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Programma di ricerca scientifica per una laguna “regolata”

Linea 2.1

*Qualità del sedimento lagunare a supporto
della sua gestione sostenibile*

D2.1.2.1

*Caratterizzazione chimica del
sedimento*

Metalli in traccia

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1 Caratterizzazione chimica del sedimento

1.1 Summary in Inglese

This document reports the results of the chemical characterization of lagoon sediments related to the two sampling campaigns of Task 2.1.2 (within Line 2.1). SELC Soc Coop performed the samplings of sediment cores from Venice lagoon waterways in November 2020 and March 2021, as commissioned by the Ca' Foscari University of Venice (Università Ca' Foscari Venezia - Dipartimento di Scienze Ambientali, Informatica e Statistica), by the University of Padua (Università degli Studi di Padova - Dipartimento di Biomedicina comparata e alimentazione) and CORILA. For each sampling campaign, six sediment cores (1m in length from the bottom of the channel) were collected in five sampling sites along the Vittorio Emanuele III channel and one sampling site in the San Felice channel.

The chemical characterization plan included the analysis of total concentrations of nine trace elements (As, Cd, Cr, Cu, Hg, Ni, Pb, V, Zn) and their geospeciation. Assessing the geospeciation of trace elements means measuring the concentrations of each element in the different chemical species/fractions, which have different bioaccessibility, mobility, and therefore a different bioavailability. These elements may exert toxic effects, representing an environmental threat to biota.

The results of this activity are reported in the following paragraphs. In Annex I (Allegato 1) in EXCEL format, two tables report the concentrations of trace elements in each sediment core for both sampling campaigns, both as total concentration and in the different fractions obtained by the geospeciation assessment. The following sections describe the analytical methods applied to determine these concentrations and present and discuss representative graphs of the first and second monitoring results. Values in red refer to concentrations Under LOQ (limit of quantification) and are reported as LOD/2 (limit of detection).

Regarding the total concentration of the trace elements studied, while all the sediments collected in the first campaign (cold season) complied with the values of Class A, those sampled in the warmer season (second campaign) showed an increment so that values of Class A were overcome and sediments complied with class B. The study of geospeciation has shown that the bioaccessible fraction and/or the two mobile fractions were predominant for all the trace elements studied at the six sites in both sampling campaigns. Besides, the study of geospeciation has highlighted that the increment in the total concentration observed in the second campaign was consistent with an increase in the bioaccessible fraction and the two mobile fractions; the sum of these three fractions always outweighed the residual concentration. Site VI is the reference site for the Water Framework Directive in the Venice Lagoon; although the total concentration of the trace elements studied met the EQSs and showed the lowest total concentration, their bioaccessibility and mobility were relevant. Geospeciation allows a more reliable assessment of the actual hazardousness of sediments.

This Deliverable does not report the sediment chemical characterization for organic contaminants, which was commissioned by UNIPD (Massimo Milan) to Laboratorio del Provveditore, as such analyses were not completed so far.

1.2 Sintesi in Italiano

Il presente documento riporta i dati sulla caratterizzazione chimica dei sedimenti lagunari relativi ai due campionamenti della Task 2.1.2 (Linea 2.1). Il prelievo di carote di sedimento dai fondali dei canali navigabili della laguna di Venezia è stato eseguito da SELC Soc. Coop a novembre 2020 e marzo 2021 su commissione dell'Università Ca' Foscari di Venezia (Dipartimento di Scienze Ambientali, Informatica e Statistica), dell'Università degli Studi di Padova (Dipartimento di Biomedicina comparata e alimentazione) e

di CORILA. Per ogni campionamento sono state prelevate sei fustelle da 1 m (dal piano fondale) da cinque siti nel Canale Vittorio Emanuele III e da un sito nel Canale San Felice.

La caratterizzazione chimica dei sedimenti campionati include la determinazione analitica delle concentrazioni totali di 9 elementi in traccia (As, Cd, Cr, Cu, Hg, Ni, Pb, V, Zn) e della loro geospeciazione, ovvero le concentrazioni di ogni singolo elemento analizzato nelle diverse forme chimiche/frazioni, che si distinguono le une dalle altre per differente bioaccessibilità, mobilità, e quindi biodisponibilità per il biota. Questi elementi potrebbero avere effetti tossici e rappresentare un pericolo per l'ambiente ed il biota.

Nei seguenti paragrafi vengono descritte le procedure analitiche che hanno portato alla determinazione di queste concentrazioni e vengono presentati e discussi i grafici relativi ai risultati ottenuti dai campioni della prima e della seconda campagna. La presente Deliverable include inoltre due tabelle (Allegato 1), in formato EXCEL, che raccolgono i risultati in termini di concentrazioni dei metalli nei campioni di entrambe le campagne, sia come concentrazione totale, sia nelle diverse frazioni ottenute tramite geospeciazione. I valori in rosso si riferiscono alle concentrazioni inferiori al LOD (limite di quantificazione) e sono riportati come LOD/2 (limite di rilevabilità).

I valori di concentrazione totale degli elementi in tracce studiati nei sei siti in esame nella prima campagna (stagione fredda) rientravano nella Classe A del Protocollo Fanghi; invece, nella seconda campagna (stagione calda) è stato osservato un incremento della concentrazione totale nei sei i siti studiati, tanto che si è osservato un superamento dei valori di Classe A; i sedimenti rientravano quindi in classe B. Per quanto riguarda lo studio di geospeciazione, la somma della frazione bioaccessibile e delle due frazioni mobili superava sempre la concentrazione residua in tutti i siti in entrambe le campagne. La geospeciazione ha evidenziato che l'incremento della concentrazione totale osservato nella seconda campagna era in linea con l'aumento della frazione bioaccessibile e delle due frazioni mobili. Il sito VI è il sito di riferimento per la Water Framework Directive nella laguna di Venezia; la concentrazione totale degli elementi in tracce nei sedimenti di questo sito era la più bassa e anche gli standard di qualità ambientale erano sempre rispettati. Ciononostante, lo studio di geospeciazione ha mostrato che la bioaccessibilità e la mobilità degli elementi in tracce nei sedimenti di questo sito era comunque significativa. Grazie allo studio di geospeciazione è possibile valutare in modo più affidabile l'effettiva pericolosità dei sedimenti.

La presente Deliverable non riporta invece la caratterizzazione chimica dei sedimenti relativa ai composti organici in quanto le analisi commissionate al Laboratorio del Provveditore da parte di UNIPD (Massimo Milan) non sono ancora state completate.

2 Methods

2.1 Sampling

Two sampling campaigns were carried out by SELC Soc. Coop. in November 2020 and March 2021, as commissioned by the Ca' Foscari University of Venice (Università Ca' Foscari di Venezia - Dipartimento di Scienze Ambientali, Informatica e Statistica), by the University of Padua (Università degli Studi di Padova - Dipartimento di Biomedicina comparata e alimentazione) and CORILA, in two different waterways of the Venice Lagoon: Vittorio Emanuele III Channel (sites I-V) and San Felice Channel (site VI) (Figure 1). In both campaigns, the sampling of the six sediment cores was performed starting from the bottom plane down to a depth of 1.0 m through a vibrating core barrel.

The one-meter sediment cores were then delivered to the Laboratory of Ecotoxicology of the Ca' Foscari University of Venice, where they were quartered, homogenized, and then apportioned in various subsamples. These tasks were carried out in a controlled atmosphere (under nitrogen flow) to preserve all the equilibria in the sediments.



Figure 1. Sampling sites.

2.2 Chemical quality of sediments: trace elements

Chemical characterization of the sediments samples was performed by analysing the total concentrations of trace elements and their geospeciation. Wet acid digestions and sequential extraction procedures were performed at the Laboratory of Analytical Chemistry of the Ca' Foscari University of Venice, while analyses via ICP-MS were performed at the Institute of Polar Sciences (CNR-ISP).

Sediment samples were quartered and then subdivided into three aliquots:

- An aliquot of each sediment sample was weighed, dried on stove at 105 °C for 48 h, and weighed again to calculate the sediment's relative humidity (Table 1 and Table 2, Annex 1).
- A second aliquot for the assessment of the total concentration of the ten elements was freeze-dried and then powdered with a ball mill (capsules and balls were made of Teflon to minimize contamination). 0.3 g of pulverized sample were then mineralized by wet acid digestion, employing TFM (tetrafluoro methoxy) "vent and release" vessels using a microwave mineralization system (high-pressure rotor, Ethos 1, Milestone). A mixture of strong oxidants (HNO₃: HF: H₂O₂, PlasmaPure PLUS, and Ultra purity Reagents, Romil) was employed for the wet acid digestion. Digested samples were then recovered and diluted 25:1 and stored at - 20 °C till the analysis. The diluted samples were then analysed by ICP-MS (Inductively Coupled Plasma-Mass Spectrometry, iCAP RQ, Thermo Scientific) with autosampler (ASX500 CETAC). At least three replicates of each sample were digested and then analyzed. Accuracy and precision were regularly checked by analysing a certified reference material (MURST-ISS-A1), digested as the samples.
- The third aliquot, for the geospeciation analysis, has been used as it is, without any pre-treatment, following a procedure harmonized and developed by Corami et al. (2020), according to the Sequential Extraction Procedure (SEP) by Tessier et al. (1979) and Argese et al. (2003). Also, for the geospeciation study, at least three replicates of each sample were digested and then analyzed

During each phase, reagents with a high purity level were used (Ultra Purity reagents, Plasma Pure PLUS SCP Science) to avoid contamination.

