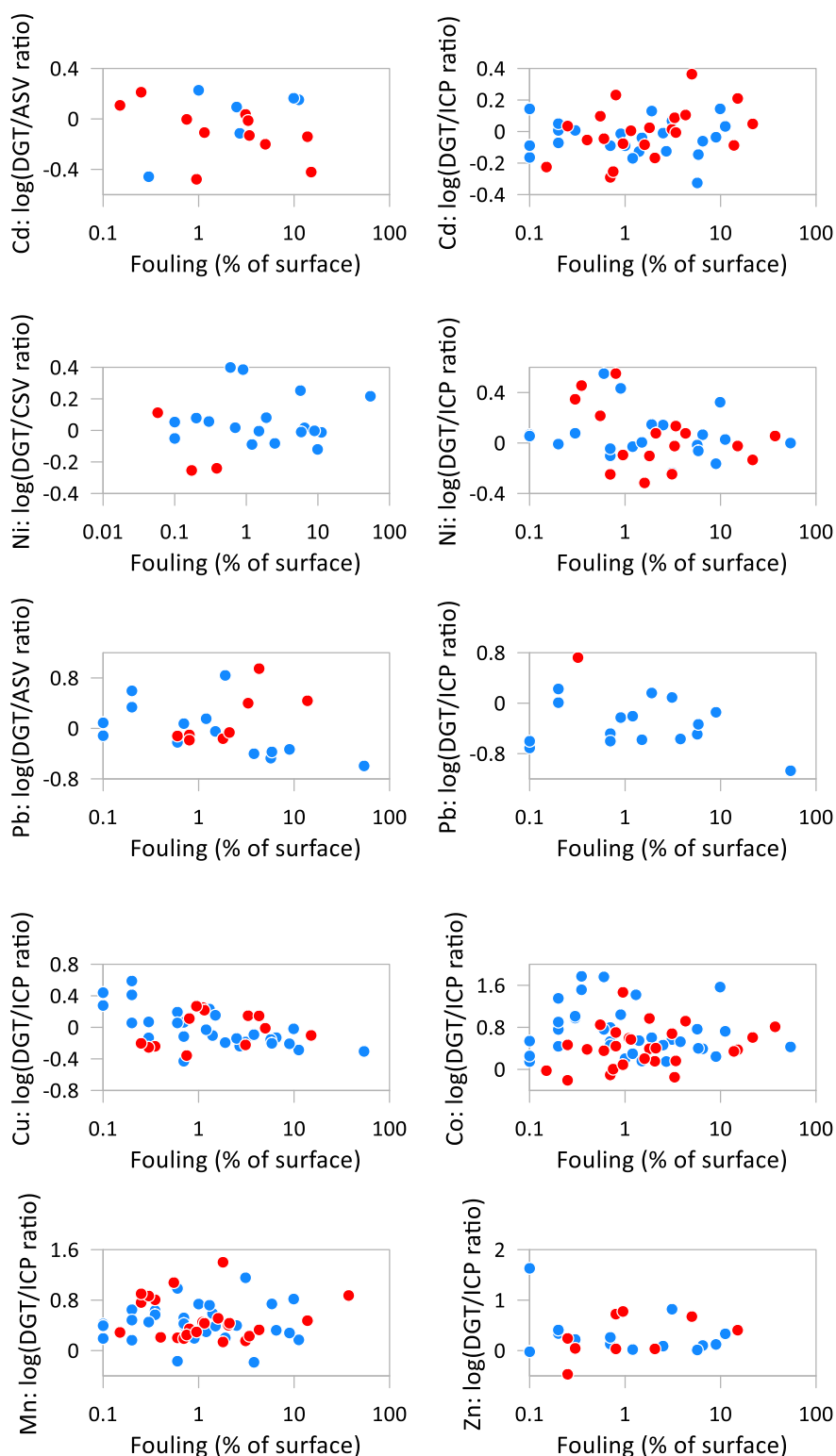
**Figure 21.** Pb: DGT/(spot sampling) ratios. Biplots of the ratio of the concentration of metal obtained by means of DGT to the mean concentration of metal obtained by spot sampling at two sampling dates. Key: DGT – concentration of a metal obtained by means of DGT passive sampler, CSV – mean concentration of a metal measured in spot samples using cathodic stripping voltammetry on filtered seawater, ICP – mean concentration of a metal measured in spot samples using ICP-MS on filtered seawater. The blue diagonal line represents a hypothetical 1:1 ratio.



**Figure 22.** Cu, Co, Mn and Zn: DGT/(spot sampling) ratios. Biplots of the ratio of the concentration of metal obtained with DGT to the mean concentration of metal obtained by spot sampling at two sampling dates. Key: DGT – concentration of a metal measured by means of DGT passive sampler, ICP – mean concentration of a metal measured in spot samples using ICP-MS on filtered seawater. The blue diagonal line represents a hypothetical 1:1 ratio.

## 9.2 Fouling

This section explores the possible relationship between the fouling coverage observed in DGTs (displayed in parallel to the DGTs in which metals were measured) vs. the DGT/spot sampling ratios. It is observed that in general there is no clear relationship (Figure 23). In the case of Cu there is a significant but weak inverse relationship (Spearman rho = -0.37).



