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Metals and PAHs in surface sediment and biological effects on the amphipod *Corophium orientale* and on embryos of the oyster *Crassostrea gigas*

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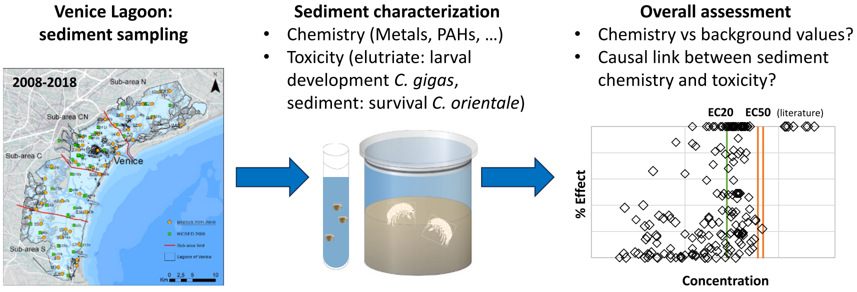
HIGHLIGHTS

- Analysis of causal links between toxicity and sediment chemistry in the Venice lagoon
- No relevant toxicity observed on the amphipod *C. orientale* exposed to whole sediment
- Elutriates determine embryotoxicity on *C. gigas*, likely due to high ammonia level

GRAPHICAL ABSTRACT



Venice Lagoon: sediment sampling

Sediment characterization
- Chemistry (Metals, PAHs, ...)
- Toxicity (elutriate: larval development *C. gigas*, sediment: survival *C. orientale*)

Overall assessment
- Chemistry vs background values?
- Causal link between sediment chemistry and toxicity?

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ABSTRACT

Surface sediments of the Venice lagoon were monitored in 2008 and 2011-2018 to evaluate sediment chemistry (with focus on metals and PAHs) and their toxicity on target organisms. The large dataset resulting from these investigations is evaluated in this study with respect to spatial distribution and background concentrations, chemical patterns and relationships of investigated chemicals with biological effects observed on the amphipod Corophium orientale (exposed to sediments), and on embryos of the oyster Crassostrea gigas (exposed to elutriates). The evaluation is performed considering mechanistic sediment quality guidelines and, for elutriate, toxicity data available in scientific literature (EC50, Effective Concentrations derived single substance laboratory test).

Although exceedance of the background concentrations defined in previous studies were observed for Zn, Cu, Pb, Cd and Hg (but not for As, Cr and Ni), tested sediments generally do not display relevant toxicity to C. orientale, whilst elutriates prepared from surface sediments can determine toxic effects on C. gigas, most likely due to the high level of ammonia. The concentrations of metals in elutriates generally appear lower than the EC50 reported in literature but their influence on C. gigas toxicity cannot be totally excluded. PAHs, evaluated on

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the basis of the TU approach, are not a stressor of main concern in the surface sediments investigated in the surveys. The results can support further evaluations aimed at sediment management actions in the Venice lagoon, as well as sediment assessment in other areas characterized by similar conditions.

1. Introduction

Over the years, several studies investigated sediments of the Venice lagoon, with the aim of assessing sediment quality and chemical contamination patterns, as well as sediment toxicity, grain size distribution, accumulation rates and erosional/depositional processes (e.g., Apitz et al., 2007, 2009; Losso and Ghirardini, 2010; Picone et al., 2018; Zonta et al., 2018). In recent years, the Minister of Infrastructure and Transport (Ministero delle Infrastrutture e dei Trasporti – Provveditorato Interregionale per le Opere Pubbliche del Veneto – Trentino Alto Adige – Friuli Venezia Giulia, formerly known as Magistrato alle Acque di Venezia, until 2014) promoted and funded whole-lagoon scale projects (HICSED survey, performed in 2008, and MODUS surveys performed in 2011–2016 and 2018), executed through its concessionaire Consorzio Venezia Nuova, with the aim of evaluating the sediment quality under the context of the monitoring activities related to the Water Framework Directive (Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy).

In these projects, sediments were investigated both for chemistry (with focus on metals and PAHs, that were always detected and relevant in terms of concentrations) and toxicity; to our best knowledge, the reported data set is the first to document spatial and time distribution of the priority organic pollutants included in the WFD and recorded in the entire lagoon of Venice. The overall results represent a valuable dataset and are discussed in this study to investigate relationships and causal link between exposure to metals and PAHs and observed effects.

Specifically, in this study chemical concentrations are first discussed in comparison with background concentrations determined in previous studies for the Venice lagoon (Apitz et al., 2009; Marchese et al., 2022), in order to identify the most relevant contaminants and to verify chemical patterns in surface sediments. As second step, chemical and toxicity data from the HICSED and MODUS projects are evaluated jointly; among available data, results of toxicity tests performed on the endemic Mediterranean amphipod *Corophium orientale* (exposed to whole sediment) and on embryos of the oyster *Crassostrea gigas* (exposed to elutriates) represent the most consistent dataset and were selected for this study as biological indicators for the evaluation of bedded and resuspended sediments. Under this context, the overall results are discussed to provide first insight on the causal link between chemical concentrations and observed effects. In this sense, sediment data are here discussed on the basis of mechanistic sediment quality guidelines (Burgess et al., 2013; McGrath et al., 2019) and not on the mere comparison of sediment concentration with empirically based sediment guidelines (such as Effect Range Low – ERL, Effect Range Median - ERM, Threshold Effect Level – TEL, Probable Effect Level - PEL), known to be useful for conservative screening but not based on a measured relationship between exposure and toxicity (Burgess et al., 2013, Burton Jr, 2002, Chapman and Mann, 1999, Conder et al., 2015, Fuchsman et al., 2023, McGrath et al., 2019, Wenning, 2005). Specifically, mechanistic sediment quality guidelines consider aqueous toxicity of chemicals to different biota coupled with site specific sediment characteristics (specifically, Total Organic Carbon, TOC, for non ionic organic chemicals and Acid Volatile Sulfide, AVS, for metals) known to influence bioavailability; the approach is based not on correlation, but rather on strong theoretical foundations and can therefore support the identification of sediment toxicity drivers (Burgess et al., 2023, Chapman and Mann, 1999, Di Toro et al., 1991, McGrath et al., 2019). In this sense, since sediment investigations in Italy are generally based on the use of empirically based sediment guidelines (Bizzotto et al., 2023), the approach adopted in this work is useful to provide a different perspective to better address and inform sediment assessment as well as to support future research aimed to optimize sediment management in the Venice lagoon.

Additionally, the discussion of chemical concentrations in elutriates represents an original element for a proper evaluation of the observed toxicity. Toxicity tests on elutriate have been extensively used to study sediment quality of the Venice lagoon (Losso and Ghirardini, 2010) and several studies investigated the contributions of ammonia, sulfides and sediment particles in elutriate toxicity (Batley and Simpson, 2009, Carr and Chapman, 1995, Kennedy et al., 2015, Losso et al., 2007a, 2007b, Sartori et al., 2024, USEPA, 1993, van den Hurk, 1994); however, metals in elutriate are not routinely investigated and, to the best of our knowledge, this study represents therefore an important contribution to support the overall evaluation of the Venice lagoon sediment quality, being relevant to both the scientific community and the stakeholders and regulators of coastal aquatic environments. In summary, this study aims to investigate the distribution of metals and PAHs in surface sediments of the Venice lagoon and to assess the sediment toxicity considering two different environmental matrices (whole sediment and elutriate, considered as proxy of resuspended sediment). Mechanistic sediment quality guidelines and, for elutriate, toxicity data available in scientific literature (i.e., effective concentration 50 (EC50) derived from water-only exposure to single contaminants) are considered for the evaluation. The results of this study, in addition to providing specific knowledge and preliminary insights for the evaluation of the causal link between sediment chemistry and observed toxicity for the Venice lagoon, provide useful information also for sediment assessment in other transitional environments characterized by similar conditions.