2.3 Geospeciation of metals via sequential extraction procedure (SEP)

Geospeciation was studied via SEP, following the procedure developed by Corami et al. (2020).

In order to preserve the distribution of fractions of the nine studied elements, the harmonized SEP was performed on wet samples of homogenized sediments. The four different fractions assessed via SEP are the following:

1. First fraction (F1) bioaccessible and labile: this fraction is composed of the readily exchangeable fraction and the exchangeable fraction, which is bound to carbonates, and both are bioaccessible and bioavailable to the biota. The trace elements bound to this fraction are considered mostly anthropogenic, and they may pose a significant and continual hazard for the biota and the environment. In F1, the sorption and the retention of trace elements are weak, and they can be released by ion exchange processes or precipitated and co-precipitated with carbonate, from which in turn they can be easily leached in neutral or slightly acidic waters or the gut of the biota.
2. Second fraction (F2) acid reducible, bound to Fe/Mn oxyhydroxides fraction: this second fraction is not directly bioaccessible, but it is mobilizable.
3. Third fraction (F3) oxidizable, bound to organic matter and sulfide: this third fraction is not directly bioaccessible and less mobilizable than F2. These two fractions are considered scavengers and may provide a sink for trace elements. However, the elements in these fractions may be mobilized anew in relation to changes of oxygen rate, temperature, pH, and redox potential, which could be caused by different activities of organisms and by some enzymes in the gut of organisms (e.g., bacteria and benthic invertebrates) and by activities such as dredging. Hence, these two mobilizable fractions may become accessible to biota and, consequently, bioavailable; furthermore, the mobility of trace elements from these two fractions represents a hazard for the biota and the environment.
4. Fourth fraction (F4) residual fraction: this is the last fraction extracted; it may be defined as an inert fraction since its mobility is null and is not mobilizable and bioaccessible. In this fraction, trace elements are retained in the crystal lattice of minerals and/or in crystallized oxides and may be mobilized only by long-term processes such as weathering. The concentration of trace elements in the inert fourth fraction is considered an evaluation of natural sources' contribution.

The detailed SEP procedure, with all the chemical details, is outlined in Figure 2.

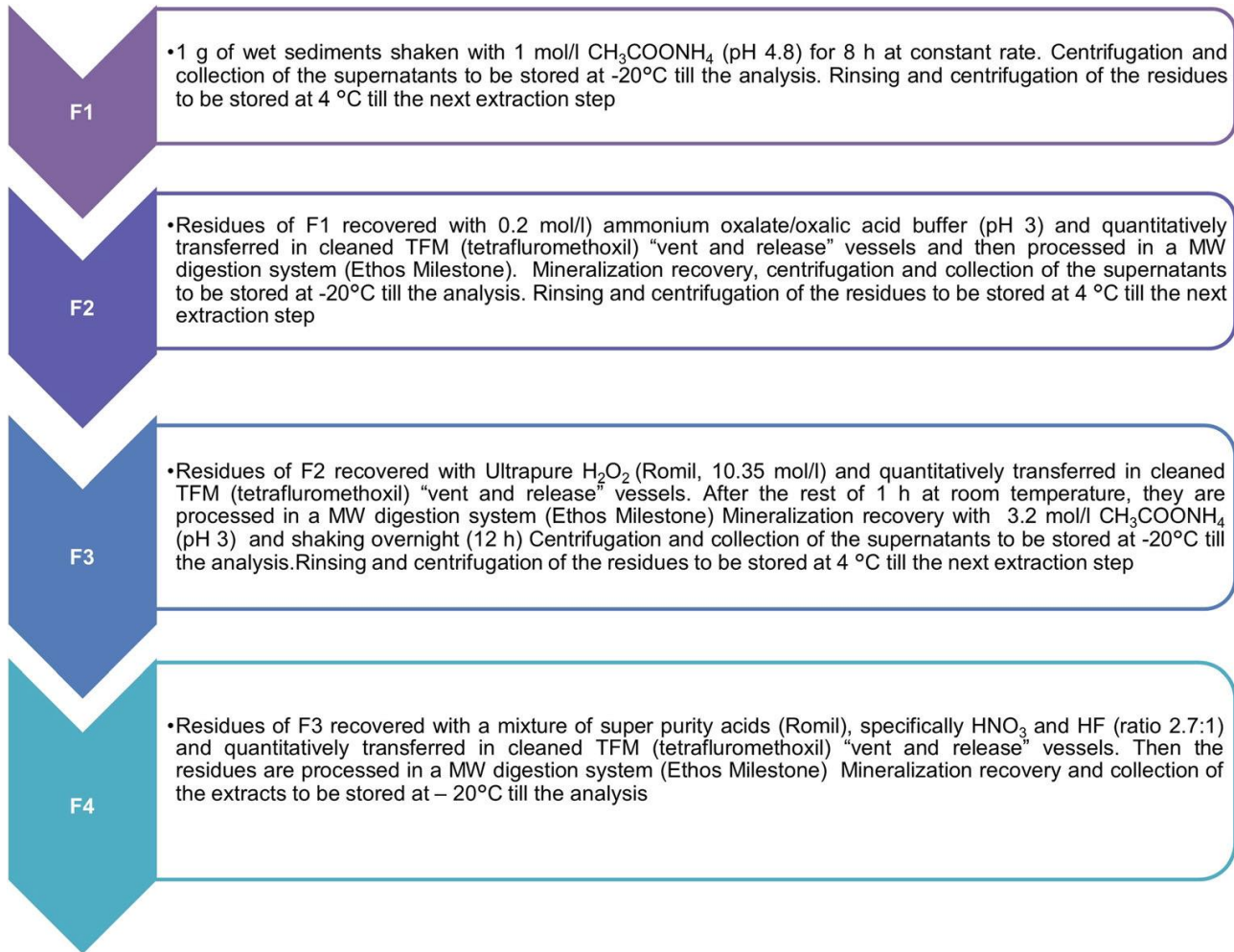


Figure 2. Sequential Extraction Procedure (SEP) (Corami et al., 2020).

3 Results of the two sampling campaigns: trace elements

3.1 Total concentrations analyzed in the two sampling campaigns

Trends of the total concentration of the ten trace elements investigated in the two campaigns are shown in Fig. 3 (a-j). Different concentration trends are observed according to the element considered. Measurement error of total concentration, expressed as the percentage of the relative standard deviation (RSD %), is $\leq 10\%$, and it is reported as an error bar in all the graphs.

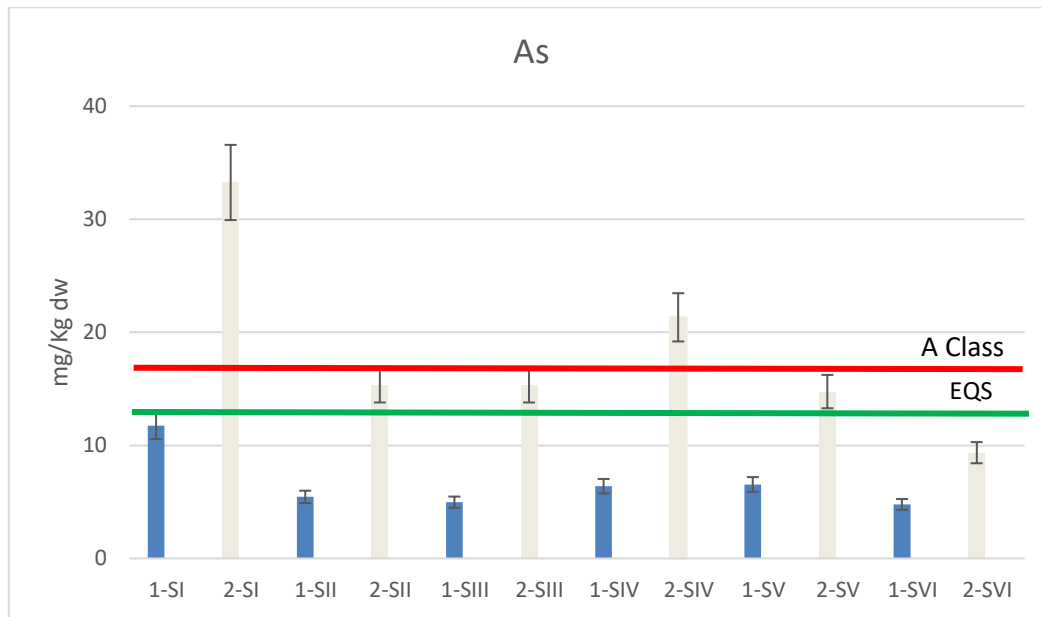
Total concentrations were compared with the regulatory thresholds defined in Protocollo Fanghi 1993 and Decree 172/2015, where *Standard di Qualità Ambientale* (SQA, translation of Environmental Quality Standards EQSs) for sediments are reported (Table 1). It is worth noting that the sediment quality classes of Protocollo Fanghi were defined with the objective of supporting sediment management and specifically to define the possible use/destination of dredged sediment. EQSs were set to evaluate the quality of surficial sediment to support and maintain a good ecological status of a water body.

