Venezia 2021

Programma di ricerca scientifica per una laguna "regolata"

Linea 2.1

Qualità del sedimento lagunare a supporto della sua gestione

D2.1.1.4

Stima dei valori di fondo

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1   Introduction

A robust assessment of the environmental quality of Venice lagoon should consider the concentration of trace elements naturally occurring in the sediment as a combination of waterborne (freshwater and seawater) and atmospheric inputs. Such concentrations, also called background values, are useful to support data evaluation and time trend analysis in order to understand the extent of anthropogenic influence on the chemical status. The assessment of sediment quality is indeed essential to confirm the achievement of the good ecological status for transitional water bodies as required by the EU Water Framework Directive (EC, 2000). In addition, sediment quality is crucial for the lagoon management and especially to allow the reuse of dredged sediments while preserving the quality and the overall biodiversity of the lagoon ecosystems.

In this context, task T2.1.1.2 aims to i) collect and analyse the background values available in the literature for selected metals (i.e. As, Cd, Cr, Cu, Hg, Ni, Pb, Zn) in the Venice lagoon; ii) review approaches and methods used to derive such background values; iii) process data available in the literature (e.g. undisturbed radio dated cores from the Venice lagoon), and finally iv) propose ranges of background values for the entire lagoon as well as its sub-basins.

1.1   Background concentration: definition and implementation

The term ''natural background'' refers to the concentrations of microelements present ''by nature'' in the minerals and their weathering products that are transported from the catchment basin by erosion and accumulated in a given sedimentary deposit. The term ''natural background'' is generally used in juxtaposition with ''anthropogenic input'', which is defined as the presence of microelements due to chemical inputs as the direct or indirect consequence of human activities (Apitz et al., 2009).

However, although some authors (Filzmoser et al. 2005, Apitz et al. 2009, Guerzoni et al., 2007) indicate that the term "natural background" should exclude the presence of any anthropogenic activity, the estimation and application of a value which totally excludes any anthropogenic contribution implies several difficulties and represents a conceptual challenge for practical application and management purposes, as recognized also by several environmental agencies (UK Environment Agency 2003, USEPA 2002, European Commission 2003, 2011)[1].

Specifically, in Europe, although the WFD advocates the consideration of the natural background values (defined as "pre-industrial levels"), the same European Commission recognized the difficulties in the

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[1] The United Kingdom Environment Agency (2003) proposed the following definition of background concentration: "The concentration of an element or compound in an environmental compartment before significant anthropogenic additions. For practical purposes, it is taken to equal pre-industrial revolution concentrations".

The United States EPA (2002) differentiates natural (pristine) background from anthropogenic background, considering the influence of diffuse contamination, distinguishing: "i) naturally occurring: substances present in the environment in forms that have not been influenced by human activity; ii) anthropogenic: natural and human-made substances present in the environment as a result of human activities".

Similarly, the same European Commission (EC, 2003) defines two background components: the "natural background concentration" is "the concentration that is present due to natural causes only", whilst the "ambient background concentration" is "the concentration that is present due to natural background plus the concentration due to contaminant release derived from diffuse sources of human origin" (including, as example, the influence of human activities on atmospheric deposition, historical land use and land management etc).

estimation and application of these values and allows the use of an "ambient background", as reported below (EC, 2011):

The general definition of natural background level is the concentration that is present owing to natural and geological processes only, i.e. the background level with no anthropogenic contribution ('pre-industrial' levels). In reality, true pristine areas are rare within Europe, and it must be considered on a case-by-case basis whether a given area represents a pristine condition for a specific metal.

In most areas in Europe, any estimate of a natural background concentration will inevitably include a small contribution from anthropogenic sources because much of Europe's landscape has been altered by man's activities for mineral extraction, agriculture or habitation for millennia and this historical contribution may be obscure. In addition, long-term anthropogenic activities, such as drainage, irrigation and special crops (e.g. conifers creating acid soil conditions), may influence environmental release of metals. This contribution is difficult to quantify and distinguish from what concentrations might have been in the absence of such activities. Finally, contributions from diffuse anthropogenic sources, e.g. aerial deposition, maybe impossible to eliminate entirely.

Therefore, an estimate of a background concentration will more likely be an 'ambient' background concentration rather than a value relating to a purely natural pristine environment."

The issue of the sediment background is therefore complex, both considering methods and approaches for its derivation but also general meaning and application in sediment management. Specifically, although background values are sometimes used to derive Sediment Quality Guidelines or similar concentration limits (Kwok et al., 2014, Apitz et al., 2007a) and to support the assessment of anthropogenic contributions to the overall level of pollution (Degetto et al., 2005, Chapman, 2007), it must be noted that exceedance of background value does not necessarily imply a biological effects or toxicity (Chapman and Wang, 2001). Additionally, since metal availability is strongly influenced by site-specific conditions and total metal concentration is a poor predictor of sediment toxicity for aquatic biota[2], the use and relevance of background values in the sediment management is still under discussion. In the context of the WFD, the same European Commission (EC 2011) indicates that sediment quality standards set below the natural background level would have a little regulatory purpose and are scientifically indefensible (unless an 'added risk' approach is to be adopted; further details in Box 1).

Under this context, in the last years, several studies investigated the sediment quality in the Lagoon of Venice and, in some cases, proposed also site-specific sediment background values to support environmental assessment and data interpretation. However, since an overall evaluation of the previous studies is still missing, this study aims to critically review existing data for the lagoon, with a focus on the meaning of background values, the approaches adopted for the derivation of site-specific background values and a comparison of these values with range of metal concentrations observed in pre-industrial age (pre 1910s), selected in this study as additional proxy of "background value" (further details in Chapter 2).

The following chapters will illustrate the main processes and factors that should be considered for the derivation of background values and that were evaluated in the literature review of existing studies on the Venice Lagoon.

BOX 1: Relevance of metal background concentrations under the WFD

Although background values are sometimes used to derive Sediment Quality Guidelines (SQGs) (Kwok et al., 2014) and similar screening benchmarks, it must be noted that neither background nor enrichment metrics take into account, or imply, biological effects or toxicity (Chapman and Wang, 2001). Additionally, since metal availability is strongly influenced by site-specific conditions and total metal concentration is a poor

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[2] Additionally, since metals are naturally occurring, many organisms may have evolved mechanisms to adapt to exposure of naturally occurring chemicals.

predictor of sediment toxicity, the use and relevance of background values in the sediment management is still under discussion.

In Europe, the Water Framework Directive explicitly acknowledges the issues of naturally occurring concentrations for metals and bioavailability. The Daughter Directive to the WFD on Environmental Quality Standards (EQS) (2008/105/EC) (EC, 2008) states in Annex I, part B.3:

"Member States may, when assessing the monitoring results against the EQS, take into account:

(a) natural background concentrations for metals and their compounds, if they prevent compliance with the EQS value; and

(b) hardness, pH or other water quality parameters that affect the bioavailability of metals."

As recognized by the European Commission (EC, 2011) the derivation of environmental quality standards for metals should require an explicit consideration of bioavailability (e.g. using speciation models or, failing that, utilising dissolved concentrations instead of total concentrations)[3] and of background concentrations. Specifically, sediment quality standards should not normally result in values below the natural background level unless an 'added risk' approach (ARA) to compliance assessment is to be adopted (EC, 2011). Setting quality standards below the natural background level would result in a value that serves little regulatory purpose and is scientifically indefensible; furthermore, many waterbodies would fail the quality standard even though there is no risk to biota.

The technical guidance for EQS derivation (EC, 2011) recognized that metal quality standard values below natural background levels may be generated if:

1.   The EQS has been set to an unrealistically low level simply because of a (too) conservative approach adopted in the quality standard derivation (i.e. a large Assessment Factor) to compensate for uncertainties arising from a lack of reliable (eco)toxicological data.

2.   The EQS was set using ecotoxicity tests with organisms cultured/tested under conditions of low metal concentrations compared with the surface water background levels (i.e. organisms locally may have adapted to higher natural concentrations).

The EC document suggests two possible approaches as a pragmatic way in case the metal EQS is below the background level:

•   to evaluate the scope for refining the EQS by reducing uncertainty (including making a correction for bioavailability) and/or

•   to use the added risk approach (ARA) (although the total risk approach would be preferential).

The ARA was discussed for the purpose of setting EQSs by Lepper (2005). The ARA requires the calculation of a maximum amount (maximum permissible addition, MPA) of a metal that may be added to the local background concentration of this metal without adversely affecting the assessed ecosystem. However, correct determination of the natural background level is key in this approach, and this may not be easy to achieve; additionally, ARA is not without flaws because added and background metal concentrations will behave as a single pool, and exposed organisms will not be able to distinguish between them. Currently,

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[3] Specifically, the technical guidance for derivation of the EQS specifies: "when evaluating toxicity data to derive quality standards for metals, total metal concentrations are not usually directly related to ecotoxicological effects because many abiotic and biotic processes can modify the venailability of metals, even rendering them unavailable for uptake. This means that the fraction available for uptake and toxicity may be a very small part of the total metal present." (EC, 2011)

some authors commented that there is little scientific evidence to support the assumptions underlying this approach, therefore still under discussion (EA, 2008).

Finally, it must be noted that the EC guidance for derivation of EQS (EC, 2011) allows also the use of sediment quality standard set on the basis of field thresholds (such as 'threshold effect levels' - TEL, 'effect range low' - ERL or 'no-effect level' - NEL), referring to concentrations where biological effects are unlikely or low (indicatively, not more than 20-25% of samples should display a toxic effect, as specified in ERL or TEL definitions). However, the EC guidance highlights that none of these approaches should be used without a thorough assessment of the reliability of the data and their relevance and, specifically, entries associated with an effect for a given chemical are relevant if the concentration for this chemical is at least 2-fold above the background (EC, 2011, McDonald et al. 1996).