2. Dataset and methods

2.1. Study area

The Venice lagoon is a coastal transitional environment with a surface of about 549 km^2 located in North-Eastern Italy. In this area, estuarine and marine environments, pristine salt marshes and shallows coexist with reconstructed marshes, reclaimed land, and human environments such as the city of Venice and the Porto Marghera industrial district. The lagoon is connected to the Adriatic Sea by 3 sea inlets that allow for the exchange of about 60 % of the water in any 12-h cycle. Twelve main tributaries drain the catchment, providing a mean freshwater discharge of about $\sim 1{,}1 \times 10^9$ m^3/yr to the lagoon (Zuliani et al., 2005). The associated annual sediment input was calculated at 33–35 × 10^3 tons/yr (Collavini et al., 2005; Molinaroli et al., 2009). Sedimentation and resuspension are very intense in the lagoon (settling rate up to 1,0 cm/yr) because about 72 % of the lagoon is shallow water with a depth range between 0,7–1,5 m (Carniello et al., 2016; D'Alpaos et al., 2013; Ghinassi et al., 2019; Madricardo et al., 2017; Molinaroli et al., 2009). Hydrologically the lagoon can be divided into four sub-areas (Fig. 1) (Molinaroli et al., 2009; Solidoro et al., 2004; Tagliapietra and Ghirardini, 2006): the northern (N) sub-area (Treporti, total area 88km^2), the central-northern (CN) sub-area (Lido, total area 86 km^2), the central (C) sub-area (Malamocco, total area 121 km^2) and the southern (S) sub-area (Chioggia, total area 111 km^2). Point and nonpoint sources of pollution flowing into the lagoon include industrial waste from the area of Porto Marghera, municipal wastewater from the Venice municipal area, streams inputs from the drainage basin, agricultural runoff, boat traffic, atmospheric deposition, increased harbour activities, growing fishing and aquaculture, and unprecedented levels of tourism (Zonta et al., 2018).

Most of the sediment sampled in the lagoon have silty grain size (average silt content of 72 %), while the sandy fraction is, in most samples, 25 % of the total and the clay fraction varies between 0.02 % and 3.6 %. Historically, the granulometry of the lagoon sediments showed a decrease in the fine fraction (< 22 μm) in all the lagoon sub-areas between the 1970s and 2000 (Molinaroli et al., 2009; Zonta et al., 2018), with the exception of the northern part of the lagoon, characterized instead by a slight increase of the clay fraction. Consequently, a general increase in the sand content in the sediments of the central and southern lagoon was observed. Sfriso et al. (2005) shows that the decrease of the pelitic fraction in the central lagoon was related to the fishing effort exerted on the *Tapes* in that area. Zonta et al. (2018) reported a strong depletion of fine particles (<31 mm in diameter) in sediments down to 10 cm depth in comparison to deeper layers.

2.2. Sampling campaigns and dataset

The dataset considered for this study includes sediment data detailed in the final reports of HICSED and MODUS projects (data source detailed in SM). The HICSED sampling campaign was conducted in 2008 (Picone et al., 2018) investigating 48 sites, while the MODUS sampling campaigns were performed on an annual basis in 2011–2016 and in 2018 (on 30–48 sampling sites, depending on the year) under the context of the monitoring activities related to the Water Framework Directive. Sampling sites are reported in Fig. 1.

Both these whole-lagoon scale projects were promoted and funded by the Minister of Infrastructure and Transport through its concessionaire Consorzio Venezia Nuova, with the aim to monitor and study sediment chemistry and toxicity.

The dataset evaluated in this study includes >300 sediment samples collected for chemical analysis; sediments were tested for both chemistry and toxicity. Specifically, most of the sediment samples (93 %) were tested on *C. orientale*; a subset of sediment samples (55 %) was also used to test elutriates with *C. gigas* (further details in Section 2.3).

Only surficial sediments (top 15–20 cm in the HICSED sampling campaign and 5 cm in the MODUS sampling campaigns) were investigated for chemistry and toxicity; therefore, the HICSED data are likely to represent sediment older than the ones studied in the MODUS campaigns.

Sediments were analyzed for metals (As, Cd, Cr, Cu, Hg, Ni, Pb, Zn, whose concentrations were expressed on a dry weight basis, mg/kg dw, and also as Simultaneously Extracted Metals, SEM, representing the bioavailable and mobile fractions), Acid Volatile Sulfides (AVS), PAHs, TBT, pesticides (DDx, Andrin, Dieldrin, HCHs and HCB); total PCB and PCDD/F were analyzed only on a subset of sediment samples. Within the MODUS project, chemical analyses were performed also on elutriates to determine metals (As, Cd, Cr, Cu, Hg, Ni, Pb, Zn), total ammonia nitrogen, and sulfide.

The present study focuses on the evaluation of metals and PAHs, since within the MODUS campaigns TBT and pesticides were generally not detected (detection limit: 0.65 μg/kg for TBT and 0.025 μg/kg for

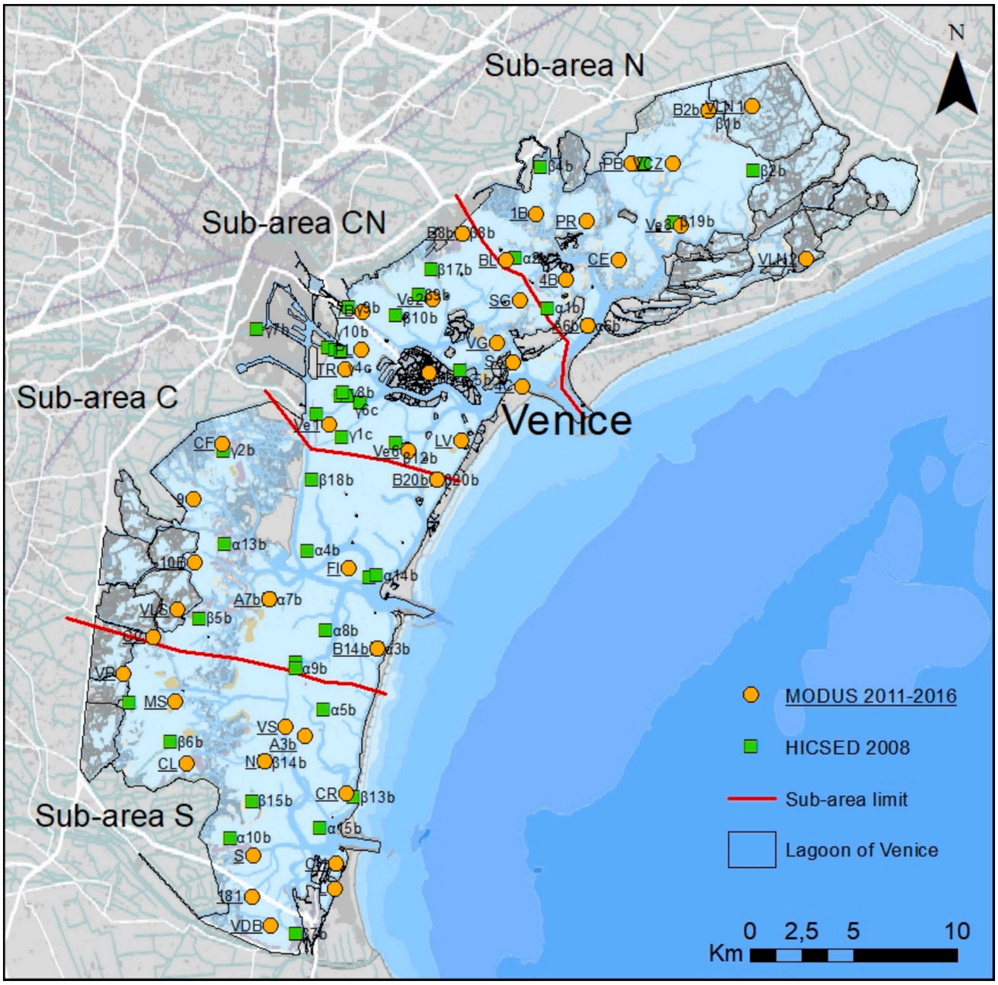

Fig. 1. Sediment sites sampled during the HICSED and MODUS campaigns. The figure shows also the subdivision of the Venice lagoon in the sub-areas North (N), Central-North (CN), Central (C), and South (S).

pesticides) or sporadically detected in few samples at very low concentrations. Similarly, data on total PCB and PCDD/F were not evaluated in this study due to the limited available dataset. Detection limits and methods used for chemical analyses on sediments and elutriates are reported in Table 1-SM.