Table 1. Regulatory thresholds for sediment quality classification defined in Protocollo Fanghi 1993 and EQSs of Decree 172/2015.

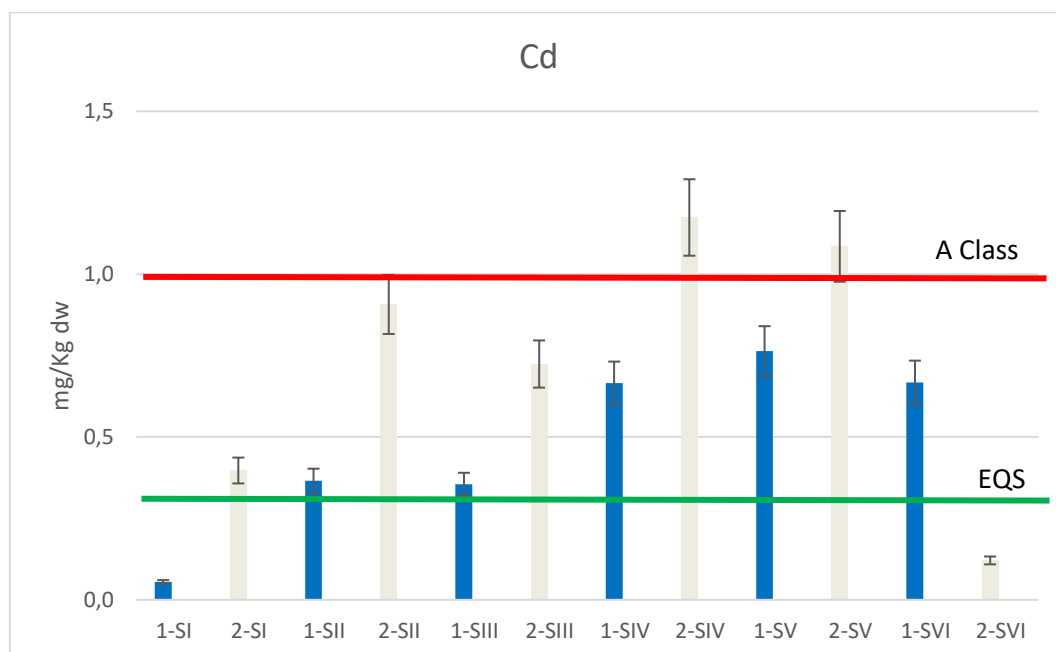
	Protocollo Fanghi			Decree 172/2015
	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw
	Class A	Class B	Class C	EQS
Hg	0,5	2	10	0,3
Cd	1	5	20	0,3
Pb	45	100	500	30
As	15	25	50	12
Cr	20	100	500	50
Cu	40	50	400	
Ni	45	50	150	
Zn	200	400	3000	

The six samples are SI, SII, SIII, SIV, SV, SVI, where S stands for sampling site; the two campaigns are called 1 and 2, respectively.

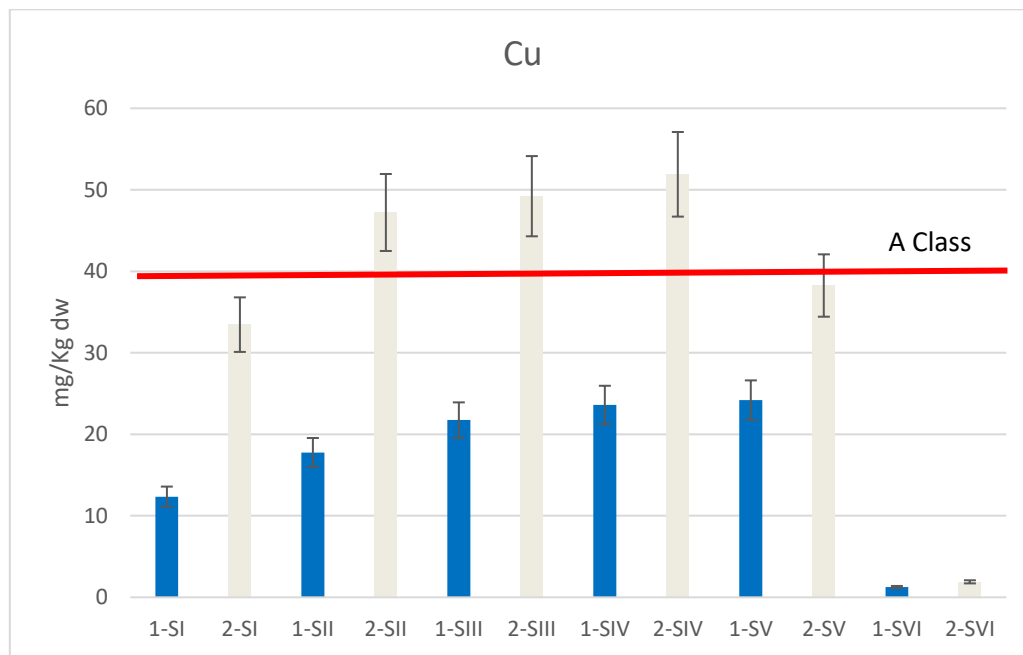
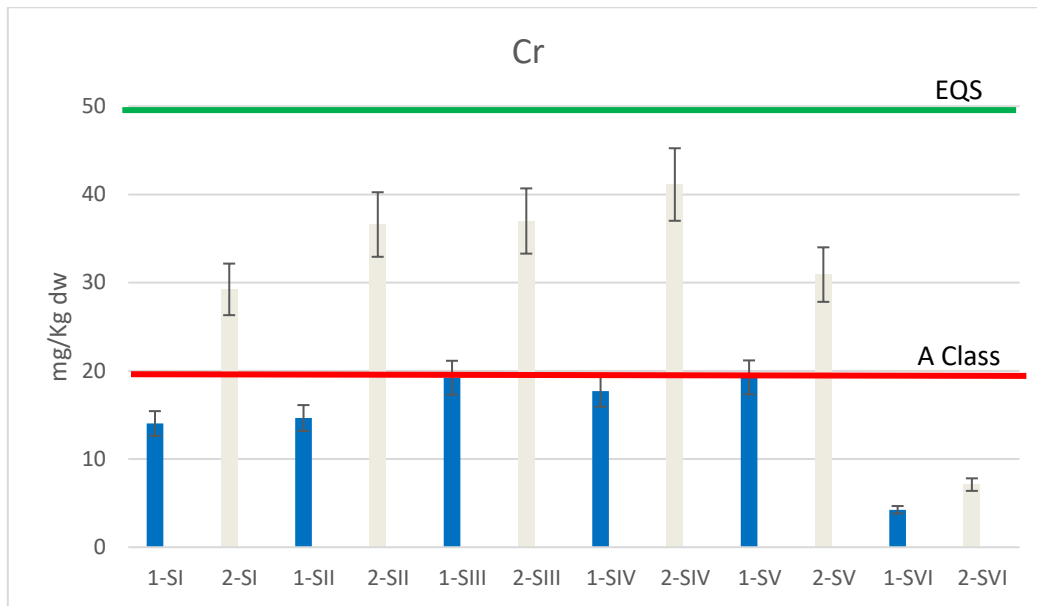
In the graphs of the trace elements analyzed, the value of the A Class limit (red line) and the value of the environmental quality standard (EQSs, green line) are shown for those elements regulated by Protocollo Fanghi and Decree 172/2015. Otherwise, the A Class limit value only is present. Vanadium is a trace element that has already been analyzed in previous studies in the lagoon but is not regulated.

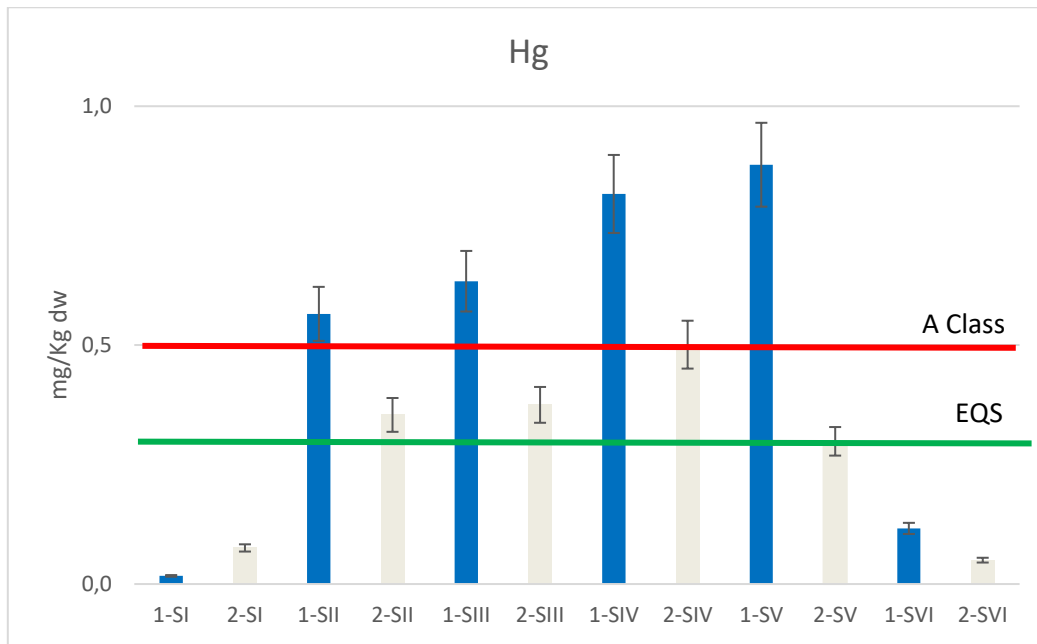


(a)