1.2 Environmental processes and factors affecting sediment background concentration

Several factors can influence background chemical concentrations (meant as pre-industrial or ambient background). They are summarized below and can be related to human activities (e.g. land use, urbanization, diffuse pollution) but also to natural processes and environmental variability (e.g. sediment physical properties, hydrodynamic conditions, geochemistry). Natural processes and environmental variability can influence significantly also the range of "natural" background values (meant as pristine concentration).

Specifically, key complexities that can strongly influence sediment concentration and that should be considered when developing the study design for representative sediment background determination include (SMWG, 2018, Geiselbrecht, 2019):

- Land use: the degree of urbanization and its evolution over time, intensity of land use, waterfront development and land cover patterns are correlated with chemical input to watershed sediment. Generally, urbanization and land use determine chemical release by soil erosion, urban runoff, diffuse and direct discharge (e.g. agricultural practices, wastewater discharge, stormwater release to water bodies) and positively correlates the chemical input that can migrate in the watershed. Natural or artificial changes to land cover within a watershed may alter the concentration of organic carbon in sediment; similarly, land erosion can change over time influencing the input of naturally occurring chemical. Consequently, historical (and current) land use within a watershed has a direct and potentially major influence on background conditions (considering both anthropogenic and naturally occurring chemical);
- Geological characteristic of the basin: concentrations of naturally occurring chemicals in sediments are controlled by the chemical composition of the parent rocks and the geochemical processes that occur during soil formation, sediment transport, and sediment deposition; therefore, certain metals tend to occur together in natural sediments, and metal/metal concentration ratios often are restricted to relatively narrow ranges. The use of catchment geology can support the derivation of background metal values for estuarine sediments although requires knowledge of the surrounding geology, especially in mineralised regions;
- Atmospheric deposition: atmospheric deposition is a recognized pathway of contamination, particularly for chemicals ubiquitously found in the environment (including metals). The impact of atmospheric deposition can be challenging to ascertain since it will vary depending on atmospheric conditions (e.g., wind speed, temperature, and rainfall, deposition patterns) and particle characteristics (size and shape). The relevance of atmospheric deposition has significantly increased during the last centuries due to the industrial growth and it is likely to represent a significant input to watershed sediment;
- Sediment transport processes: sediment sites are dynamic in nature, as they are consistently receiving suspended sediments from off-site areas that can contain background concentrations of trace elements from diffuse anthropogenic sources but also of naturally occurring metals. It is

therefore important to understand the diversity of depositional environments and the many varying factors such as current directions, tidal pumping, erosion and resuspension dynamics, and constant or episodic sediment transport processes. Consideration should be given to multiple potentially significant factors influencing sediment transport at coastal/tidal sites, including the effects of flood events and storm surges;

- Biological community: the watershed biological community and its temporal evolution can play an important role by influencing deposition rate (e.g. in the case of primary production), sediment disturbance (e.g. bioturbation process and feeding habits) but also chemical bioavailability (e.g. due to organic matter, anoxia, etc.) and should be considered in the general framework. More details about the influence of these aspects are reported below;

- Vertical profile and sediment disturbance: the vertical profile of sediment may vary significantly in composition, texture, chemicals, and biological characteristics. Changes in the hydrodynamic environment and sediment sources can result in distinct layering. Change in land use and land cover over time, such as increasing urbanization, may produce layers with different compositions, texture, organic content and concentrations of anthropogenic background chemicals and naturally occurring chemicals. All of these factors can influence the distribution of chemicals along with sediment depth. Sediment disturbance processes (deposition, erosion/removal, but also mixing due to natural process or human activities) affect chemical distribution in sediments. Pore space and volume of the water within sediments is decreased by compaction as sediments are buried; during this process, chemicals present in sediments may be vertically redistributed by mixing of surface and deeper sediments. Sediment mixing may also occur through bioturbation, that may increase pore space, water fraction, and organic content, affecting the partitioning of chemicals between aqueous and solid phases. Age dating and chemical analysis of sediment core samples may indicate chemical concentrations that are associated with sediment layers deposited and may be helpful in estimating representative background concentration ranges;

- Physical properties of sediment: the physical properties of sediment (such as grain size and density) strongly influence the distribution of naturally occurring and anthropogenic background chemicals in the environment. Sediment consists of organic material, inorganic material, and pore water. The relative abundance of these components varies vertically and horizontally within a sediment body, resulting in variable distribution of chemicals at a sediment site. Sediment texture has a substantial effect on the distribution of chemicals of concern in sediment: fine-grained sediments, particularly those with a high percentage of clay-sized particles and organic content, have greater surface area, so they typically have greater sorption capacity than medium and coarse-grained sediments. Silts typically have moderate sorption capacity, while sands and gravels have lower sorption capacity. In addition to sediment texture, sorption capacity of some fine-grained sediment is enhanced by surface charge. For example, clays and organic colloids tend to be highly charged relative to their surface areas. Clay minerals are typically negatively charged under normal pH conditions, so they attract positively charged trace metals ions for sorption. This results in clay-rich, fine-grained sediments that have greater trace and reference metal concentrations. In addition, metal concentrations (in particular) tend to be inversely proportional to grain size;

- Geochemistry: geochemical processes relevant to sediment background evaluation include association of elements with minerals, sorption of elements on mineral surfaces, water chemistry, and water-mineral interactions. Chemical properties of sediment particles and the surrounding aqueous phase strongly influence the distribution of metals: key properties include metal solubility, pH of the aqueous phase (including the overlying water column and pore water), redox potential of the aqueous phase, metal affinity for organic carbon, TOC concentrations and pore water, and reactions of metals with sulphide (that can strongly influence also metals bioavailability). Additional details on the geochemical processes are reported in Box 2.

The overall variability and complexity of the above-illustrated processes may hinder the ability to identify sediment homogeneous area and to define a range of reference conditions (defined as chemical conditions used for comparison with the investigated site/area, subject to anthropic pressure[4]). Under this context, several methods and approaches have been developed to reduce environmental variabilities and to allow the estimation of background values, as summarized in Chapter 1.3.

Box 2. Focus on metals and sediment geochemistry

In sediments, metals concentrations are controlled by dissolution/precipitation reactions and adsorption/desorption ("sorption") reactions processes; the water fraction plays an important role in filling pore space within the sediment, allowing for the transport of dissolved chemicals, and is subject to geochemical conditions that strongly influence the transport and sorption of metals[5].

In addition to these factors, sorption is influenced by changes in pH, oxidation potential, salinity, concentrations of competing ions, the nature of sorbent phases and their surface areas, and surface site densities.

Highly soluble metals can remain mobile in the aqueous phase and can be dissolved from the sediment, while low solubility metals can precipitate and accumulate in sediments. The solubility of a metal is highly dependent on characteristics of the aqueous phase including pH, redox potential, and ionic strength. While elements differ in their response to changing pH, acidic conditions tend to dissolve and mobilize some metals, while basic pH conditions can precipitate other metals (resulting in greater concentrations in sediment). The pH also controls the net surface charge of particles, which is an important factor in determining sorption of metals on mineral surfaces. This is important due to the presence of clay minerals and metal oxides that have strong affinities to absorb specific trace metals.

Oxidizing conditions cause many metal ions (e.g., iron and manganese) to precipitate as oxides. Reducing conditions, such as in anoxic sediments, tend to keep specific elements in solution and mobile. In addition to naturally reducing conditions associated with peat or other organic materials in wetlands or similar

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[4] Reference conditions are generally defined on the basis of following data:

- Chemical concentrations observed in one (or more) reference area, that should have similar physical, chemical, geological, and biological characteristics of the investigated site, but should not have been affected by punctual anthropic activities or release. However, this reference area should include anthropogenic inputs that are reflective of the larger region (USEPA 2002, Geiselbrecht et al., 2019). These reference conditions can be therefore considered representative of ambient background values;

- Chemical concentrations observed in older sediments, e.g. deposited in pre-industrial period (and therefore representative of ambient background values) or deposited in previous age (and therefore considered representative of "natural" background values), although several factors (summarized in Chapter 1.2) can influence and determine temporal evolution of these reference conditions.

[5] Specifically:
- Speciation/complexation is the distribution of a given constituent among its possible chemical forms, including metal complexes, which have differing tendencies to be adsorbed or desorbed;
- Precipitation is the process by which dissolved species exceed the solubility limits of their solids, so that some of the species precipitate from solution;
- Colloid formation can result in metals being sorbed or coprecipitated with colloidal-sized particles;
- Biofixation occurs when biological processes (usually involving microorganisms or plants) result in the binding of metals to solid materials; interactions with natural organic matter can also result in sorption.

environments, releases of organic contaminants can stimulate microbial activity, resulting in local reducing conditions and the mobilization of select metals.

Reducing conditions can cause the reductive dissolution of iron and manganese oxides, which may mobilize adsorbed trace elements. Reducing conditions may also directly reduce arsenic, selenium, antimony, molybdenum, and vanadium to more mobile valence states. Sulfate-reducing conditions in sediment can cause specific metals (e.g., arsenic, mercury, copper, lead, and zinc) to precipitate as (or with) insoluble sulfide phases. Sulfide ions, produced from the reduction of sulfate associated with the breakdown of organic compounds and as measured by acid-volatile sulfide (AVS), are usually associated with higher metals concentrations in sediment.