2.3. Sediment chemistry assessment

To support the evaluation of chemical contaminants measured in sediments, in this study metals and PAHs concentrations were evaluated according to the USEPA EqP-procedure (Burgess et al., 2013; USEPA, 2003, 2005) and considering site specific sediment characteristics contributing to control chemical bioavailability. Sulfides represent the phase that relates most directly to the bioavailable fraction of divalent metals (Cd, Cu, Pb, Ni, Zn): specifically, in the SEM-AVS model, the sediment Acid Volatile Sulfide (AVS) is considered the principal binding phase in reduced sediments. Cationic metals released from the sediment during the extraction and measurement of the AVS are called Simultaneously Extracted Metal (SEM); in the presence of excess AVS, cationic metals will form non-bioavailable (and insoluble) metal sulfides rather than partition into the dissolved phase in the interstitial waters (and becoming bioavailable and potentially toxic to sediment organisms) (Burgess et al., 2013; USEPA, 2005). Thus, metals in sediment are predicted as not toxic when the molar concentration of AVS is higher than that of SEM. Under this contest, since the existing dataset includes both SEM and AVS concentrations, the ratio $\sum$SEM/AVS was calculated for each sediment sample.

PAHs measured in sediments were used to estimate PAH Toxic Unit, adapting the USEPA (2003) methodology to the existing dataset. First, the dry weight concentrations for each PAH were converted to μg PAH/g organic carbon (COC, μg/gOC) by dividing by the fraction of organic carbon (= %TOC/100) measured in each sediment sample; since the MODUS analytical profile evaluated a lower number of PAHs than the HICSED project, we used the HICSED data to estimate concentration of benzo,a,anthracene, chrysene, phenanthrene, fluorene and pyrene (not investigated in MODUS), being the ratio of these single PAHs relatively constant with respect to the sum of the other PAHs concentrations.

Second, the organic carbon normalized PAHs concentrations in the sediment were divided by the PAH-specific sediment concentration of concern (as defined in USEPA, 2003 to protect benthic organisms), to derive the toxic unit (TU) for each individual PAH; the values were then added and extrapolated using the uncertainty factor reported in USEPA, 2003 (confidence level of 95 %) to estimate the TU for the complete PAHs mixtures (including unmeasured PAHs). A PAH TU value or a $\sum$SEM/AVS ratio greater than one suggests the potential for adverse effects from PAHs or from divalent metals, while values lower than one indicate that these chemicals are likely not the main toxicity driver.

2.4. Toxicity testing

Toxicity data about *C. gigas* and *C. orientale* represent the most consistent available dataset; these species were then selected as biological indicators for the evaluation of resuspended and bedded sediments of the Venice lagoon. Both species are relevant components of the Venice Lagoon benthic communities (Sconfietti et al., 2003; Tagliapietra et al., 1998). Furthermore, tests with *C. orientale* and *C. gigas* were already evaluated for their application and discriminating ability towards sediments of the Venice Lagoon (Losso et al., 2007a, 2007b; Picone et al., 2016) and included in the list of the preferred test methods for assessing the toxicity of dredged sediments according to the Italian Law.

Regarding the Pacific oyster *C. gigas*, for the present study we considered the toxicity tests performed on elutriate prepared from field collected sediments (HICSED and MODUS project).

Specifically, in the period 2013–2016 the embryotoxicity tests on *C. gigas* were performed on aqueous phase (elutriate) prepared from field collected sediment, diluting the sediment samples with artificial seawater at a sample dilution of 1:4 (sediment:water) and then stirring the sediment–water mixture for a prolonged period. Specifically, in the MODUS project elutriates were prepared according to the procedure set by ISPRA (and recently described in ISPRA, 2021). The mixture was let to settle and then centrifuged to separate the supernatant. Elutriate toxicity was then investigated with the protocol ASTM E724 (1998), evaluating effects on the larval development of *C. gigas* after a 48 h-exposure; testing conditions were characterized by pH in the range 7.3–8.4 and salinity in the range 28–31 ‰ (MODUS project). Toxicity test on *C. gigas* exposed to elutriate can be useful to study water column impact during scenarios characterized by a relevant presence of resuspended sediments within the water column (e.g., as in the case of dredging activities and of sediment disposal in open-water, as well as during flood events and for sediment resuspension by boat and ship traffic in shallow areas) (Haring et al., 2010; Kennedy et al., 2015; USEPA USACE, 1998), although the realism and usefulness of elutriate testing has been questioned and discussed elsewhere (Anderson et al., 2004; Chapman et al., 2002; Lotufo et al., 2014; Word et al., 2005).

Toxicity testing on the autochthonous Mediterranean amphipod *C. orientale* was carried out exposing organisms to whole sediment, following the ISO 16712 (2005) protocol (further details in Picone et al., 2018, 2008). The test evaluates a 10-day exposure under controlled lab conditions, after which mortality is determined. The toxicity tests on *C. orientale* allow to evaluate potential impacts posed by contaminants in bedded sediments; moreover, whole-sediment exposure is considered a more realistic testing alternative than aqueous phase (Ireland and Ho, 2005; Lotufo et al., 2014).

For both the tested species, QA/QC control included negative control and reference toxicant testing, with respect of the acceptability criteria defined by the protocol and the intra-laboratory control chart and literature data. Reported results were corrected for effects in the negative control by applying Abbott's correction.

2.5. PCA and spatial interpolation

In this study, a Principal Component Analysis (PCA) was first conducted to identify the elements that most affect the spatial distribution of investigated chemicals. PCA examines the set of continuous attribute variables (e.g., chemical concentration, SEM/AVS index, TOC%) measured at the sampling sites in the lagoon. This statistical analysis was performed using the R-Studio software (https://www.rstudio.com/), an open-source environment for R statistical language (https://www.r-project.org/). The PCA was performed only on the MODUS dataset, considered more representative of the chemical status of the lagoon sediments today.

The PCA considers chemistry data grouped in the sub-areas North (N), Central-North (CN), Central (C), and South (S). Together with the PCA, the correlation between the considered variables was carried out and only the correlations with $p < 0.01$ were retained.

Geographical maps were created for the most influential variables by interpolation of the concentrations at each sampling site for a specific contaminant. The maps were obtained through the “Inverse Distance Weighted” (IDW) methodology using the ESRI Arcmap 10.4 GIS software. IDW interpolation explicitly assumes that things that are close to one another are more alike than those that are farther apart. To predict a value for any unmeasured location, IDW uses the measured values surrounding the prediction location. The measured values closest to the prediction location have more influence on the predicted value than those farther away. IDW assumes that each measured point has a local influence that diminishes with distance.

3. Results and discussions

Sediment concentrations are discussed in Section 3.1 considering the observed chemical range in comparison with metal background concentrations and, for PAHs, protective screening benchmarks, and evaluating spatial distribution and chemical patterns. In Section 3.2, relationships of sediment chemistry with observed toxicity are discussed considering also mechanistic sediment quality guidelines.

3.1. Metals and PAHs concentrations in surface sediment of the Venice lagoon and comparison with background concentrations

The descriptive statistics of chemical concentrations in surface sediments are presented in Table 1 (mean, standard deviation, minimum and maximum); detailed information concentrations observed in the different sampling campaigns are reported in Table 2-SM.

A first evaluation of the sediment quality can be made by comparing metals concentrations observed in the Venice lagoon with the background concentrations determined by Marchese et al. (2022) and Apitz et al. (2009) (Fig. 2). This comparison is useful as preliminary assessment, since it is generally accepted that metal background concentrations are protective (and not predictive) towards biological effects or toxicity (Chapman and Wang, 2001; EC, 2011; MacDonald et al., 1996). For PAHs, in absence of a reliable background concentration and to allow a preliminary evaluation, a first comparison was performed considering the range of protective Sediment Quality Guidelines reported in McGrath et al. (2019), defined as concentrations below which adverse effects are unlikely. These SQGs represent empirically derived values and are useful only for preliminary screening due to their conservative nature (McGrath et al., 2019).

With regard to metals, the background concentrations proposed by Marchese et al. (2022) have been derived from a critical review of literature data based on radio-dated sediment cores and represent the upper bound of the pre-industrial (i.e. pre-1910) background range. The proposed values are the following (mg/kg d.w.): As 15.9; Cd 0.6; Cr 38; Cu 18.1; Hg 1.1; Ni 32.9; Pb 29.4; Zn 94.5. Authors concluded that the pre-industrial concentration (named 2σ-pIC) are in good agreement with previous studies that investigated the background values of metals in sediment of the Venice lagoon, with the exception of Hg whose 2σ-pIC value was probably influenced by limitations and uncertainties in the dataset and adopted method.