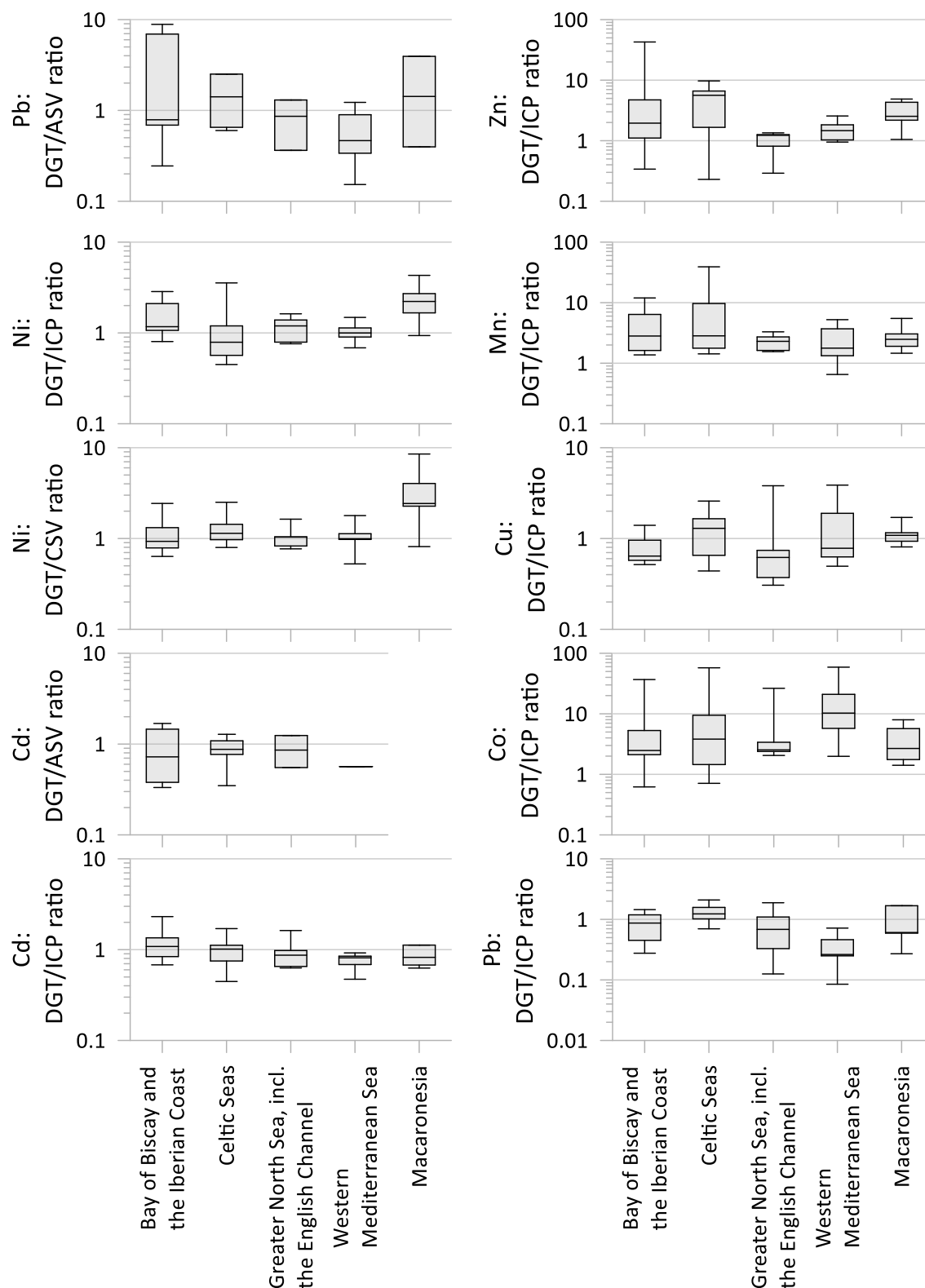
**Figure 23.** Biplots of the ratio of the concentration of metal measured in DGT to the mean concentration of metal measured in spot samples vs fouling measured in DGT. Key: DGT – concentration of a metal measured by means of DGT passive sampler, ASV – mean concentration of a metal measured in spot samples using anodic stripping voltammetry on filtered seawater, CSV – mean concentration of a metal measured in spot samples using cathodic stripping voltammetry on filtered seawater. The blue dots correspond to coastal areas and the red dots to estuaries.