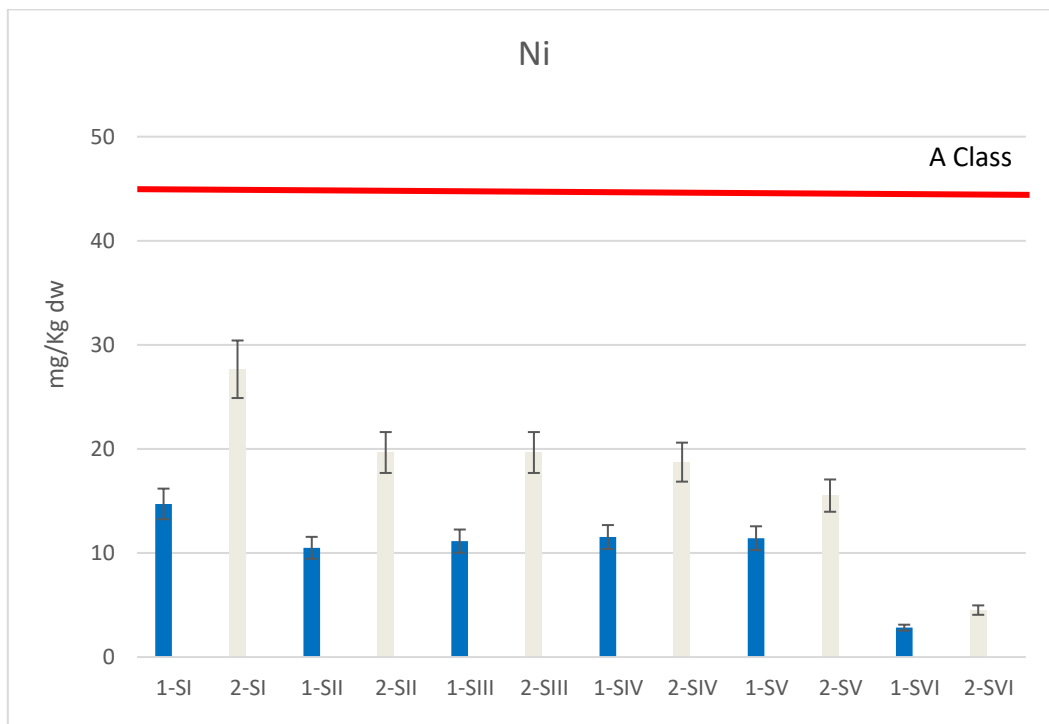


(b)

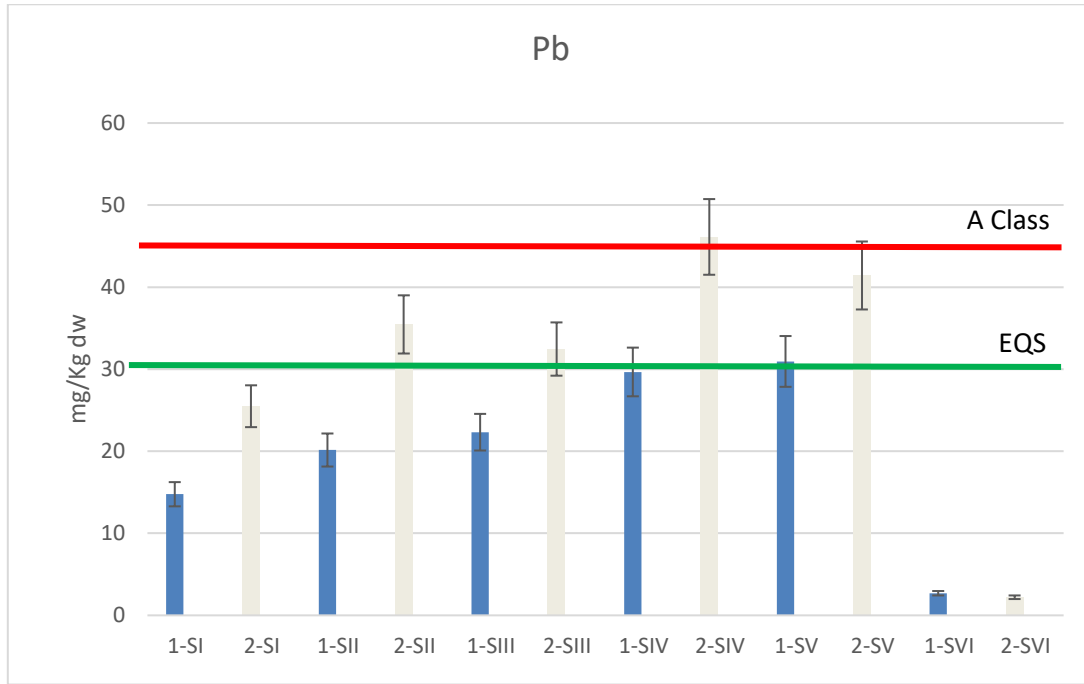




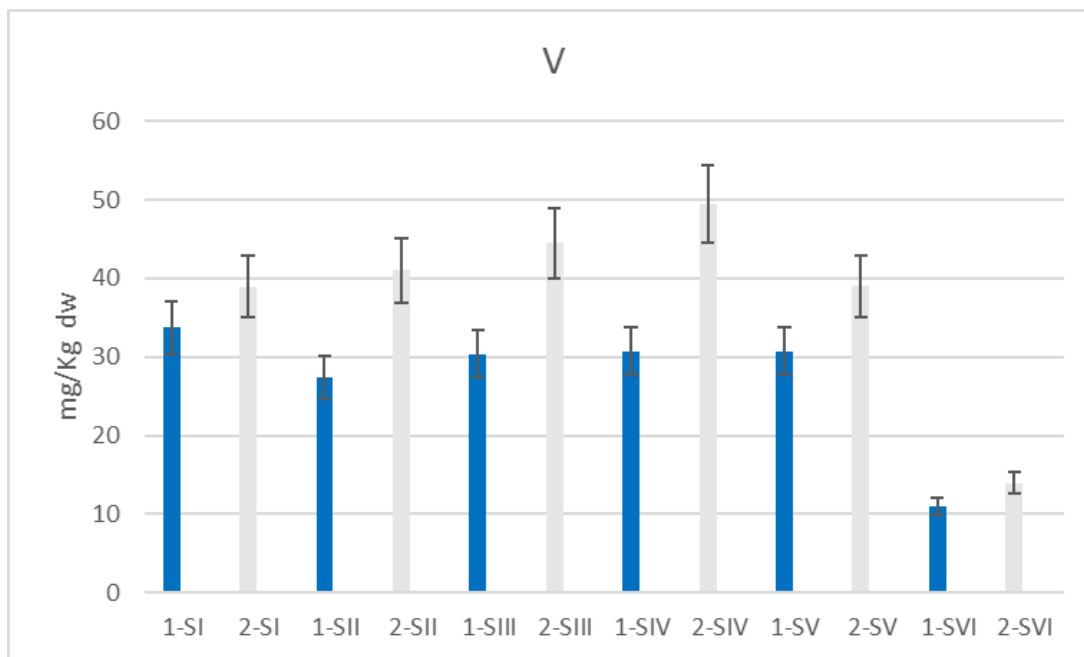
(e)