As further reference, Apitz et al. (2009) studied sediments of the Venice lagoon and applied a statistical method to separate background concentrations (expressed as a range of values) from anthropic concentrations using a dataset of sediment core distributed over the entire lagoon. For comparison, the values proposed by Apitz et al. (2009) are the following (mg/kg d.w.): As 5–35; Cd 0,1-1,2; Cr 4–80; Cu 5–40; Hg 0,2-0,3; Ni 5–45; Pb 5–50; Zn 40–130.

As shown in Fig. 2, the concentration of As, Ni and Cr measured in surface sediments sampled in 2008–2018 were generally in the same range of the background concentrations available for the Venice lagoon, indicating absence of relevant input and of enrichment process for these metals in the sampled sediments. Instead, concentrations of Hg, Pb, Cd, Cu and Zn showed exceedance of the background concentrations defined by Marchese et al. (2022) and Apitz et al. (2009); higher values were mainly observed in the sub-areas CN and C, near the coast and the industrial site of Porto Marghera. Exceedance of the metal background concentrations were observed also in few sites located in the northern part (Pb) and in the southern part of the lagoon (mainly Cu and Zn).

With special regard to Hg, most of the sediment (60 %) exceeded the background range (0.2–0.3 mg/kg dw) identified by Apitz et al. (2009), suggesting a diffuse presence in the lagoon; in few sites Hg values were also higher than the 2σ-BC defined by Marchese et al. (2022), that represents the upper bound of the pre-industrial background range. With regard to PAHs, the 60 % and 35 % of sediments were respectively lower or in the range of protective Sediment Quality Guidelines reported for PAHs in McGrath et al. (2019), suggesting a diffuse but not relevant presence of PAHs in the investigated area (Fig. 2). Exceedances of the protective SQGs were observed only in two sites in the HICSED campaign, while in the MODUS campaigns the highest PAHs concentrations were consistently detected, among years, in the historical center of Venice, probably due to the intense boat traffic. Further exceedances of the SQGs were sporadically detected in two sites in the sub-areas CN and N and in the southern part of the lagoon. Overall results are consistent with distribution patterns observed in previous studies conducted in the Venice lagoon (further details in supplementary material, Fig. 1-SM and 2-SM). Specifically, Zonta et al. (2018) and Apitz et al. (2007) indicated that Cr and Ni can be considered as prevalently lithogenic elements, as well as As, although for this metalloid the existence of anthropic sources in both the drainage basin and industrial zones should be considered (Apitz et al., 2007; Zonta et al., 2005, 2018). The same authors indicated that Cu, Hg, Pb, Cd and Zn can be considered mostly of anthropic origin; shallow waters on the landward side (particularly close to freshwater inputs), the area nearby the industrial district of Porto Marghera and a small zone adjacent to the city of Chioggia were identified as the main pollutant accumulation sites.

The spatial distribution was confirmed also by a PCA that was applied to recognize distinct groups of variables and to highlight relationship between chemical variables (Fig. 3).

The PCA was applied only to the samples from the MODUS sampling campaigns, considered more representative of the chemical status of the lagoon sediments today, since the MODUS sampling campaigns specifically investigated only the first 5 cm of surface sediments. Moreover, a deep analysis of the HICSED dataset has been recently published by Picone et al., 2018, which is in good agreement with the following results.

Table 1
Mean values and concentration range observed in sediments sampled in 2008–2018 in the Venice lagoon. Data are grouped in the sub-areas North (N), Central-North (CN), Central (C), and South (S); in parenthesis, the number of samples. Metals values are expressed in mg/kg d.w., PAHs in μg/kg d.w.

Sub-area		As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	PAHs
N (79)	Mean	8	0.2	22	20	0.5	15	19	63	306
	Dev st	3	0.1	10	6	0.2	4	11	15	832
	Min	3	0.1	7	5	0.0	4	6	15	6
	Max	17	0.6	61	36	1.0	29	57	115	7060
CN (112)	Mean	9	0.7	20	37	0.9	14	27	170	4476
	Dev st	6	1.1	13	41	0.8	5	22	258	18,377
	Min	3	0.0	5	3	0.1	4	4	25	6
	Max	38	7.6	81	194	7.3	38	143	1921	119,482
C (66)	Mean	11	0.4	28	23	0.3	19	20	109	214
	Dev st	5	0.4	15	12	0.2	7	10	66	197
	Min	4	0.0	7	5	0.0	6	5	24	6
	Max	30	2.0	84	59	1.0	39	44	275	947
S (78)	Mean	12	0.3	34	28	0.2	23	21	94	642
	Dev st	6	0.2	17	23	0.1	7	11	41	1103
	Min	3	0.0	6	3	0.0	5	3	26	6
	Max	38	0.9	99	122	0.5	50	60	209	6021

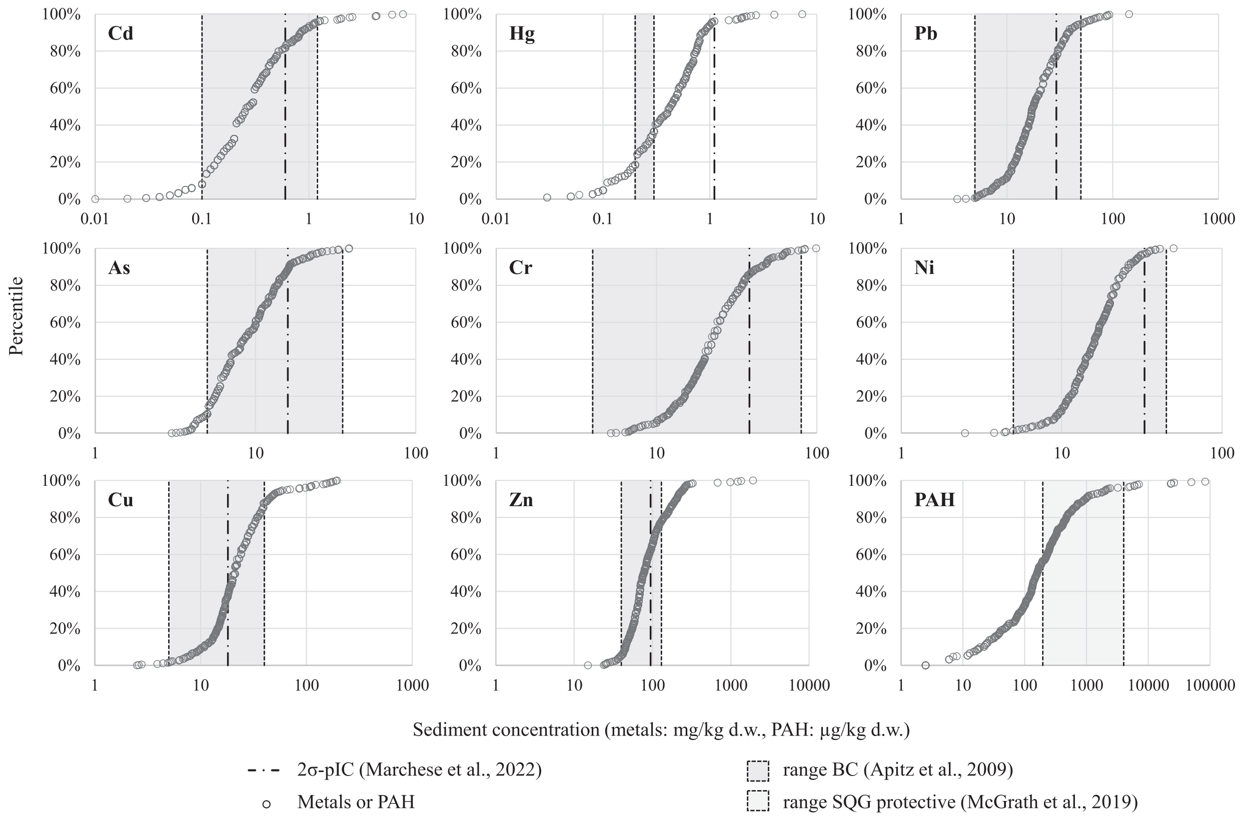

Fig. 2. Distribution of metals concentrations observed in surface sediment of the Venice lagoon in comparison with metals background concentrations determined for the lagoon by Marchese et al., 2022 (pre-industrial concentration, 2σ-pIC) and Apitz et al. (2009) (range of background concentration, BC). For PAHs, the graph indicates a range of protective Sediment Quality Guidelines (SQG, 197–4022 µg/kg d.w.), as reported in McGrath et al. (2019).