Finally, sediments with greater TOC concentrations typically have greater concentrations of specific trace elements (e.g., mercury, copper, tin, and uranium), because the organic particles have a greater sorptive capacity for these elements. However, greater TOC concentrations may be associated with reducing conditions, so the metals associated with the TOC may be less bioavailable. This complexity determines that concentration of metal in bioavailable form is typically not proportional to the total concentration of the metal; as a consequence, total concentrations of metals are recognized as poor predictors of toxicity for aquatic biota (and especially, benthic organisms). Additionally, since metals are naturally occurring, many organisms have evolved mechanisms to adapt to exposure of naturally occurring chemicals.

1.3 Review of existing methodologies for the determination of sediment background concentrations

1.3.1 Techniques for background values estimation

There is a number of methodologies used to differentiate between anthropogenic and "naturally" occurring concentrations. They can be divided into three categories: empirical, statistical and integrated techniques.

Empirical methods (Geiselbrecht et al., 2019) include several approaches, based on i) calculation of global averages of metal concentration in upper crust and marine shale, ii) identification of pristine areas (which requires identification of uncontaminated areas), iii) use of catchment geology, soils, shales and fluvial sediments and iv) analytic determination of metal concentrations in sediment core data.

Statistical methods aim at the differentiation of the initial observed chemical concentration data into natural and anthropogenic subsets and at establishing a threshold dividing the two groups. Among statistical methods for establishing natural concentrations the cumulative frequency, the modal analysis or outlier testing are used (Matschullat et al., 2000). More techniques used in deriving background values were reviewed by Birch (2017) and include regression techniques, cluster/factor analysis, multi-fractal analysis, maximum likelihood mixture estimation, population clustering, gradient method, sorption hypothesis and specific surface area methods. Most of these statistical techniques require data to be normally, or log-normally distributed. However, this is often a requirement difficult to meet, due to various processes affecting the distribution of the substance concentration and leading to anomalies in observed data. Detection of such anomalies is frequently performed throughout the identification of outliers (Reimann et al., 2005).

For the so-called **integrated method**, the samples are collected in pristine areas and the analytical results are subjected to statistical calculations. Non–polluted samples from an area located at a certain distance from sources of pollution or deep core samples can serve as a basis to derive background values. With this method, data are less affected by differences in site sampling because of the representativeness of the samples for the study area (Thuong et al, 2013). Furthermore, data processing is less complex due to the fact that a restricted amount of data is obtained with this method (Gałuszka, 2007).

All the methods listed above present some limitations. Empirically derived background values can be significantly affected by local geological mineralization, making the use of a single background value

problematic for wider spatial assessments (e.g. at regional scale). On the other hand, statistical techniques applied to distinguish background values are adversely affected by multiple distribution modality and require large data sets. Finally, the integrated method requires a real pristine area to be identified: this can be difficult for several reasons, such as the presence of several human activities or the influence of the long-range transport of atmospheric deposition of heavy metals. Among empirical methods, the use of sediment cores seems to be the most attractive one, providing that sedimentary deposits are homogeneous (Degetto et al., 2005; Frignani et al., 2001). Additionally, the technique allows the evaluation of the historical trend of contamination. As indicated in technical documents for the WFD implementation (EC, 2011), the analysis of deeper, undisturbed sediments, combined with radio-isotopic techniques (see Box 3), may allow one to estimate historical environment concentrations, and thus to judge 'pre-industrial' levels. The potential contribution of erosion on deeper sediments can be also estimated from national or international databases or geological modelling. The combination of empirical and statistical methods (i.e. integrated methods) offers the best trade-off for the determination of background values since a sufficient number of samplings could help reducing the uncertainty associated with radio-isotopic techniques as well as the identification of undisturbed sediments.

Box 3 Sediments Radio dating

Sediments are excellent environmental indicators that record not only past climatic and geological events but also environmental perturbations produced by anthropogenic polluting activities that involve the water body from which they are deposited. Sediments preserve the memory of the processes of introduction, dispersion and deposition of chemical substances, of anthropic or natural origin, and with them the main phenomena occurring in the basin. Moreover, for many substances, they constitute a reservoir that can affect the water column, depending on hydrodynamic conditions (e.g. deposition/erosion rates) and sediment transport processes.

The chronology of metals in sediments can be determined by methods of radio dating (time scale of 100-200 years) which use numerous radioactive isotopes of both natural and anthropogenic origin. The most used for these purposes are ^{210}Pb, ^{7}Be, ^{137}Cs and ^{134}Cs.

The ^{210}Pb ($t_{1/2}$ = 22.3 years) is a natural radioactive isotope belonging to the ^{238}U decay series and derives from ^{226}Ra; it provides the accumulation rates of sediments on a time scale of about 100 years.

The ^{7}Be ($t_{1/2}$ = 55.3 days) is used on short time scales in the determination of accumulation rates in the case of rapid deposition of sediments and the mixing speed.

The ^{137}Cs is an artificial radionuclide that allows the dating of some levels in the sedimentary column based on the course of its atmospheric relapses. For example, the emission peaks correspond to 1963, the year in which the maximum number of nuclear experiments in the atmosphere occurred, and to 1986, the year of the Chernobyl accident. The profile base of the ^{137}Cs can identify the sediments deposited in 1954 (Frignani et al., 1991; Degetto, 1997).

1.3.2   Techniques for data normalization

As defined by Kersten and Smedes (2002), normalization is a procedure to correct both background and contaminant concentrations for the influence of the natural variability in sediment granulometry and mineralogical composition mediated by the ambient energy of the aquatic system.

Normalization methods are commonly divided into granulometric and geochemical methods, with the aim to correctly evaluate the physical variability (granulometric normalization) and/or the chemical variability (geochemical normalization), respectively.

- Granulometric normalization: as anticipated, fine-grained sediments have greater sorption capacity than medium and coarse-grained sediments. Specifically, trace elements concentrations are generally higher in areas with sediments rich in clays than those in sandy regions, where the granulometric dilution effect causes lower and variable contaminant concentrations in the sediment (Kersten and Smedes 2002). Granulometric normalization can be done adopting the following approaches:
  - The empirical approach requires the separation of different grain size fractions (eg. <2μm clay or, alternatively, <20μm or <64 μm, depending on the characteristics of the samples and the desired level of effort) and subsequent chemical analysis (Herut and Sandler, 2006). However, this method might suffer some disadvantages, since it is very laborious and requires an elevated sample manipulation (susceptible to contamination). Additionally, in cases of highly variable mineralogical composition, this method would not reflect this variability. Therefore, most environmental studies dealing with polluting metals use the composition of the total sample;
  - The computational approach needs that the value of a specific chemical is calculated by dividing the measured concentration to the fine fraction content (Loring and Rantala 1992, Thuong et al., 2013). The selection of the proper fine fraction should be done considering the grain size variability in the sample. However, this method is not recommended for sediments that are heterogeneous in grain size (e.g. sediments/soils derived from glacial erosion of igneous and metamorphic rocks)(Loring and Rantala 1992; UNEP 1995).
- Geochemical normalization: geochemical normalization commonly uses a conservative element as a reference, assuming that the reference element is insensitive to inputs from anthropogenic sources and stable to environmental influences such as reduction/oxidation, adsorption/desorption and other diagenetic processes. In the case of trace metals[6], the element used as normalizer should be a main constituent of the heavy metal carrier and it should reflect the granulometric variations in the samples, representing, therefore, a geochemical normalizer or ''co-factors'' for grain-size/compositional variation (Loring, 1990, Herut and Sandler, 2006). This is based on the assumption that there are conservative (i.e. "reference") elements, like Al or Li[7], which represent proxies for the clay mineral content. In this context, Al has been most frequently used in estuarine and coastal environments, although normalization with Al is not valid in sediments with variable feldspar content or in metamorphic sediments. Similarly, Si represents a metal proxy for the quartz grain content. Components like organic matter, Fe/Mn oxides, or sulfide minerals may also serve as hosts for trace elements (although Fe and organic matter can be significantly influenced by early diagenetic processes, or redox and precipitation effects which are frequently observed in estuarine and coastal sediments). Accordingly to Herut and Sandler (2006), chemical normalization has the following advantages: a) a single analytical procedure is practised for the determination of all needed elements, the pollutants and those used for normalization; b) minimal manipulation of the sample

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[6] Much less experience is available on normalization of trace organics as compared to metals. Knowing the phase distribution of organic contaminants is a crucial prerequisite for understanding and predicting their environmental behaviour. As example, there is a well-known strong affinity to organic matter (OM) for organic chemicals like polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs). Consequently, the mobility and partitioning of these chemicals in the environment can be predicted based on their partitioning into the bulk organic carbon in the sediment. Since OM content varies within sediments, this co-factor has occasionally been used for geochemical normalization. This is of particular interest in areas affected by anthropogenic inputs, in order to evaluate chemical distribution caused by variation in the OM content.

[7] The examination of aluminium (Al) and lithium (Li) concentrations indicates that Li is superior to Al for the normalization of the metal data from sediments derived mainly from glacial erosion of crystalline rocks. Lithium is of equal merit, or superior to Al, for the normalization of metal data from most other silicate sediments. Lithium normalization provides an alternative procedure to those used previously for the identification and estimation of relative anthropogenic trace-metal contributions to estuarine and coastal sediments (Loring, 1991).

minimizes contamination; c) the chosen element, or elements, is supposed to normalize both the grain size and the composition variability. The main modes of geochemical normalizations include the following (Thuong et al., 2013):

o   By dividing the raw concentration of heavy metals to the concentration of the normalizer. This method is applied to compare the results with geo-accumulation index (I_{geo}) or enrichment factor (EF) since these indices are used to determine the pollution status (I_{geo}) or degree of enrichment (EF) in sediments/soils;

o   By calculating the linear regression equation of a heavy metal concentration versus the normalizer concentration or a ratio of heavy metal concentration and normalizer concentration;

o   By calculating the regression line between heavy metal and normalizer through a pivot point (non-polluted sand is commonly used) and selecting the standard sediment/soil composition;

o   Multi-parameter normalization: using the combination of clay fraction and normalizing elements to build up a multi regression equation with high regression coefficient.