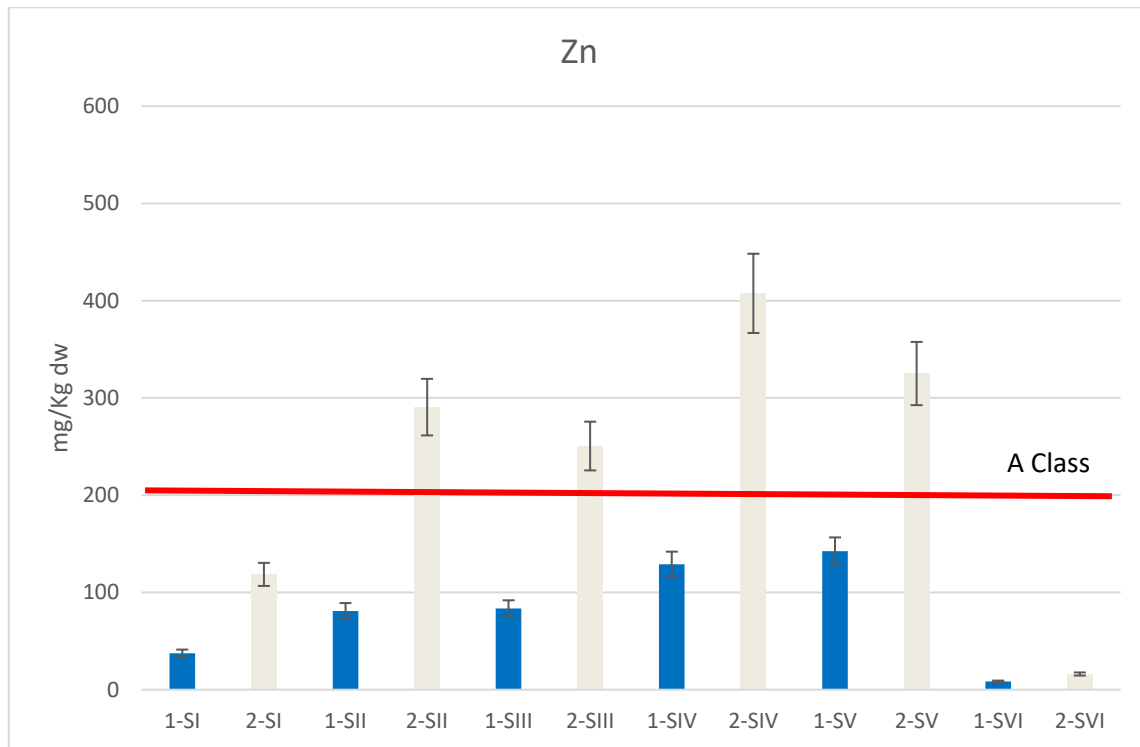
(f)



(g)



(h)



(i)

Figura. 3 (a-i). Total concentrations (mg/Kg dw) of trace elements analyzed in the sediments collected in the six sites in the two sampling campaigns (1 and 2), the error bar is expressed as RSD%.

In the first campaign, while the EQS for Pb is exceeded only in Site V, Site I is the only site where the sediment concentration complies with the EQS for Cd. On the other hand, Site I and Site VI respect the EQS of Hg. Moreover, for all sites, total concentrations of metals meet the threshold values reported in column A of Protocollo Fanghi 1993, except for Hg.

Except for Cd, Site VI, which is the reference site for the Water Framework Directive 2000/60/CE in the Venice Lagoon, shows the lowest total concentrations.

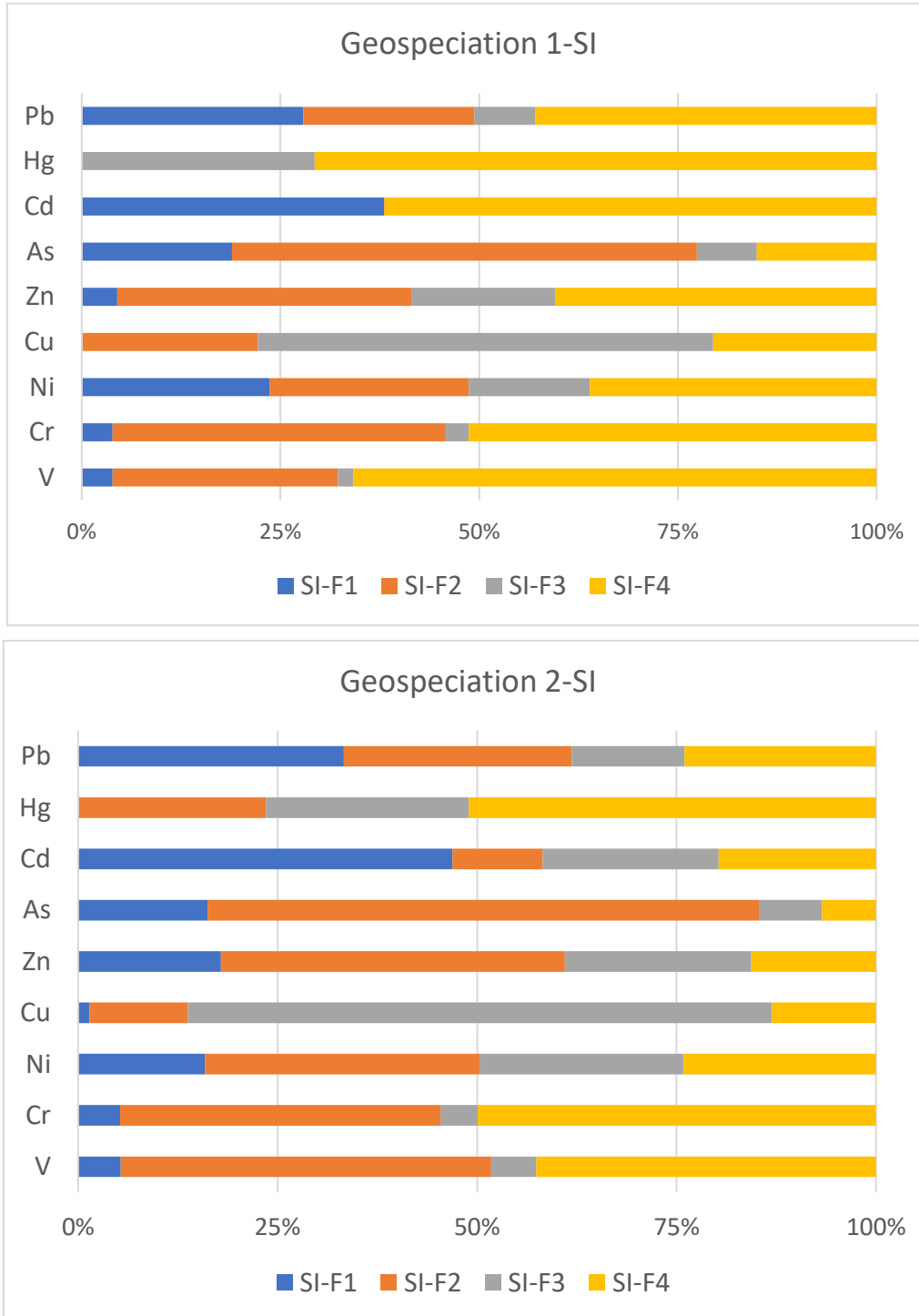
In the second campaign, the total concentration of the selected elements is higher than what was observed in sediment cores from the first campaign, except for Hg.

According to the Venice Sediment Management Protocol - Italian Ministry of the Environment 1993, an excess of 10% of the tabular limit is allowed for a single parameter of the list of pollutants. Considering only trace element concentrations in the first campaign, the sediments fall into Class A. On the other hand, in the second campaign, again regarding trace elements, sediments belong to class B (exceeding 10% by more than one parameter, except for Ni and Pb).

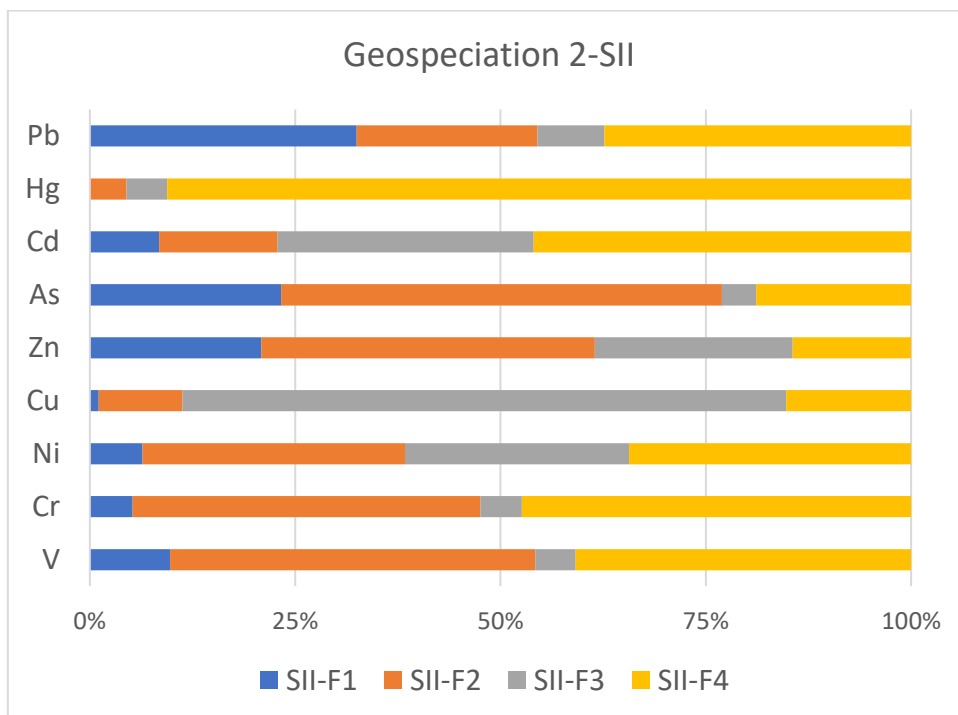
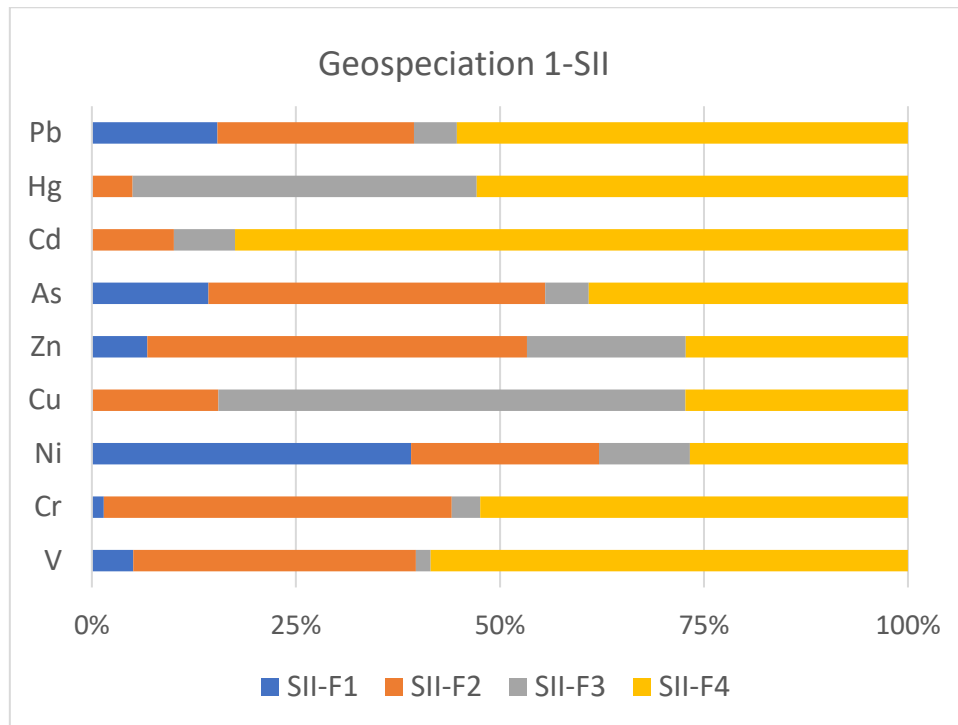
The EQSs for all elements under study are met only by the sediment sample from Site VI. Although, according to Decree 172/2015, it is permissible to exceed 20% of the EQS in sediments, if the precautionary principle was applied (European Commission, February 2000), most of the investigated sites would not meet the EQS for at least one contaminant.