The first two principal components (PCs) explained ~65 % of the total variance of the data (Fig. 3). The most significant parameters (i.e., the parameters with the highest factor loadings) of these two PCs are Anthracene, Hg, Pb, Zn and Cr (and Cr VI). Another important result from the application of PCA is the scattergram of "factor scores" for each sampling locations. All samples, except those of the sampling station "A", tend to scatter around the center of the Cartesian plane. Results show that there is a clear division and grouping of the points included in the four sub-areas. Almost all the samples from the sub-area CN are horizontally distributed along the PC1 line (influenced by metals of anthropic origin), in the quadrant Q3 and Q4. A group alone is composed by the "A" samples, located in the Venice historical center. The samples from sub-area N are mainly concentrated in Q3, while samples from sub-areas S and C are mainly distributed in Q2 and Q1.

An increase of the second PC is associated with an increase of the Cr concentrations (element considered of lithogenic origin in the Venice lagoon). A decrease in the first PC is associated with an increase of Pb and Zn concentrations. A decrease in both first and second PCs is associated with an increase in Hg and Anthracene concentrations.

3.2. *Toxicity observed on C. orientale and C. gigas*

The overall toxicity test results are summarized in Table 2; to illustrate distribution and intensity of the observed effects on *C. orientale* and *C. gigas*, results are grouped in four classes, ranging from negligible toxicity (<20 %) to high toxicity (effects ≥50 %) (Chapman, 2016; Thursby et al., 1997).

Within the HICSED campaign, results indicated acute toxicity towards the amphipod *C. orientale* only in few sites, located close to the industrial area and in northern part of the lagoon; specifically, sediment displayed a high toxicity (observed mortality >50 %) in 2 sites, while among the other tested sediments only 3 samples indicated a moderate toxicity (observed mortality 26–31 %).

Similarly, the MODUS dataset displayed relevant toxicity (mortality >50 %) on *C. orientale* only in one site in 2011 and 2018, while in 2012 an increased sediment toxicity was observed (12 samples displayed a mortality on *C. orientale* in the range 50–80 %, Table 2). Sediments sampled in 2013–2018 at the same sites did not display significant toxicity on *C. orientale*.

Regarding *C. gigas*, toxicity tests were done by exposing the tested organisms to elutriate, evaluating effects on larval development. Within the HICSED project (2008), most of the elutriate samples (81 %) did not determine a relevant toxic effect (>50 %) on *C. giga*. Regarding data collected within the MODUS project, a certain variability was observed between toxicity test performed at the same sites in different years, with an increase of diffuse toxicity for *C. gigas* in 2016 with respect to 2013 data (Table 2); most of the samples displayed a toxic effect on at least 50 % of tested organisms (58 samples on a total of 186 elutriates tested on *C. gigas* in 2013–2016).

Overall results suggest therefore that most of the lagoon surficial sediment is not toxic towards *C. orientale* in the short-term, whilst elutriates can determine toxic effects; toxicity test results were then evaluated considering the chemical concentrations measured in sediments and in elutriates (to support the interpretation of bioassays on *C. gigas*).

3.2.1. *Toxicity vs metals and PAHs concentration in sediments*

The toxicity observed on *C. orientale* and *C. gigas* is not correlated to metals concentrations measured in bulk sediments (considering a *p* value<0.01), indicating that metal concentrations expressed on a dry weight basis (mg/kg d.w.) are not a good metric to assess toxicity. The lack of a specific relationship between metals and observed toxicity was determined both for divalent metals (Cd, Cu, Ni, Pb, Zn), which can be better assessed by the approach SEM/AVS, and for metals that cannot be fully assessed by the SEM/AVS approach (As, Hg, Cr, Fig. 3-SM) (USEPA,

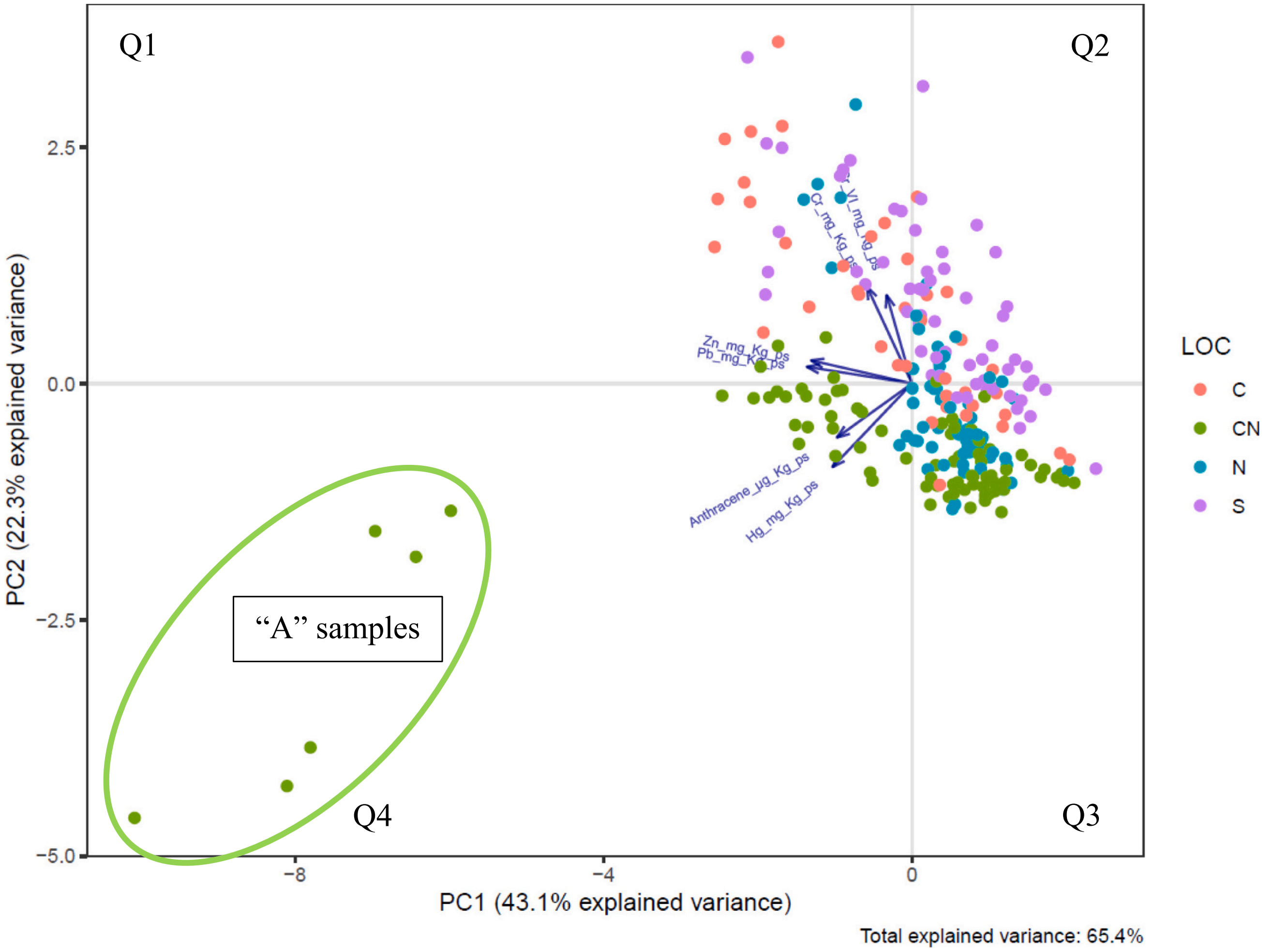

Fig. 3. PCA performed considering sediments (MODUS survey, 0–5 cm sediment depth) in different sub-areas of the Venice lagoon.