Overall, geochemical normalization appears to be more appropriate than granulometric methods because it compensates for the mineralogical as well as the natural granular variability of trace-metal concentrations in sediments (Loring et al 1991). However, often most environmental studies dealing with polluting metals do not investigate all the elements needed for the geochemical normalization (e.g. Al), so this method can rarely be applied on existing datasets.

2   Methods

The review of available studies and data and the definition of new background values in the sediments of the Venice lagoon was based on the following approach, represented in Fig. 2.1:

1) collection and critical analysis of available studies including the determination of concentration profiles of metals in radio-dated sediment cores and/or estimation of background values for metals in the Venice lagoon and extraction of relevant data (detailed methods described in Chap. 2.1);
2) data sorting and preparation of the following data sets:
   a. background values as reported in available studies and scientific papers (lBV dataset) (methods in Chap 2.1.1);
   b. range of metal concentrations observed in the local pre-industrial period (i.e. before 1910), considering existing data related to radio-dated sediment cores (RDC dataset) (Chap. 2.1.2);
3) quality evaluation of data included in RDC dataset in order to select data from the most robust and representative studies, followed by their inclusion in the sRDC dataset (other data were excluded from further analysis and stored in the dRDC dataset) and comparison to literature background values (lBV) (selection criteria in Chap. 2.2);
4) application of a statistical method (2sigma method) to the sRDC dataset to propose new Background Values (nBV) (methods in Chap. 2.2), later compared to literature background values (lBV).
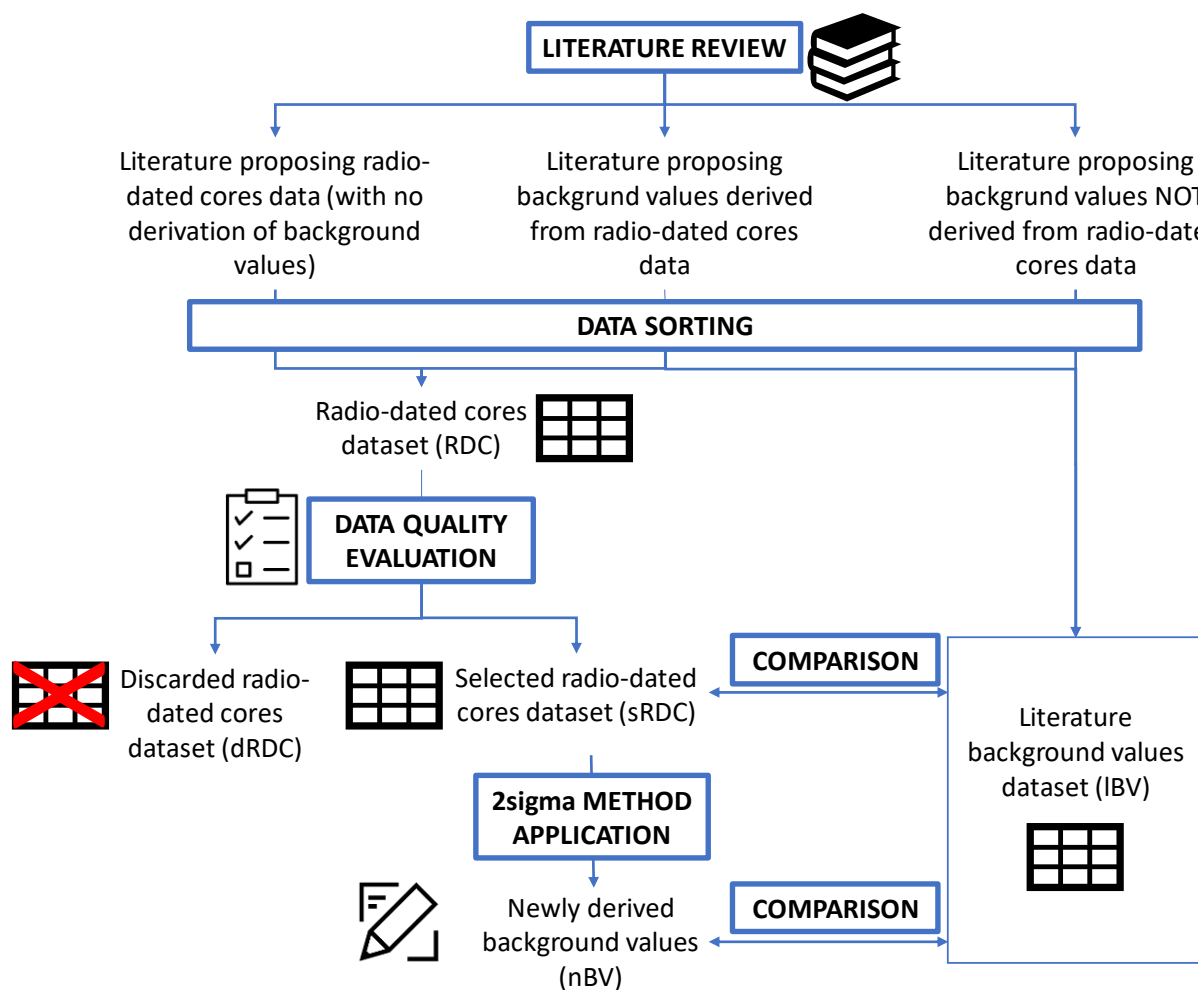

Figure 2.1. Scheme of the methodology adopted in this work for literature review and for the determination of new background values.

2.1 Literature review and data sorting concerning the Venice lagoon

A literature review was conducted with the aim to i) collect scientific papers and reports proposing background values for the lagoon of Venice; ii) collect scientific papers and reports describing data on radio-dated sediment cores collected in the lagoon of Venice.

The keywords used for searching within the "Scopus" database were "Venice Lagoon", "Natural background", "Background values", "Radio-dated cores", "Sediments", "Heavy metals", and the considered timespan was from the 1980s to present days. An additional search was done in order to identify the most important technical reports and grey literature written in Italian (as result of investigations performed by environmental agencies and public authorities) and not published in scientific journals.

All the collected studies were evaluated in order to understand the aims of the work, the data used/generated through experimental activities and the general approach adopted for the derivation of Background Values, considering the key factors described in Chapter 1.

Specifically, both peer-reviewed articles and project reports were analysed in order to present: i) an overview of the methodologies applied to distinguish background concentrations of metals from anthropogenic inputs, ii) different meanings attributed to background values and their estimated ranges for the sediments of the lagoon of Venice, and iii) existing information on radio-dated cores collected in different areas of the lagoon of Venice.

Available information was systematically processed, dividing the collected data into two Excel tables:

- the "literature Background Values" (lBV) dataset, composed of the background values proposed in the selected works, and
- the "Radio-Dated Cores" (RDC) dataset, reporting sediment core data extracted from selected papers. This dataset was prepared considering only sediment cores investigated with both radio dating analysis and chemical analysis, in order to evaluate metal concentrations in sediment deposited in the pre-industrial age (i.e. before 1910).

For this work, it was decided to report only the metal concentrations of the most studied and available elements in the datasets, although some authors also have analysed other elements (e.g., Ag, Mn, V). Therefore the metals considered in this analysis are Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Mercury (Hg), Nickel (Ni), Lead (Pb) and Zinc (Zn).

2.1.1 Literature Background Values dataset (lBV)

The lBV dataset includes all the available data proposed as background values for the Venice lagoon in the selected literature. Available sources were processed in order to extract and report in a table general information about the study (investigated area, sampling year, etc.) and the range (min-max, if present) of the proposed background values. It was also reported whether the collected background value referred to a particular area of the lagoon or to the entire lagoon basin. Additionally, the studies were analysed in order to identify the method adopted for the background values determination and related information (such as normalization procedure, etc).

2.1.2 Radio-dated cores dataset (RDC)

The RDC dataset was prepared including all the data related to sediment cores subject to both chemical analysis (at different depths) and geochronological analysis aimed to determine sediment age and sedimentation rate. The data were organized in columns showing all the important information related to the radio-dated cores, in particular about the area of core sampling (e.g., northern lagoon, central lagoon), the morphological unit of extraction (shallow water or salt marsh), the year of sampling, the labelled name of the core, the analysed layer thickness with the associated radionuclide, the Sediment Accumulation Rate

(S.A.R.), the age and the year of the analysed thickness. Information about the S.A.R. and/or the sediment age, if not available, were calculated reciprocally from available data: if the S.A.R. was available, the date and year of the relative core layer have been calculated and, vice versa, if the date/year was available, the S.A.R. was estimated. Moreover, for those studies that reported many S.A.R. values derived from different methodologies (Constant Flux (C.F.); Constant Initial Activity (C.I.A.); Constant Initial Concentration (C.I.C.); Constant Rate of Supply (C.R.S.); Constant Sedimentation (C.S.)., see Table 3.1.2) for the same core, an average value for the whole core profile was reported. In addition, the dataset included also ancillary parameters useful for the data evaluation (i.e., sediment grain size data, TOC and, when available, chemical normalizer).

2.2   Data quality critical evaluation

The large number of sediment cores data collected from the literature allowed the use of pre-industrial (before 1910) concentrations (estimated from undisturbed sediment cores, subject to both geochronological and chemical analysis) as a possible indicator of the "background value" for target metals.

Accordingly, data from the RDC dataset were processed as follows. First, concentrations before the 1910s were selected from each radio-dated core profiles. Then, the RDC dataset was divided into two distinct datasets, one with the data of the works considered "robust", called "selected radio-dated cores" (sRDC) and one with all the "discarded radio-dated cores" (dRDC) dataset.