3.2 Geospeciation from the two sampling campaigns

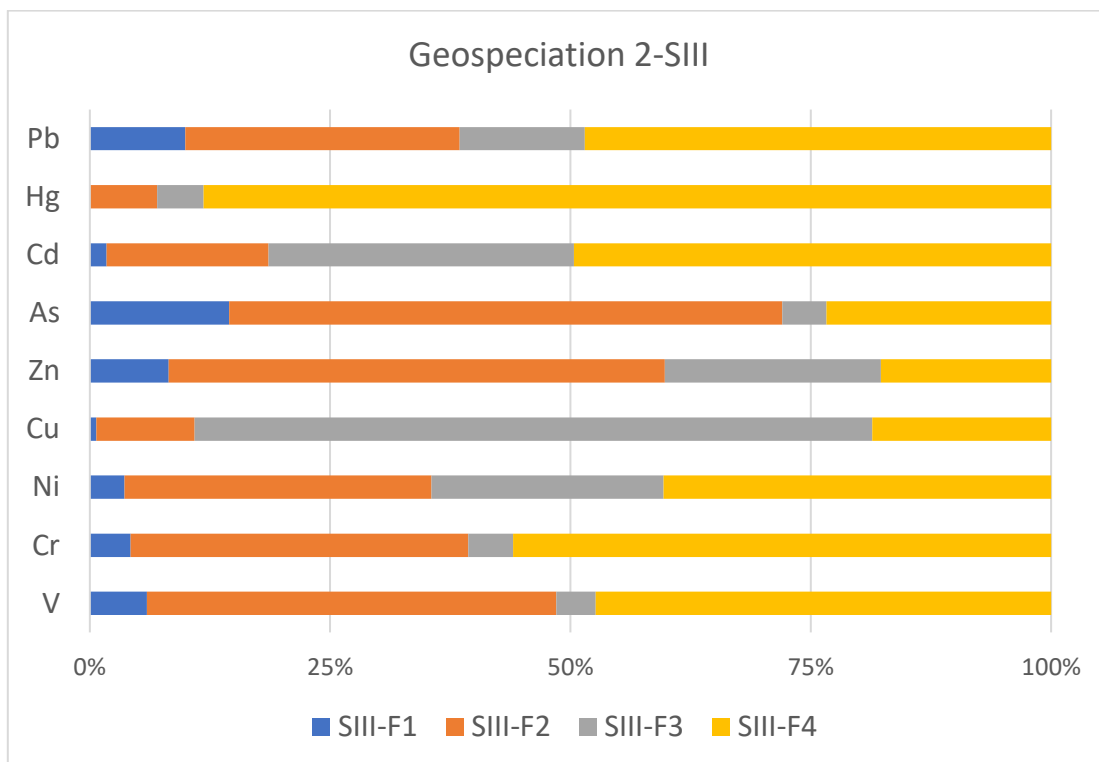
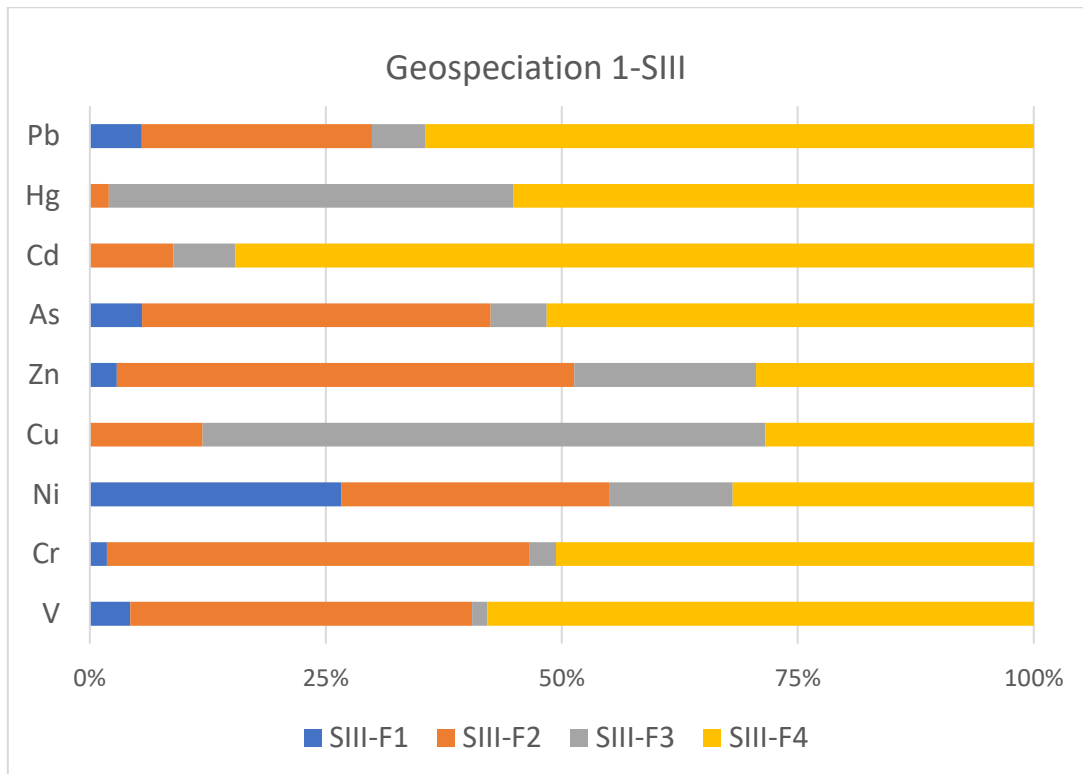
Geospeciation results for the nine elements for the six sampling sites in the two sampling campaigns are shown in Fig. 4 (a-f). The graphs show the percentage of the individual fractions (calculated on concentrations expressed as mg/kg dw). As mentioned for total concentrations, the measurement error for each fraction of every studied trace element is $\leq 10\%$ (RSD %).