Table 2

Distribution (% samples) of the toxicity test results among different toxicity classes (effect% <20, 20–50, 50–80, >80) in the HICSED and MODUS campaigns.

		Toxicity observed on *C. orientale* (10-d sediment exposure, effect on survival)				Toxicity observed on *C. gigas* (48-h elutriate exposure, effect on larval development)			
Toxic effect		<20 %	20–50 %	50–80 %	>80 %	<20 %	20–50 %	50–80 %	>80 %
Hicsed 2008	*n* = 48	90 %	6 %	4 %		56 %	25 %	2 %	17 %
Modus 2011	n = 48	73 %	25 %		2 %				
2012	*n* = 36	53 %	14 %	33 %					
2013	*n* = 37/42°	92 %	8 %			76 %	10 %	5 %	10 %
2014	*n* = 42	95 %	5 %			21 %	31 %	12 %	36 %
2015	*n* = 24	92 %	8 %			17 %	42 %	17 %	25 %
2016	*n* = 30	90 %	10 %			17 %	10 %		73 %
2018	n = 48	88 %	10 %	2 %					

n = number of tested samples.

°: in 2013, embryotoxicity tests on *C. gigas* were performed on 37 samples of elutriates, while tests with *C. orientale* were performed on 42 sediment samples.

2005).

The SEM/AVS ratio was therefore analyzed to better evaluate the potentially bioavailable fraction of Cd, Cu, Ni, Pb, Zn and its influence on tested organisms (Fig. 4).

Metals in sediment are predicted as not toxic when the molar concentration of AVS is higher than that of SEM; however, it is generally recognized that the SEM/AVS concept does reasonably well in predicting the absence of toxicity ($\sum$SEM/AVS <1) but is less useful to predict metal related toxicity ($\sum$SEM/AVS > 1) (Burgess et al., 2013; USEPA, 2005).

As first observation, it must be noted that $\sum$SEM/AVS ratio indicates a low bioavailability of divalent metals in sediments of the Venice lagoon, since most (i.e., 73 %) of the sediments were characterized by values <1 (Fig. 4). The highest values of the $\sum$SEM/AVS ratio were observed in 2016, due to very low levels of AVS measured in that year; in this context, further research is recommended to investigate seasonal variations of AVS concentration in the Venice lagoon since they may change the potential toxicity of metals in sediments.

With regard to biological effects, the overall results suggest that the model $\sum$SEM/AVS (Fig. 4), when applied to sediment in Venice lagoon, works better for *C. gigas* (although exposed to elutriate prepared from sediments, thus under conditions that not necessarily run counter to the

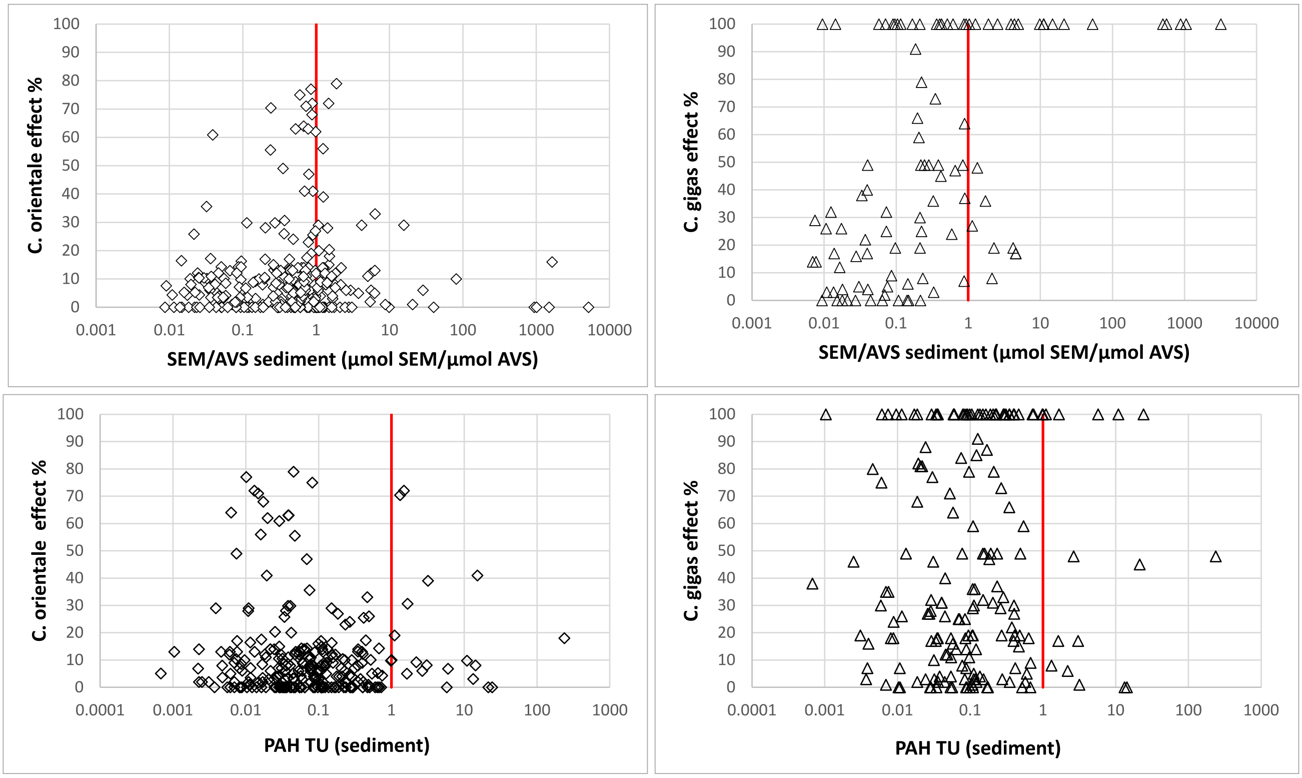

Fig. 4. Toxicity observed on *C. orientale* and *C. gigas* plotted against SEM/AVS and PAH TU values measured in sediments. If a sediment shows toxicity but has SEM/AVS or PAH TU values<1, it is likely that the cause of toxicity is a different chemical or group of chemicals. In other instances, it may be that a SEM/AVS or PAH TU value is >1, but the sediment is not toxic for that species under that test protocol, since the approach is protective of most species and the level of protection applies to both acute and chronic effects. It is also possible for a sediment with SEM/AVS or PAH TU >1 to be non-toxic if there are site-specific partitioning conditions that run counter to the equilibrium partitioning model and its assumptions (USEPA, 2003, 2005).

equilibrium partitioning model and its assumptions) than for *C. orientale* (exposed to bulk sediment).

Specifically, the $\sum$SEM/AVS ratio measured in tested sediment does not appear to influence the low-moderate toxicity observed on the tested amphipod *C. orientale*; among sediment sites characterized by the presence of potentially bioavailable fraction of Cd, Cu, Ni, Pb, Zn ($\sum$SEM/AVS > 1), only the 13 % displayed some toxic effects (mortality >20 %) to *C. orientale*, while most of the sediments toxic for *C. orientale* was characterized by $\sum$SEM/AVS < 1. These results suggest therefore that metals were not the main driver of the low-moderate toxicity observed on *C. orientale* (Fig. 4). Instead, the $\sum$SEM/AVS ratio seems to work better as toxicity predictor for *C. gigas*, since toxic effects on *C. gigas* were observed in 63 % of samples with $\sum$SEM/AVS > 1 and *C. gigas* embryotoxicity appears weakly correlated (Pearson's correlation $= 0.19$, $p < 0.01$) to the $\sum$SEM/AVS (Fig. 4). However, the overall results indicated also the presence of other factors influencing the biological effects on *C. gigas*, since relevant toxicity was observed also in samples characterized by $\sum$SEM/AVS < 1.

Further evaluations can be done considering PAHs, although the PAH Toxic Unit (TU) values are to be considered a preliminary estimate (due to extrapolation methods adopted to fill data gaps). Results indicate that PAHs in surface sediments are likely not of relevant concern for benthic invertebrates (Fig. 4), since the estimated PAH TU values appear to be >1 in few sites and do not appear to determine a significant effect on *C. orientale* neither on *C. gigas*. The PAH TU approach is protective of most species and the level of protection applies to both acute and chronic effects (McGrath et al., 2019).