Data included in the sRDC dataset were evaluated and selected from the RDC according to the following criteria (yes/no):

1. Does the study provide an estimate of sediment background values? If yes, which method was used and was it including data normalization?
2. Does the study include radionuclides analysis and provide an estimate of the S.A.R.? If yes, which method was used?
3. Does the study provide ancillary parameters (i.e., vertical concentration profile, granulometry, mineralogy, organic content) useful for the evaluation of sediment variability? If yes, which ones?

The evaluation criteria were used in order to establish a dataset of robust and comparable data, to reduce data variability and to increase the representativeness of data for the entire lagoon. Selected studies were only those in which all 3 criteria were met (i.e., YES for the 3 questions).

2.3   Comparison between collected dataset, definition of new background values and confrontation with former background values

A comparison was made between the distribution of the sRDC and lBV dataset data in order to highlight main similarities and differences. Environmental Quality Standards (EQS) and similar benchmarks (i.e. L1) for metals available from national regulations were used as a comparison for the distribution of the background values collected from the literature and radio-dated cores (i.e. lBV and sRDC datasets, respectively).

More specifically, we selected as reference values for this comparison the Environmental Quality Standards for sediments set in Italy under the context of the Water Framework Directive 2000/60 (D. Lgs. 172/2015) and the sediment benchmarks L1 (National chemical reference levels[8]), set in Italy for sediment

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[8] The Chemical Level L1 is the concentration of a certain substance present in the sediment matrix, mixed with other possible contaminants, at which generic toxic and bioaccumulation effects are expected with low probability.

management and defined as concentrations that are unlikely to cause a toxic effect in sediments (Decreto 173/2016). It is worth to note that, according to the Decreto 173/2016, L1 values can be modified on a site-specific basis, and specifically considering local sediment background conditions. The EQS and L1 values set in Italy to support sediment assessment for metals considered in this work are reported in Table 2.1.

Table 2.1 Environmental Quality Standards (EQS) expressed as an annual average value (D.Lgs. 172/2015) and sediment benchmark (L1) (Decreto 173/2016)

As*°	Cd*°	Cr(tot)*°	Cu°	Hg*°	Ni°	Pb*°	Zn°
mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw
12,0	0,30	50,0	40,0	0,30	30,0	30,0	100,0

Note:

*EQS-AA set in Italy under the WFD (D.Lgs. 172/2015)

°L1 set in Italy for sediment management (Decreto 173/2016)

The obtained dataset is extensive (prepared based on several studies), therefore, due to the overall uncertainty related to data elaboration and the need to find a simple and robust statistical test, it was decided to adopt a statistical procedure to determine the new background values.

In the work of Matschullat et al. (2000) the 2σ method is mentioned as a valid and robust statistical approach among others tested by the authors for the quantification of background values. For this reason, the iterative 2σ method proposed by Matschullat et al. (2000) was applied to the sRDC dataset to derive "new Background Values"(nBV) for the lagoon of Venice. The 2σ-technique aims to derive realistic data for the geochemical background and to define the background values by approaching a normal range distribution. Mean and standard deviation are calculated for the original data set. All values beyond the mean±2σ interval are omitted. This procedure is repeated until all remaining values lie within this range.

For the sRDC dataset, the mean value, the standard deviation (σ) and the 90°and 10° percentiles were calculated as general statistical descriptors. In order to reduce the variability of the distribution, it was decided to remove outlier data above and below 75° and 25° percentiles according to Romano et. al. (2015) (who performed a simplified procedure with respect to Apitz et al., 2009) and in order to reduce uncertainty and sample sediment heterogeneity. Then the 2σ methodology was applied: on this reduced dataset, all values beyond the mean±2σ interval were omitted. This procedure was repeated a second time until all remaining values lied within this range. The mean±2σ calculated from the final "sRDC" is considered to reflect the geogenic background (Matschullat et al., 2000). With this procedure, the background value is defined as the upper limit of the sub-dataset variability (i.e. the "nBV"), defined by the mean+2σ. In the present study, the "nBV" is considered, according to Matschullat et al. (2000), as the upper threshold of the "sRDC" concentrations after the second iteration, where 97% of cases lies under such threshold.

Finally, the nBV were compared to the sRDC and lBV: for both datasets, the mean, standard deviation (σ) and minimum and maximum values of the distribution were calculated. As a reference for the proposed background values, we compared also the values proposed by Apitz et al. (2009) and the national benchmarks (i.e. EQS-AA and L1 reported in Table 2.1). The comparison of the nBV concentrations with the Italian benchmarks (EQS and/or L1) is more noticeable if a confidence interval of the EQS(L1) value is set. For this reason the following thresholds are defined: the nBV can be confirmed if the value is the same (confidence interval ±10% of the EQS(L1)), the nBV value is statistically similar if the value falls in the confidence interval of ±10%<EQS(L1)<±50% and the nBV concentration is significally different if the value is >±50% of the EQS(L1).

3   Results and discussions

3.1   Literature review and data sorting for the lagoon of Venice

The literature review identified seven articles proposing background values derived from radio-dated cores data, seven documents proposing background values not derived from radio-dated cores data and four documents reporting radio-dated cores data with no derivation of background values. Bibliographic references are included in the Bibliography and a brief description of such studies is reported in Annex A, providing the chronology of the main sediment studies found in literature, a summary of temporal evolution of sediment quality in the Venice lagoon and a summary of the environmental complexity of the Venice lagoon and morphological characteristics. Moreover, in order to offer an overview of the methods used in each of the selected literary works, table AP1 (in Annex A) reports information regarding the analytical methods used to determine: i) metal concentrations in sediments; ii) isotopes used for the radio dating of cores.

The two datasets resulting from the literature review included in total 143 entries: 111 layers (chemical concentration in sediment deposited pre-1910) for the RDC dataset and 32 entries (background values) for the lBV dataset. Table 3.1.1 reports information about the spatial distribution of data included in the two datasets, referring to investigated geographical area of the lagoon (i.e. N-North, CN-Central-North, C-Central, S-South) and lagoon morphologies (i.e. shallow water or salt marsh) studied with sediment core sampling or for background values derivation.

As can be observed in Table 3.1.1, there is a considerable difference in the number of entries between the RDC and the lBV dataset; additionally, information regarding N and CN areas of the lagoon are abundant whilst C and S areas are less studied. Indeed, articles and reports published before the 1999s often refer to values related to a specific position in the lagoon basin, mainly northern and central-northern basins.

Regarding the morphology, it can be observed that shallow waters morphologies are well represented for both the datasets, while saltmarsh morphologies are generally less studied and were investigated mainly in the northern basin, with the exception of three cores collected in the southern basin.

Table 3.1.1 Spatial distribution of data included in the RDC and IBV datasets, in relation to geographical areas of the lagoon (i.e. N-North, CN-Central-North, C-Central, S-South) and lagoon morphological units (i.e. shallow water or salt marsh).

Basin	RDC dataset		IBV dataset	
	shallow water	salt marsh	shallow water	salt marsh
N	43	13	13	1
CN	43	0	17	0
C	5	0	1	0
S	4	3	0	0

3.2   Data quality critical evaluation

The quality of data present in the RDC dataset was evaluated according to the criteria set out in paragraph 2.2 and resulted in a reduction of the initial dataset. The new dataset, renamed sRDC dataset, included only samples reported in literature studies that presented specific quality criteria, as the indication of the type of method used for the derivation of the background values (if any), the data normalization process and the presence of sediment concentrations dated prior to the pre-industrial period (i.e. before 1910). The complete evaluation is reported in Table 3.1.2.

Table 3.1.2 Data quality evaluation of the collected articles and reports. (°) works included in the sRDC dataset; (*) works included in the lBV dataset.

Ref.	Area	Does the study provide an estimate of sediment background values? If yes, which method was used and was it including data normalization?			Does the study include radionuclides analysis and provide an estimate of the S.A.R.? If yes, which method was used?		Does the study provide ancillary parameters (i.e., vertical concentration profile, granulometry, mineralogy, organic content) useful for the evaluation of sediment variability? If yes, which ones?			
		Background values	Method	Normalization	S.A.R. (and method)	Radionuclides	Vertical profiles of chemical concentration	Grain size	Mineralogy	Organic content
Donazzolo et al. 1982*	Northern lagoon	YES	Empirical approach - average concentrations below 80 cm sediment depth	NO	YES (n.a)	^{210}Pb	YES	YES	NO	NO
Pavoni et al. 1987a °*	Central-Northern lagoon	YES	Empirical approach - average concentrations deepest layer core (n.3 cores)	YES, considering previous background values (source not specified)	YES (C.R.S.)	^{210}Pb, ^{137}Cs	YES	YES	NO	YES
Pavoni et al. 1987b	Central-Northern lagoon	NO			NO	^{210}Pb, ^{137}Cs	NO	YES	NO	YES
Battiston et al. 1988	Northern lagoon; Central-Northern lagoon	NO			NO	^{210}Pb, ^{137}Cs	NO	NO	YES	YES
Battiston et al. 1989	Northern lagoon; Central-Northern lagoon	NO			YES (C.R.S. model)	^{210}Pb, ^{137}Cs	NO	NO	YES	YES