### 9.3 Subregions

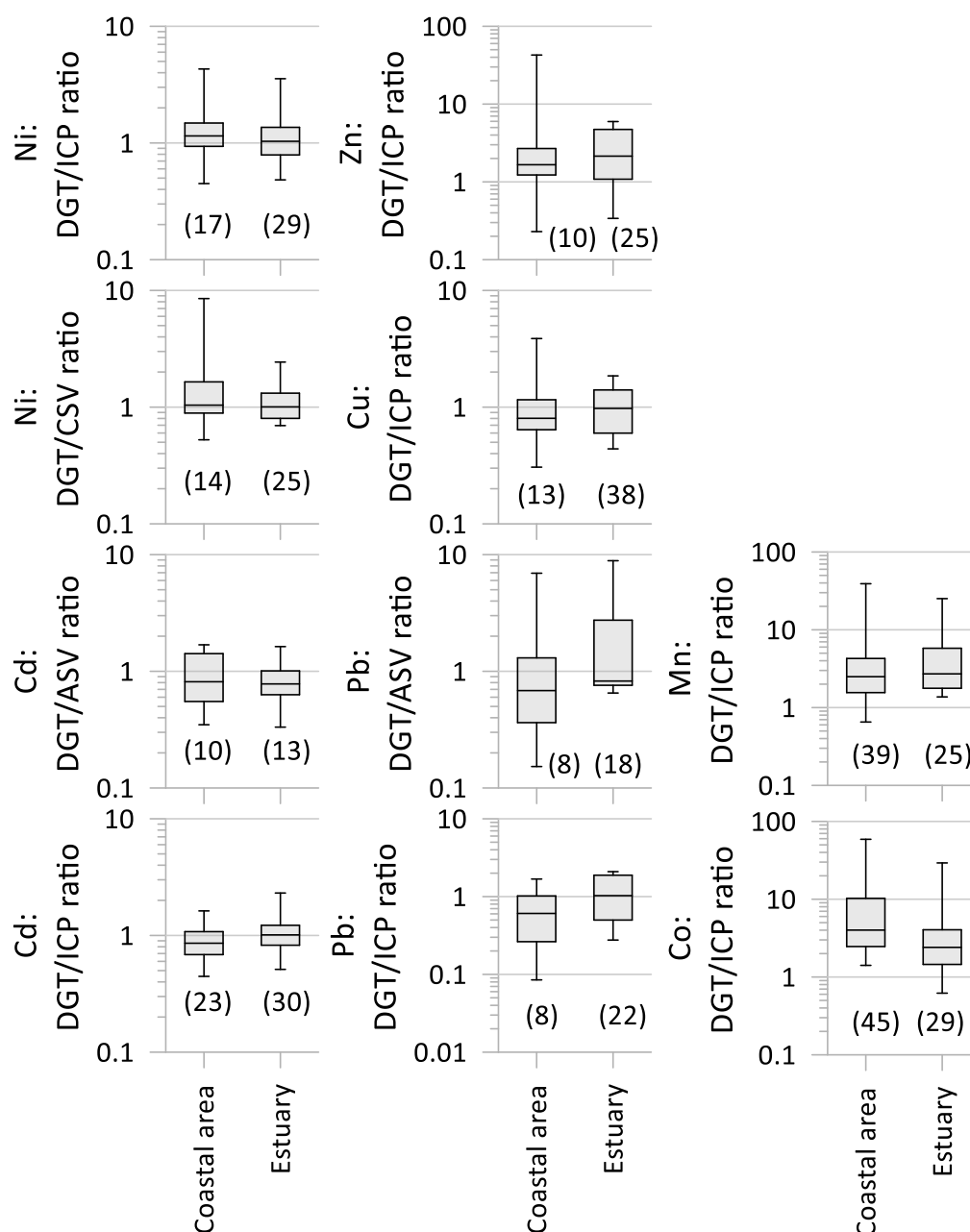
Figure 24 shows the variability among the different sub-areas studied in the DGT/spot sampling ratios. There are no significant differences in the median value between zones.

### 9.4 Coastal areas vs estuarine areas

Figure 25 shows the variability between the coastal and estuarine areas in the DGT/spot sampling ratios. There are no significant differences in the median values between both areas.



**Figure 24.** Box-plots of ratios of metal concentration measured with different methods. Key: DGT – concentration of metal obtained by means of DGT passive sampler, ICP – mean metal concentration measured in filtered spot water samples using ICP-MS, ASV (CSV) – mean metal concentration measured in filtered spot water samples using anodic stripping voltammetry (or cathodic stripping voltammetry). Whiskers indicate maximum and minimum values. Note: at Macaronesia the concentration of Cd measured by ASV was lower than LOQ, therefore no data of Cd: DGT/ASV ratio is available.



**Figure 25.** Box-plots of ratios of metal concentration measured with different methods. Number of data is indicated in brackets. Key: DGT – concentration of metal obtained by means of DGT passive sampler, ICP – mean metal concentration measured in filtered spot water samples using ICP-MS, ASV (CSV) – mean metal concentration measured in filtered spot water samples using anodic stripping voltammetry (or cathodic stripping voltammetry). Whiskers indicate maximum and minimum values.

## 10. Main conclusions

It can be concluded that the variability of the DGT/spot sampling ratios can be better explained by the fluctuations in metal concentration in waters rather than the effect of environmental conditions. The ratios were not significantly affected by temperature, salinity, pH, oxygen, DOC, SPM or fouling. For some metals (Ni, Pb, Co and Zn), in most cases, it was found that with longer exposure times the DGT/spot sampling ratio was slightly lower.

## 11. References

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