Therefore, the application of SEM/AVS and PAH TU approach for the evaluation of sediment of the Venice lagoon indicates that the mechanistic sediment quality guidelines can be considered protective. The tests performed on elutriates indicate the presence of some effects on *C. gigas* but these effects are likely not due to PAHs exposure and could be partially related to metals; in this sense, the evaluation of chemical analyses on elutriates provide a valuable tool for a better understanding of the observed toxicity (see Section 3.2.2). Additionally, most of the sediment in the lagoon is not toxic to *C. orientale*, whose tested endpoint (acute mortality) appears to be less sensitive than other bioassays commonly used for ecotoxicological surveys (Losso and Ghirardini, 2010; Picone et al., 2008). The low sensitivity of *C. orientale* to the sediment of the Lagoon was previously observed and related to the lower sensitivity of the *Corophium* genus compared to other amphipods commonly used for acute toxicity tests (i.e., *R. abronius* and *A. abdita*). However, the lower sensitivity could be partly explained by different ecological characteristics (i.e., *R. abronius* is a free-burrowing amphipod directly exposed to pore-water and sediment and not a tube-dweller like *Corophium*) and the different test-temperature often used when testing sediments (*A. abdita* is tested at higher temperatures compared to *Corophium*) (Picone et al., 2008). Furthermore, it should be noted that the acute test with amphipods is as a reliable tool only for the identification of hot-spot of contamination and its ability to discriminate among sediments characterized by low to moderate contamination is uncertain, as in the case of the samples collected within the MODUS project, independently from the species used as indicator (Picone et al., 2016; USEPA, 2001).

3.2.2. *Toxicity vs ammonia and metals in elutriates*

Total ammonia (expressed as total ammonia nitrogen) was investigated in all elutriate samples used in toxicity testing (Fig. 5). Additionally, in the MODUS project elutriates were also analyzed for metals (As, Cd, Cr, Cu, Hg, Ni, Pb, Zn and sulfide) (Table 3); these results provide valuable information for the evaluation of *C. gigas* embryotoxicity test, as discussed below.

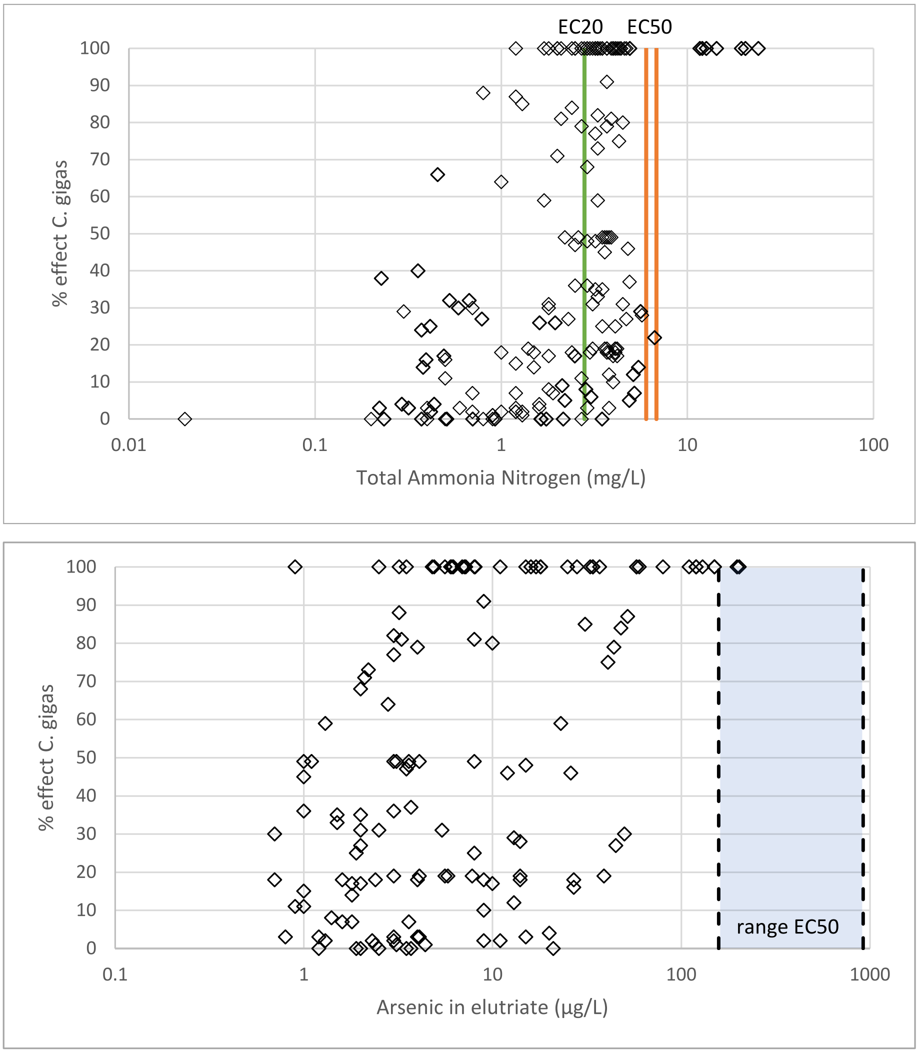

Fig. 5. Toxicity observed on *C. gigas* plotted against total ammonia and As measured in elutriate. For ammonia, the figure reports also the EC20 (in green, Geffard et al., 2002) and the range of EC50 values reported in literature for *C. gigas* (in red, Picone et al., 2019, USEPA, 1993).

Table 3
Range of metal concentrations (µg/l) in elutriates (MODUS 2013–2016) and range of effect concentrations (EC50) reported for *C. gigas* embriotoxicity in literature (further details in SM).

	Cd	Ni	Pb	As	Zn	Cr	Cu	Hg
%detected	1 %	99 %	42 %	100 %	17 %	22 %	32 %	1 %
Mean (µg/l)	–	2.6	1.5	19.3	8.6	0.5	1.6	–
Max (µg/l)	1.6	19.0	46	203	90	3.2	29	0.1
Limit of Detection (µg/l)	1	1	0.5	0.5	10	0.5	1	0.1
EC50 (µg/l) *C. gigas* embryotoxicity (range)	212–375 -	78	474–680	158–920	48–206.5	936	2–20.77	5–11

The evaluation of elutriate data suggests that ammonia could play a main role as toxicity driver for *C. gigas* (Fig. 5).

Elevated ammonia concentrations occur naturally in sediment and represent one of the main confounding factors to be considered for the evaluation of elutriate toxicity test, and specifically in the evaluation of embriotoxicity (Kennedy et al., 2015; Losso et al., 2007a, 2007b; McDonald, 2005; Sartori et al., 2024; USACE, 2021). With regard to total ammonia nitrogen (NH_3-N, i.e. the sum concentration of NH_4^+ and NH_3), Geffard et al. (2002) estimated an EC20 for *C. gigas* of 2.8 mg/l and Picone et al. (2019) reported an EC50 of 6.0 mg/l, while USEPA (1993) indicated a provisional EC50 of 6.83 mg/l and a NOEC of 4.68 mg/l (test condition: T 15 °C, pH 7.5–8.5); this NOEC value is also used, *ad interim*, as acceptability criteria for embryotoxicity test with *C. gigas* (ASTM, 1998).

Moreover, although total ammonia represents the parameter typically investigated in routine monitoring, it is important to underline that unionized ammonia (NH_3) is more toxic than the ammonium ion (NH_4^+) (USEPA, 1989, 1999). The fraction of total ammonia present as unionized ammonia (NH_3) is contingent on the pH, temperature, and salinity of the test water (Kennedy et al., 2015); specifically, the percentage of unionized ammonia increases with higher pH and temperature, but it decreases with higher salinity. In seawater at 20 °C, pH 8 and 30 ‰ salinity, unionized ammonia comprises ~3.8 % of the total ammonia (ANZECC/ARMCANZ, 2000; Emerson et al., 1975), with the ammonium ion contributing <1 % of the total toxicity (USEPA, 1989). Kennedy et al. (2015) reviewed existing data on acute toxicity testing on ammonia, reporting the following range (LC_{50}) for unionized ammonia (at salinity range 25–31 ppt): mysid shrimp 0.7–2 mg/l, fish species 1–3 mg/l while much lower values are reported for mussel and urchin larvae (~0.05–0.2 mg/l). Embryotoxicity tests conducted on the pacific oyster *C. gigas* (USEPA, 1993) revealed for unionized ammonia a 48-h EC50 value of 0.13 mg/l and a NOEC of 0.08 mg/l (test pH range 7.8 to 8.1 and salinity range 27 to 28 ppt); Losso et al. (2007a, 2007b), as cited in Batley and Simpson (2009), report for *C. gigas* a NOEC of 0.156 mg/l for unionized ammonia (embryotoxicity test, lab condition:18 °C and pH 8). Picone et al. (2019) indicated, for the larval development test with *C. gigas*, an EC50 of 0.29 mg/L for unionized ammonia. Finally, the USACE (2021) indicates for unionized ammonia a NOEC of 0.04 mg/l for larval test on bivalves.