Frignani et al. 1997°*	Northern lagoon; Central-Northern lagoon	YES	Empirical approach - constant concentrations considering two or more deep core layers (n. 18 cores)	YES, considering Al content	YES C.F.-C.S.; C.R.S.	^{210}Pb, ^{137}Cs, ^{210}Po	YES	YES	YES	YES
Cochran et al. 1998*	Northern lagoon	YES	Empirical approach - constant concentrations in two or more deep core layers	NO	YES (C.R.S.)	^{210}Pb	YES	NO	NO	NO
MAV-CVN 2000a°*	Whole lagoon	YES	Empirical approach - average concentrations deepest layer (n. 12 cores);	YES, considering Al content	YES (C.R.S.)	^{210}Pb, ^{137}Cs	YES	YES	YES	YES
MAV-CVN 2000b°*	Northern lagoon; Central-Northern lagoon	YES	Empirical approach - average concentrations deepest layer (n. 45 cores), dated near the end of the 19th century	Not needed, due to grain size homogeneity	YES (C.R.S.)	^{210}Pb, ^{137}Cs, ^{134}Cs, ^{7}Be, ^{226}Ra	YES	YES	NO	NO
Frignani et al. 2001	Central-Northern lagoon	NO			YES (C.R.S.)	^{210}Pb, ^{137}Cs	NO	YES	NO	NO
Lucchini et al. 2001*	Whole lagoon	YES	Empirical approach - average concentration of 2 or more levels with constant low values in the profile, normalized to Al	NO	YES (n.a.)	NO	YES	YES	NO	NO
Ciavola et al. 2002	Northern lagoon; Central-Northern lagoon	NO			YES (C.I.C.; C.R.S.)	^{210}Pb, ^{137}Cs	NO	YES	NO	NO

Degetto et al. 2005*	Whole lagoon	YES	Empirical approach - concentration observed in sediment core layers dated near the end of the 19th century	NO	YES (C.R.S.)	^{210}Pb, ^{137}Cs, ^{7}Be	NO	NO	NO	NO
Bernardello et al. 2006*	Whole lagoon	YES	Empirical approach - metal concentrations in the deepest layer of radio dated cores (pre-industrial values); from reference values (Pavoni et. al., 1992)	NO	NO	NO	NO	NO	NO	YES
Apitz et al. 2009*	Whole lagoon	YES	Statistical analysis considering chemistry data from n. 70 cores from the MAV-CVN, 2000b	YES, considering Al content	NO	^{210}Pb, ^{137}Cs	NO	YES	YES	NO
Gieskes et al. 2011	Northern lagoon; Central-Northern lagoon	NO	NO	NO	NO	NO	YES	NO	NO	YES
MAV-CVN, 2011	Whole lagoon	NO	NO	NO	YES (C.R.S.)	^{210}Pb, ^{137}Cs	YES	YES	NO	YES
Zonta et al. 2018°	Whole lagoon	YES	Empirical approach - metal concentrations in the deepest layer of radio dated cores (pre-industrial values)	Not needed, due to grain size homogeneity	YES (C.F.; C.I.A.; C.R.S.)	^{210}Pb, ^{137}Cs	YES	YES	NO	YES

According to Table 3.1.2, the works selected for the sRDC dataset are the following:

- Pavoni et al.,1987, n. of sample cores: 3, authors estimated also a background value referred to pre-industrial concentrations;
- Frignani et al., 1997, n. of sample cores: 18, authors estimated also background values referred to pre-industrial concentrations;
- MAV-CVN 2000a, n. of sample cores: 12, authors calculated also background values as pre-industrial concentrations;
- MAV-CVN 2000b, n. of sample cores: 45, grain size-homogeneous cores (normalization not required), background values estimated as pre-industrial concentrations;
- Zonta et al., 2018, n. of sample cores: 12, authors did not directly report background values.

Among the selected works, the approach mostly used for the determination of background values is the empirical approach, based on the determination of the deepest layers of sediment cores. The only exception is the approach proposed by Apitz et al. (2009), based on a statistical analysis of a large dataset of sediment cores. Because of the application of such robust approach, the background values proposed by Apitz et al. (2009) can be considered as a reference among those included in lBV, i.e. the most representative ones for the entire lagoon.

As a final observation, all the collected background values exclusively refer to local pre-industrial concentrations (before 1910); indeed, none of the available articles and documents report data, information and/or analysis of deeper sediment layers (i.e. > 50-80 cm depth) or any reference to background values in ancient periods (i.e. before the 18th-19th century).

3.3   Comparison between collected dataset, definition of new background values and confrontation with former background values

The comparison between the background values proposed in the literature (lBV dataset) and the data available from the selected radio-dated cores (sRDC), composed by 68 layers, is graphically presented in Fig. 3.2.1. Descriptive statistics of the datasets are available in Annex A-Table AP2.
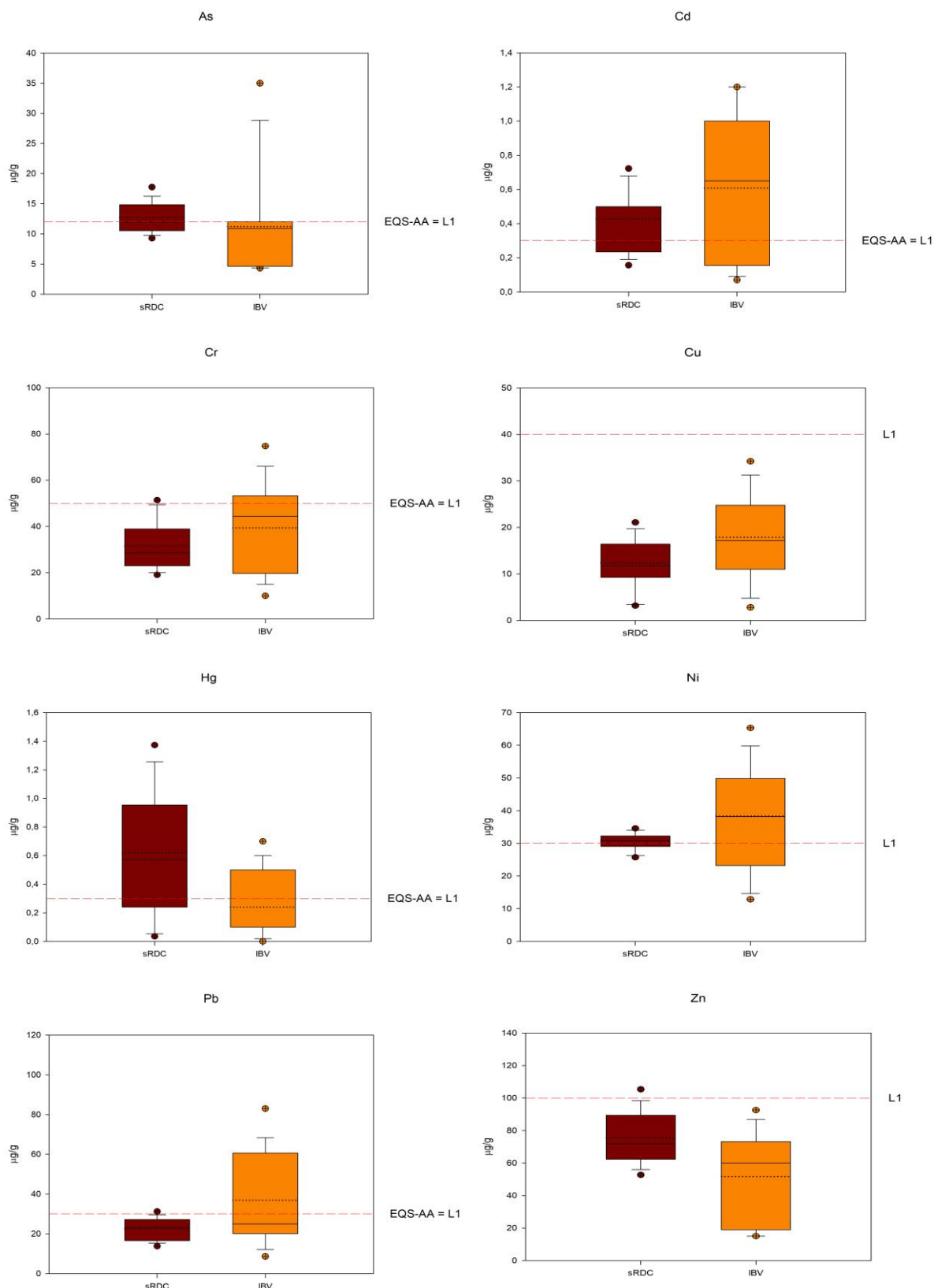
Figure 3.2.1. Charts presenting the comparison between the data from the selected radio-dates cores (sRDC) and the literature background values (lBV) for eight metals. Red-dashed line shows the Italian sediment benchmarks (Environmental Quality Standard and/or L1 value). Dotted line inside the boxplot shows the mean value. Black line shows the median value. Crossed-circles show 90° and 10° percentile.

In this comparison, it appears that the considered sediment benchmarks are generally exceeded (considering the mean concentration values) for the following metals:

- As and Hg: the mean values of sRDC exceed the sediment EQS-AA and the L1 values, while the mean values of lBV are below these benchmarks; the 75th percentile is above the benchmark for both the dataset;
- Cd and Ni: the mean values and the 75th percentile of both sRDC and lBV exceed the sediment EQS-AA and/or the L1 values;
- Cu and Zn: both the mean value and the 75th percentile are below the L1 benchmark;
- Cr: the mean value is below the benchmark but the 75th percentile exceed the EQS-AA benchmark;
- Pb: the mean value and the 75th percentile of lBV distribution exceeds the sediment EQS-AA and the L1 values, while the mean value and the 75th percentile of sRDC is below such benchmarks.

The analysis of the distribution reveals that, for some elements, geochemical enrichments from natural or pre-industrial (i.e. before 1910) origin are possible. On the other side, the EQS(L1)are in some cases below the mean value of the dataset distribution.