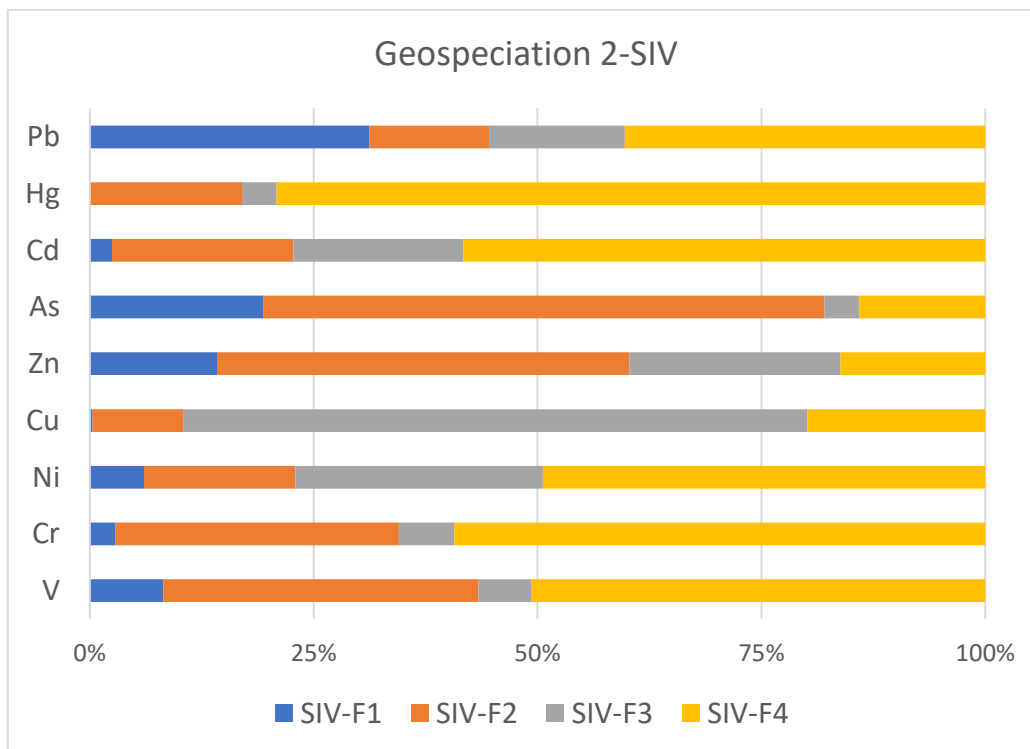
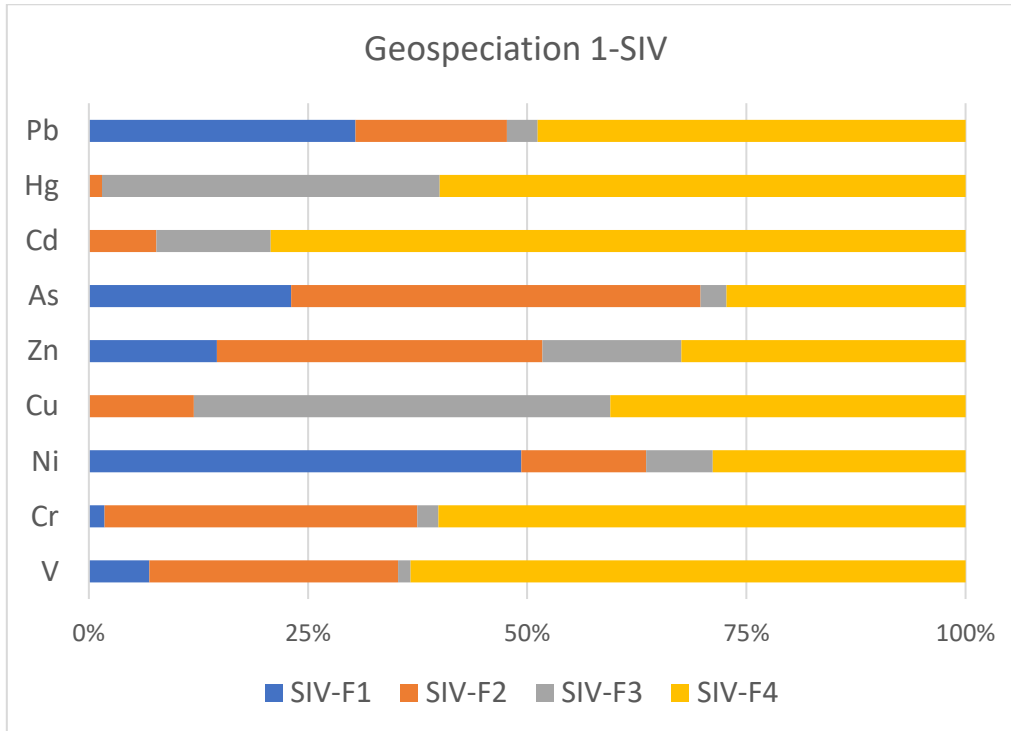
(a)



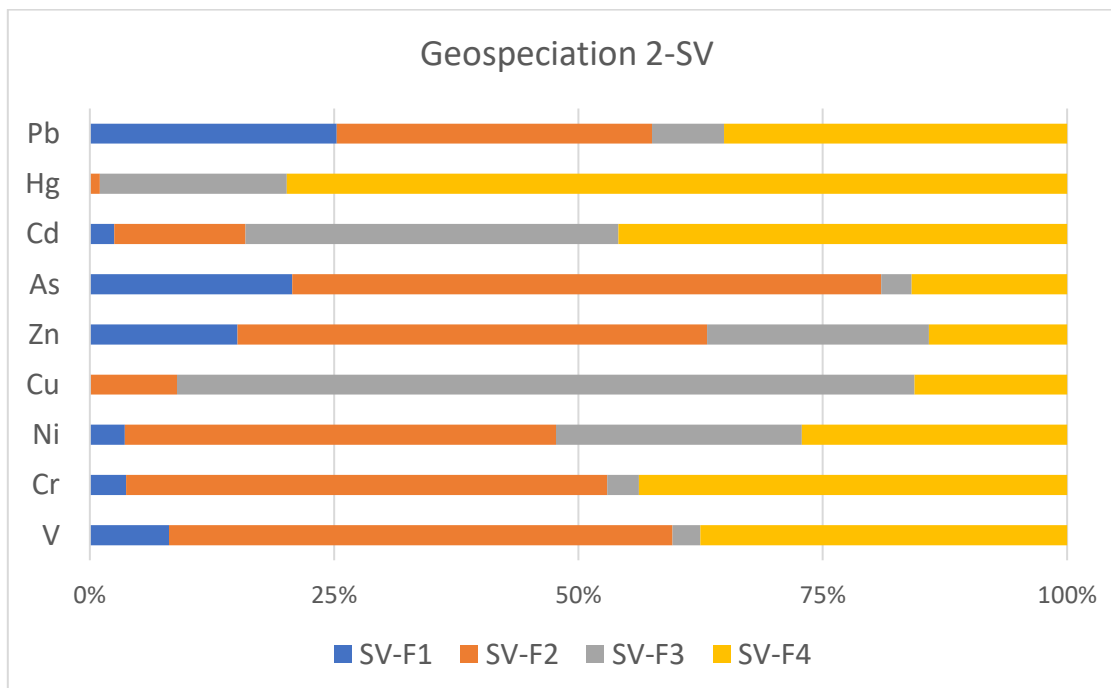
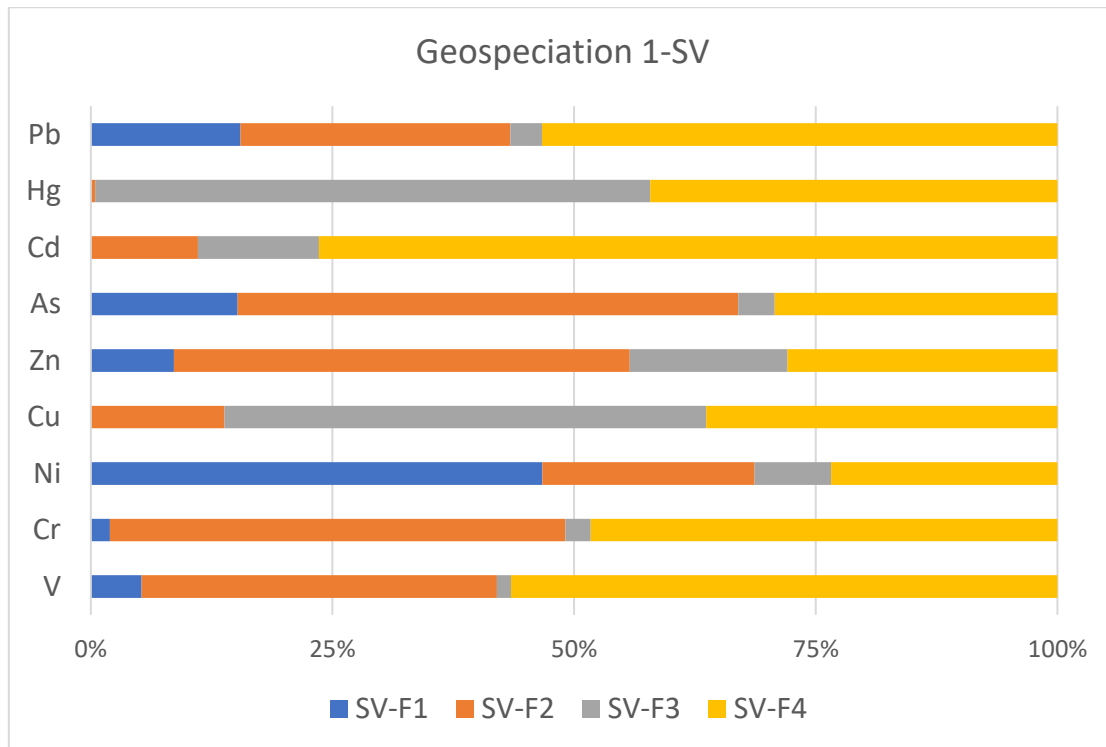
(b)