Available data measured in elutriate of the Venice lagoon and tested for *C. gigas* are expressed as total ammonia; these values, as well as the concentrations of unionized ammonia estimated considering the pH registered during the lab testing (and assuming a temperature of 20 °C under laboratory condition), are in the same range of the effect concentrations reported in literature, being the mean and maximum value of total ammonia respectively 3.3 and 30.8 mg/l (Fig. 4-SM) and mean and maximum estimated values of unionized ammonia 0.16 and 1.47 mg/l. Specifically, toxic effects observed on *C. gigas* are correlated with total ammonia concentration (Pearson's correlation 0.79, considering the HICSED data, and 0.39 considering the MODUS data, p value$<$0.01) (Fig. 5). However, the existing dataset does not allow us to evaluate the origins of the ammonia levels measured in the tested samples (natural vs anthropic origins, or laboratory artifacts).

Further evaluations can be done considering metals concentration in elutriates (Table 3), that were not correlated to sediment concentrations, suggesting therefore a low metals bioavailability.

Among chemicals (Cd, Ni, Pb, As, Zn, Cr, Cu, Hg) tested in elutriate, only Ni and As were always detected whilst Cd and Hg were generally below the detection limits (1 μg/l for Cd and 0.1 μg/l for Hg); therefore, the role of these metals do not appear relevant for the tested organisms, since not detected in elutriate and both *C. gigas* and *C. orientale* toxicity data were not correlated to Hg and Cd concentration in sediment. Detected concentrations in elutriates are well below the EC_{50} values reported in literature for *C. gigas* (embryotoxicity test) for Cd, Ni, Pb, Cr, Hg, whilst in few samples Cu values and, to a lesser extent, Zn and As values fall in the range of the EC_{50} reported in literature and determined in single substance water-only exposures (Beiras and His, 1994; Brooks et al., 2007; Coglianese and Martin, 1981; Dinnel et al., 1983; His et al., 1999; Knezovich et al., 1981; Mai et al., 2012; Mamindy-Pajany et al., 2013; Martin et al., 1981; Moreira et al., 2018, 2018a; Picone et al., 2019; Xie et al., 2017) (Table 3-SM). Additionally, sulfide concentrations in elutriates (mean value 0.04 mg/l) were generally lower than the NOEC value reported as acceptability criteria for the *C. gigas* embryotoxicity test (0.10 mg/l, ASTM, 2021). The effects observed on *C. gigas* in the MODUS project are not significantly correlated to metal concentrations in elutriate, except for As (Pearson's correlation = 0.42, $p <$ 0.01) (Fig. 5). In this regard, it must be noted that concentrations of total As measured in elutriates are lower than the EC_{50} value reported in literature; however, it is known that the toxicity of As (as in the case of other metals) towards marine invertebrates, including the early life stages of *C. gigas*, can be widely influenced by several factors (such as chemical speciation, temperature, salinity, quantity and quality of organic matter) and available data do not permit a clear interpretation (Boukadida et al., 2016; Brooks et al., 2007; Gamain et al., 2017; Lorenzo et al., 2002; Mamindy-Pajany et al., 2013; Moreira et al., 2018, 2018a; Nadella et al., 2009; Rosen et al., 2005, 2008; Zitoun et al., 2019). Therefore, the influence of metals on *C. gigas* toxicity cannot be totally excluded, as suggested also by the evaluation of SEM/AVS ratio, previously discussed.

4. Conclusions

This work presents an independent evaluation of results of sediment surveys performed in 2008–2018 in the Venice lagoon, with the aim to evaluate jointly chemistry and toxicity data in order to identify main chemical stressors in bedded sediment and elutriate (considered as proxy of resuspended sediment).

With regard to sediment chemistry, As, Cr and Ni measured in surface sediments were generally in the same range of background concentrations defined in previous studies, while exceedance of the background concentrations were observed for Zn, Cu, Pb, Cd and Hg, mainly in the northern-central and central part of the lagoon; moreover, results indicated a diffuse but not relevant presence of PAHs in the investigated sites, with presence of local hot spots, including the historical center of Venice. Although chemical data indicated presence of anthropic pressure on sediments, the surface sediments tested in the Venice lagoon generally do not display relevant toxicity to *C. orientale*, whilst elutriate prepared from surface sediments can determine toxic effects on *C. gigas*, mainly due to ammonia exposure; in this context, chemical analyses on elutriate strongly support the evaluation of toxicity data.

Overall results indicate therefore that chemical concentrations measured in bulk sediment, with no specific evaluation of site specific sediment characteristics known to influence bioavailability (specifically, TOC for non ionic organic chemicals and AVS for metals), are not a good predictor of toxicity; in details, toxicity test results were not correlated to sediment concentrations (expressed on a dry weight basis) neither sediment concentrations were correlated to elutriate concentrations. Instead, the sediment assessment was enhanced by the application of mechanistic sediment quality guidelines: results suggest that the $\sum$SEM/AVS ratio (representing bioavailable fraction of Cd, Ni, Pb, Cu, Zn) is a better predictor for toxicity for *C. gigas* than for *C. orientale,* while the PAH TU approach indicates that, in most of the lagoon, PAHs are not a stressor of main concern and tested organisms are not particularly sensitive to these compounds when exposed at the concentration range observed in the analyzed sediment samples. Finally, results indicate that Hg, although present with diffuse exceedances of the background concentrations, does not play a relevant role as toxicity driver at the tested concentration range (up to maximum concentrations of 4–7 mg/kg d.w.).

These results represent useful information to support further evaluations aimed at sediment management in the Venice lagoon, as well as to support sediment assessment in other areas characterized by similar chemical range; specifically, the evaluation of toxicity drivers is an essential information to support scientific discussion to pursue the most sustainable sediment management (Bizzotto et al., 2023). With special regards to the Venice lagoon, results clearly indicated the need to include in sediment investigation a proper evaluation of chemical bioavailability as well as the consideration of confounding factors in toxicity testing, in order to better support the evaluation of sediment quality and the related management decisions.

However, any extrapolation of these results should be done considering also the ecological realism of tested organisms (and measured endpoints) and the representativeness of the tested conditions compared to the environmental variability in natural systems. With regard to ecological realism, larval development toxicity tests are more sensitive than lethality tests performed on adults of the same species (as well as on fish and other invertebrates); on the contrary, *C. orientale* is known to be less sensitive than other amphipod species to certain contaminants. Moreover, oyster larvae are planktonic, and thus not in direct contact with sediments; therefore, interpretation of elutriate toxicity test results should be evaluated as useful only in case of significant sediment resuspension scenarios. The toxicity test results on *C. gigas* can be therefore considered conservative and do not imply necessarily an impact on the trophic web or on mussels' population. With regard to the representativeness of tested conditions, it must be considered that the toxicity and levels of the pollutants investigated in this study can vary under field conditions, as a function of environmental conditions; finally, bioaccumulation is not specifically evaluated in this study and would require further insights.

CRediT authorship contribution statement

Elisa Chiara Bizzotto: Writing – review & editing, Writing – original draft, Visualization, Methodology, Conceptualization. **Marco Picone:** Writing – original draft, Validation, Investigation. **Elisa Giubilato:** Writing – review & editing, Validation. **Elena Semenzin:** Writing – review & editing, Validation. **Patrizia Bidinotto:** Investigation. **Valerio Volpe:** Investigation. **Antonio Marcomini:** Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2025.179164.

Data availability

Data will be made available on request.

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