As specified in paragraph 2.2, the calculation of new background values in this work was carried out on the sRDC dataset, which has been subject to the reduction of data variability (outliers) for the determination of background values through the 2σ statistical method proposed by Matschullat et al. (2000). The "newly derived Background Values" (nBV[9]) are presented in Table 3.3.1.

Table 3.3.1 New background concentrations of certain metals (nBV) compared with i) the mean (±σ) of the background values collected from the scientific literature (lBV), ii) the background values proposed by Apitz et al. (2009), and iii) the EQS(L1) values declared by the Italian legislation (Legislative Decree no. 172/2015 and Decree no. 173/2016).

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	
	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	
nBV	**15,9**	**0,7**	**36,6**	**18,4**	**1,1**	**33,7**	**30,0**	**97,3**	2sigma
lBV	11,2 (±8,3)	0,6 (±0,4)	39,4 (±20,1)	17,9 (±9,3)	0,2 (±0,2)	38,4 (±15,9)	36,9 (±23,9)	51,7 (±29,6)	Mean (±σ)
Apitz at al., 2009	5-35	0,1-1,2	4-80	5-40	0,2-0,3	5-45	5-50	40-130	Range
EQS(L1)	12,0	0,3	50,0	40,0	0,3	30,0	30,0	100,0	

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[9] Considering the sRDC dataset, it is important to underline that the newly derived background values are referred to fine particle size (<63 µm), since the sRDC core data are characterized in the bottom layers by an elevated percentage of fine particle size sediments (average value of 87,5%).

According to Table 3.3.1, for some trace elements such as As, Cd, Cr, Cu, Ni, and Pb, nBV are in good accordance with lBV mean(±σ), except for Hg and Zn concentrations which are higher than lBV mean(±σ) values. For Zn, nBV results to fall between the minimum and maximum values of the distribution of the lBV dataset while Hg exceed the maximum value of the lBV distribution (minimum and maximum values are reported in Annex A-Table AP2).

Similarly, the nBV values fall between the range of concentrations proposed by Apitz and colleagues (2009), except for Hg concentratios. However, it must be observed that the range of values proposed by Apitz et al.(2009) is quite wide if compared with the lBV mean(±σ) range, with the exceptions of the Hg range (which is very narrow) and the Cd and Pb ranges (which are comparable).

The comparison of the nBV concentrations with the Italian benchmarks (EQS and/or L1) results as following:

- The metal elements with a confirmed nBV concentration are Cr, Pb, Zn (the nBV falls in the confidence interval ±10% of the EQS(L1));
- The metal elements with a statistically similar nBV concentration are As and Ni (the nBV value falls in the confidence interval of ±10%<EQS(L1)< ±50%);
- The metal elements with a significant difference in the nBV concentration are Cd, Cu and Hg (the nBV value is >±50% of the EQS(L1)).

The nBV concentration for Cd and Hg are well above the EQS(L1) value while the Cu concentration is well below the EQS(L1). It must be observed that:

- the dataset presents an unevenly geographical distribution of samples: the number of core samples available for the C and S basins are very few in the dataset and their values are, on average, lower than those available for the N and CN basins. So, it can be questioned if the Cd and Hg values in the N and CN basins can be considered representative of the whole lagoon or if the N and CN basin may have been influenced by past activities and other factors present also in the pre-industrial period (before 1910);
- the enrichment of Hg in the sediment cores of pre-industrial period could be considered representative, as it is probably influenced by historical human activity in the study area and the drainage basin (ARPAV, 2016).Possible enrichment of Hg could derive from biogeochemical complexities related to the mercury cycle and methylation as well as from the intake of this element from the Adriatic sea, where the concentration is enriched as a result of the historical mining extraction in the Slovenian mine of Idrija (Covelli et al., 2013).

4   Conclusions

This study investigated available data from vertical radio-dated sediment cores layers and previously identified background values for a set of selected trace elements, in order to determine the metals concentration variability before the local industrial period (prior to the year 1910) in the lagoon of Venice. The definition of background values is useful to support sediment data evaluation and time trend analysis and to understand the extent of anthropogenic influence on the chemical status of the lagoon. A reliableevaluation of sediment quality is indeed crucial for the lagoon management and especially to allow the reuse of dredged sediments while preserving the quality and the overall biodiversity of the lagoon ecosystems.

Task T2.1.1.2 included the collection and critical analysis of available sediment studies conducted in the Venice lagoon over the last 30 years, with a focus on those including the determination of concentration profiles of metals in radio-dated sediment cores and/or estimation of background values for metals from non-radio dated sediment cores (i.e. statistical analysis). Existing data were organized in two different datasets, distinguishing background values reported in available studies and scientific papers (composed by 32 entries and named lBV dataset), and metals concentration observed in the local pre-industrial (i.e. before 1910) period (composed by 111 layers of sediment cores dated before the year 1910 and named RDC dataset).

The RDC dataset was then subject to a criticalevaluation, in order to select the most robust and representative studies (sRDC dataset, composed by 68 layers), used for the application of a statistical method aimed at identifying new Background Values (nBV). The use of a statistical approach on the empirical dataset was selected with the purpose of reducing the variability of data distribution and the uncertainty related to data quality. The analysis of the distribution of metal concentrations (considering both lBV and sRDC) reveals, for some elements (i.e. Hg) , geochemical enrichment; for some other metals (i.e Cd), the lBV and sRDC datasets show exceedance of the sediment EQS-AA.

From the comparison of the nBV concentrations with the lBV mean concentrations it may be observed that, the nBV values are similar to the lBV mean($\pm\sigma$) values, except for Hg and Zn concentrations which are higher than lBV mean($\pm\sigma$) values.

All the nBV values falls between the range of concentrations proposed by Apitz and colleagues (2009), except for Hg concentration that is higher than the proposed range.

Respect the EQS(L1) comparison, the background concentration are i) confirmed for Cr, Pb, Zn (the nBV falls in the confidence interval ±10% of the EQS(L1)), ii) statistically similar for As and Ni (the nBV value falls in the confidence interval of ±10%<EQS(L1)< ±50%) and iii) significantly different for Cd, Cu and Hg (the nBV value is >±50% of the EQS(L1)).Although this study presents a certain level of uncertainty (e.g. limitations due to the use of data collected from different studies), the results suggest that Hg and Zn are ubiquitous trace elements also in the local pre-industrialsediments (i.e. before 1910), likelydue to the inputof solid material from both the drainage basin (ARPAV, 2016) and the coastal northern Adriatic sea.

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6   Annex A

Literature review for background values in the lagoon of Venice

In order to evaluate the background values available for trace metals in the Venice Lagoon, a literature review was performed to identify main publications and technical reports investigating spatial and temporal distribution of metals in sediments, mainly based on the observation of concentration in sediment core profiles.

Chronology of the main sediment studies found in literature

The oldest studies date back to the 1980s (Donazzolo et al., 1982, Pavoni et al., 1987a; Pavoni et al., 1987b; Battiston et al., 1989) and were intended to reconstruct the historical evolution of sediment pollution related to industrial development in the area of Porto Marghera. Specifically, these studies investigated the pre-industrial background levels (i.e. before 1910) for metals and estimated sedimentation rates under present and past conditions. The sampling sites were located in areas considered strongly influenced by Porto Marghera as well as in those located further away from this source (Northern Lagoon). Also the later studies (MAV-CVN, 1991a; MAV-CVN, 1991b; Frignani et al., 1997; Cochran et al., 1998; Marcomini et al., 1999; MAV-CVN, 2000a; MAV-CVN, 2000b; Frignani et al., 2001) investigated, as area of interest, the central-northern lagoon and the northern lagoon, with focus on the shallow waters between Venice and the mainland. These studies provided scarce information for the central and southern areas of the lagoon.

The trends of trace elements in the sediments of industrial canals of Porto Marghera and the background values of metals have been determined more recently with the studies of MAV-CVN (2000b) and Frignani et al. (2001). Specifically, the MAV-CVN (2000a and 2000b) projects included the sampling of several dated sediment cores, providing a good dataset considering the overall number of samples collected; additionally, these projects provided information also for the central and the southern lagoon. The MAV-CVN dataset (2000b) served as the basis for different articles, with focus on the critical analysis of the method of radiological dating (Degetto et al., 2005) and the investigation of statistical methods for derivation of the background values (Apitz et al., 2009).

With a focus on the lagoon sediment quality, the QSEV 2011 project (MAV-CVN, 2011) reported a database extended to the entire lagoon, investigating metal concentrations at different depths. This study included also radioisotopic analyses (aimed to date a subset of sediment cores) and the determination of grain size. The results highlighted the lagoon erosion processes. Sediments erosion and deposition in the lagoon has been recently critically reviewed in Zonta et al. (2018). Some other authors used the Venice lagoon background values or radio dated cores for different research purposes, as i) the identification of exceptional flood events (high water) using radionuclides; ii) the assessment of sedimentation rates using benthic foraminifera (Serandrei-Barbero et al., 2006); iii) the evolution of sediments pollution in the Venice lagoon (Bernardello et al., 2006; Gieskes et al., 2011; MAV-CVN, 2004).

Considering the overall available studies, the set of metals most frequently considered by the authors mentioned above consists of Hg, Zn, Cd, Pb, Cu, because considered closely related to past and present industrial activities in the Porto Marghera area (Donazzolo et al., 1984; Pavoni et al., 1987a). Spreading of contaminants from the industrial zone towards the city of Venice and the sea inlet of Lido has been reported (Donazzolo et al., 1984) and, according to radio dated cores, a temporal increase in metals concentration was found to be chronologically related to the development of the industrial area itself (Pavoni et al., 1987; 1992).