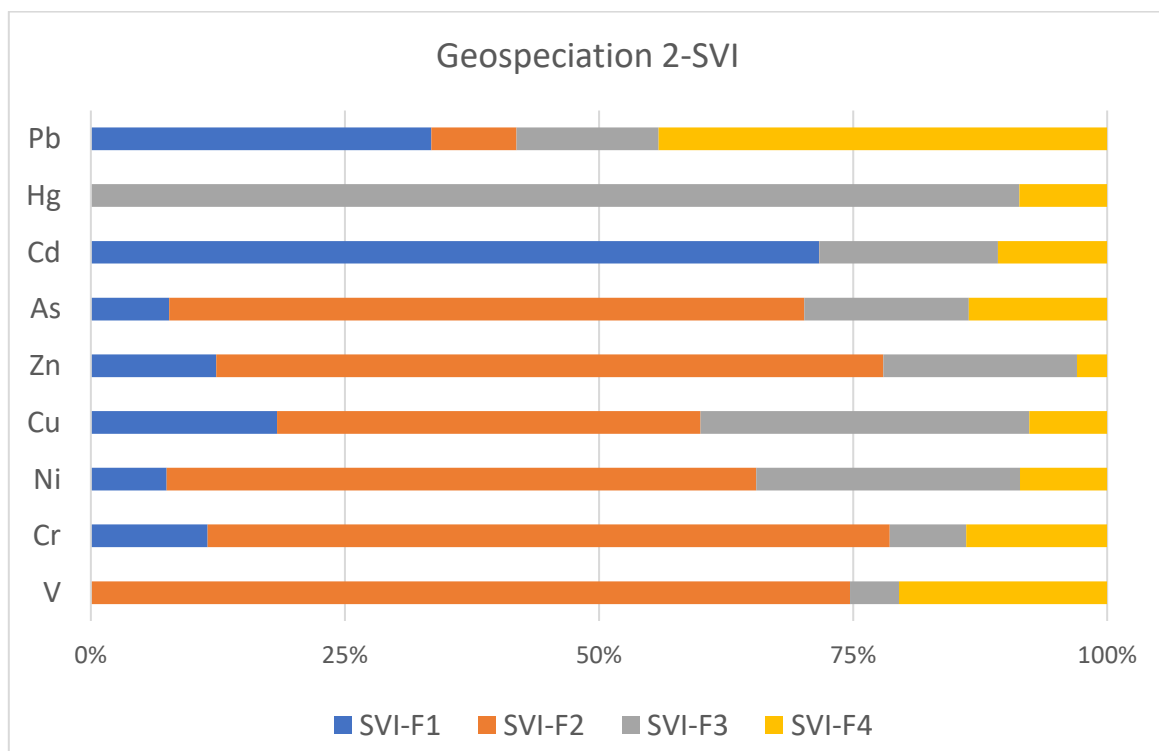
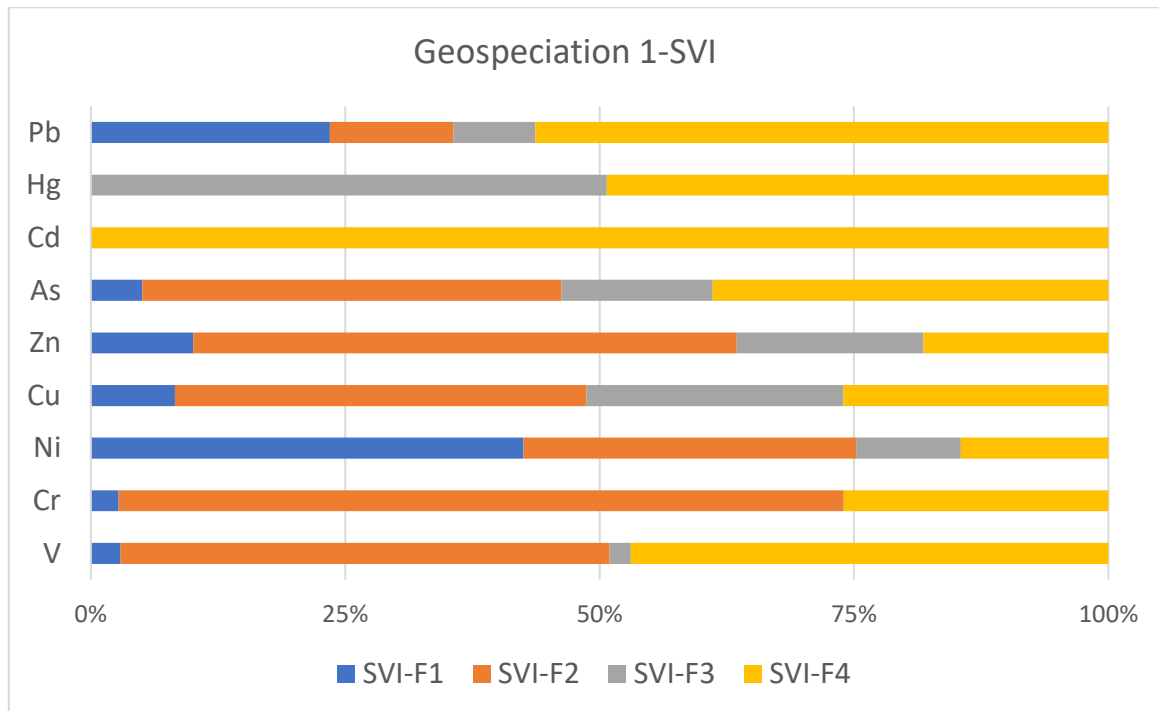
(c)



(d)



(e)



(f)

Figure 4 (a-f). Geospeciation of the trace elements analyzed in the six sites (SI-SVI) sampled in two different campaigns (1 and 2). F1 is the bioaccessible fraction (blue), F2 is the mobile fraction bound to Fe and Mn oxyhydroxides (orange), F3 is the mobile fraction bound to organic matter and sulfides (silver grey), F4 is the residual fraction or inert fraction (yellow).

Except for Cd at Site I, the geospeciation of Cd and Hg is similar for the investigated sites. In the geospeciation study of the other elements investigated at the six sampling sites, the bioaccessible fraction

and fractions with different mobility are present, and often outnumber the residual fraction. Unlike the other three fractions, F1 is considered mostly anthropogenic

Compared to the first campaign, except for Hg, the first bioaccessible fraction is present for all elements. It should be noted that the two mobile fractions are present for all elements in the sediments of the second campaign. The sum of these three fractions varies from 20% to 80 and outnumber the residual fraction, as observed in the first campaign. For instance, F1 and F3 fractions for Pb increased in the second campaign. Similar comments can be expressed for Cd or Hg. The concentration of Hg is predominantly mobile (third fraction F3), while Cd shows the highest bioaccessible fractions.

It is also worth highlighting that although the sediments at Site VI meet the EQSs and show the lowest total concentrations, the bioaccessibility and mobility of the studied trace elements are significant.

4 Conclusions

The two samplings were carried out in two different seasons. Differences in total concentrations may be likely influenced by seasonality.

Seasonality is a term that contains several factors, e.g., wet and dry seasons, temperature regime, the concentration of dissolved oxygen in the sediments, redox potentials, bacterial activity, etc. Total concentration and geospeciation of trace elements in surface sediments can be significantly affected due to changes from dry to wet seasons, resulting in relevant increases in inputs (i.e., from the drainage basin) towards the sediments. Changes in temperature from a cold season to a warm season can also influence the load of organic matter present in the water column, which then settles in the sediments; these changes can substantially affect the activity of detritivores. Besides, all these factors can influence the redox potential, the concentration of dissolved oxygen, and the equilibrium sulfate-sulfide. All factors related to seasonality can therefore result in enrichment in surface sediments.

In this study, 1m cores were collected, and the sediments were homogenized precisely to mimic what happens during an excavation. Consequently, the total concentration value observed in the cold and warm seasons is mediated. However, anything that influences the surface sediment could increase the mediated concentration due to the complete homogenization of the entire 1 m core sampled.

Sediments sampled in the cold season fell in Class A. In the warmer season (II sampling campaign), an increase in all total concentrations is observed, such that the sediments at some sites belong to class B and do not comply with the values of class A anymore.

Regarding geospeciation, an increase in bioaccessible and mobile phases is observed for all elements in the second campaign. In particular, although the sediments of site VI always meet the class A values and the EQSs, the sum of bioaccessible and mobile fractions is still relevant for all elements studied. As for the first bioaccessible fraction, it is generally considered primarily anthropogenic; however, given seasonal changes, the II and III fractions of the trace elements present in the drainage basin can mobilize and become bioaccessible, resulting in an increase of the I fraction in the lagoon sediments. Hence, the first bioaccessible fraction and the two mobile fractions can rise, and the total concentration of trace elements can increase as a result.

The results of this study corroborate the relevance of geospeciation as it provides a more accurate and trustworthy estimate of the actual threat posed by trace elements in sediments than a simple comparison between total concentrations and threshold limits. Therefore, it would be worth considering the employment of a more comprehensive approach, e.g., the TRIAD approach, in assessing the quality of sediments and the hazard they can represent, especially for their proper management and handling.

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