Summary of the environmental complexity of the Venice lagoon and morphological characteristics

For the assessment of background values, it must be kept in mind that the lagoon of Venice exhibits an extreme morphologic variability. As an open basin, it undergoes a tidal effect or rather, at every tidal cycle, it exchanges with the sea a water volume approximately equal to the same lagoon volume (Degetto et al., 2005). Similarly, the suspended particulate matter in the water column is exchanged at the mouth entrances (input+output), in amounts to approximately millions of kg/day (MAV-CVN, 1991a). Moreover, the amount of airborne sediments exchanged with the sea represents an important fraction compared to that deposited directly by the atmosphere at the lagoon surface (MAV-CVN, 2000b). It should be noted that the lagoon can be divided into four sub-basins, characterised by distinctive hydrodynamic behaviour. However, because the past fluvial diversion, the lagoon basin includes a few river inputs along its internal perimeter, which could be of some importance only in connection with episodic although very large flooding events (Degetto et al., 2005). Locally, in different areas of the lagoon, the sediment floor of the Venice Lagoon have undergone changes in their particle size composition, as highlighted in the "Project 2023 Linea F" (MAV-CVN, 2000c), which may have led to positive or negative changes in the content of metals. Recently, Degetto et al. (2005) and Zonta et al. (2018) have assessed depositional and/or erosional processes in the Venice lagoon, as identified with bathymetric methods. Radioisotopes (210Pb, 137Cs, 7Be) were used to estimate sediment deposition rates and provide tracers of depositional and erosional conditions. To avoid false interpretations, the data should be subjected to normalization operations with respect to parameters that can determine natural variations of the values of the metals (see paragraph 1.3.2). Unfortunately, in some of the selected works, normalization was not performed either the available dataset allows the normalization, due to the absence of ancillary parameters (e.g. grain size, Al values, etc). Therefore, the comparison of the metals background values must be carried out with caution because some variations could be attributed to granulometric and mineralogical changes rather than to modification of the contributions from the sources. From the studies cited above, it emerges that the application of the methods of radio-dating can highlight the presence of erosion phenomena in the lagoon, consequently, the assessment of metals background concentration in the sediments can be uncertain and misleading in the absence of radio dated cores.

Summary of temporal evolution of sediment quality in the Venice lagoon

In the Venice lagoon, between the land and the city of Venice, the beginning of industrial releases can be dated back to the 1930s and determined high concentrations of metals in the surface sediments (MAV-CVN,2004). In the examined literature, the maximum levels of concentration and flow of metals were referred to time intervals not always coinciding, due to the different location of the investigated area with respect to the polluting source. Pavoni et al. (1987a) dated the maximum concentration of Zn in Porto Marghera in the 1940s; the peak of the Hg is subsequent and referable to the 1950s. The authors' considerations were carried out on the values of the normalized metals with respect to the background values proposed in the same study. Battiston et al. (1989), analysing the profile of Pb, Zn and Cu along with sediment cores, determined that the maximum intake occurred in the period 1950-1960, corresponding to the maximum expansion of the industrial area. Marcomini et al. (1997) dated the peak concentrations of Hg, Zn, Cd, Pb and Cu around the 1960s in cores sampled from the area in front of Porto Marghera. Frignani et al. (1997), using three cores sampled in the area facing Campalto, identified a strong increase of Zn, Cu and Pb since the 1940s, as a direct effect of the metallurgical activities started in Porto Marghera in the mid-1930s, with maximum concentration reported in the mid-1970s. Also in the report "Project 2023 line B and line C" (MAV-CVN, 2000a, b) it was shown that metals concentration increased from 1930-1940 up to a maximum in the 1960s-1970s. In the following decades, the values of these metals decreased considerably as reported by the study of (Bernardello et al., 2006).

Overview of the methods used in the collected literature

In the Northern Lagoon, the most investigated area was Palude di Cona and the mouth of the Dese river (Donazzolo et al., 1982; Frignani et al., 1997; Cochran et al., 1998; MAV-CVN, 2000a, b); some saltmarsh sites have been considered in the "Project 2023" line C (MAV-CVN 2023- Linea C, Frignani et. al. 2000b), by Cochran et al. (1998) and by Lucchini et al. (2002) to determine the deposition of metals from the atmosphere. Some authors have highlighted a variable increase in concentrations of Pb, Zn, and Cu towards the surface layers and a subsequent decrease. Frignani et al. (1997) dated the beginning of the contribution of the industrial area to the 1930s. Exceptions are Hg and Cd which show an increase up to the present day (Frignani et al., 1997; Cochran et al., 1998; (MAV-CVN et al., 2000a). Cochran et al. (1998) concluded that in the areas of the northern lagoon the atmospheric contribution is relevant for Pb and, to a lesser extent, for Zn, while atmospheric Cu and Ni can contribute up to 30-40% of the total sediment concentration.

Table AP1. Analytical methods used for the determination of metal concentration and background values in sediment cores. For the radiometric dating of sediment cores, alongside the ^{210}Pb and ^{137}Cs, some works also report the use of [7]Be, [134]Cs, [210]Po and [226]Ra. The common method used for the assessment of the sediment accumulation rate (SAR) appears to be the CRS (Constant Rate of Supply). Most of the analysed works use only this approach for the determination of the SAR, while only the works of Frignani et al. (1997), Ciavola et al. (2002) and Zonta et al. (2018) present a comparison and a mix of different approaches for the SAR assessment. As already mentioned earlier, in the sediment cores the principal analysed metal elements were Ag, As, Cd, Co, Cr, Cu, Hg, Ni, Pb, and Zn, although some authors have also extended the analysis to other trace elements (see Lucchini et al., 2001 and Apitz et al., 2009). The instrumentation for trace element analysis has technologically evolved since the 1980s, from atomic absorption spectrophotometers towards the use of X-ray Fluorescence spectrometers, that guarantee greater precision of the analysis.

Authors	Year	Radionuclides	SAR method	Metals	Method	Derivation of Background values	Determination method
Donazzolo et. al.	1982	[210]Pb	n.a.	Hg, Cd, Pb, Cr, Cu, Ni, Co, Zn, Fe	Perkin Elmer Model5000 atomic absorption spemophotometer.	Yes	Metal average concentration in the sediment core layer below 80 cm depth.
Pavoni et. al. (a)	1987	[210]Pb, [137]Cs	C.R.S. model (constant rate of supply)	Hg, Cd, Pb, Cr, Cu, Ni, Co, Zn, Fe	HNO_3 (8N); H_2SO_4, HNO_3, HCl, $KMnO_4$, $K_2S_2O_8$ (Hg); Perkin Elmer Model5000 atomic absorption spemophotometer.	Yes	Metal average concentration in the deepest layer of sediment core n.3.
Pavoni et. al. (b)	1987	[210]Pb, [137]Cs	n.a.	n.a.	n.a.	n.a.	n.a.
Battiston et. al.	1988	[210]Pb, [137]Cs	n.a.	NO	n.a.	NO	n.a.

Authors	Year	Radionuclides	SAR method	Metals	Method	Derivation of Background values	Determination method
Battiston et. al.	1989	^{210}Pb, ^{137}Cs	C.R.S. model	Mg, Al, Si, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, Pb, Br, Rb, Sr	XRF	NO	n.a.
MAV-CVN (a)	1991	^{210}Pb, ^{137}Cs	n.a.	Ca, Mg, Al, Fe, Mn, Zn, Cu, Pb, Cd, Cr, Mo, Ni, Co, As	HNO_3 + $HClO_4$	n.a.	n.a.
MAV-CVN (b)	1991	^{210}Pb, ^{137}Cs	n.a.	Ca, Fe, Cu, Zn, Pb	n.a.	n.a.	n.a.
Frignani et. al.	1997	^{210}Pb, ^{137}Cs, ^{210}Po	Constant Flux-Constant Sedimentation; C.R.S. model.	Si, Al, Ca, K, Fe, Mg, Ti, Pb, Cu, Zn, Ni, Mn, Cr	XRF: Siemens sequential SRS 300.	YES	Constant concentrations in two or more depth sediment core layers.
Cochran et. al.	1998	^{210}Pb	C.R.S. model.	Mg, Cd, Ag, Pb, Cu, Zn, Ni, Mn	HCl (8N); XRF: Siemens sequential SRS 300	YES	Constant concentrations in two or more depth sediment core layers.
Marcomini et. al.	1999	^{210}Pb, ^{137}Cs, ^{134}Cs, ^{7}Be	n.a.	NO	n.a.	n.a.	n.a.

Authors	Year	Radionuclides	SAR method	Metals	Method	Derivation of Background values	Determination method
MAV-CVN (a)	2000	^{210}Pb, ^{137}Cs	C.R.S. model.	As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Zn, Zr	XRF	YES	Metal concentration similar to those found in literature.
MAV-CVN (b),	2000	^{210}Pb, ^{137}Cs, ^{134}Cs, ^{7}Be, ^{226}Ra	C.R.S. model	Pb, Zn, Cd, Ni, Cr, Hg, As, Cu, Mn	EDXRF.	YES	Metal concentration in the sediment core layers, dated around the end of the 19th century.
Frignani et. al.	2001	^{210}Pb, ^{137}Cs	C.R.S. model.	n.a.	n.a.	n.a.	n.a.
Lucchini et. al.	2001	NO	n.a.	As, Ba, Br, Ce, Co, Cr, Cu, Ga, La, Nb, Ni, Pb, Rb, Sc, Sr, Th, V,Y, Zn, Zr	XRF: Philips PW 1480.	YES	Averaging two or more levels with constant low values in the sediment core profile, normalized to Al.
Ciavola et. al.	2002	^{210}Pb, ^{137}Cs	C.I.C model (constant initial concentration); C.R.S. model.	NO	n.a.	n.a.	n.a.

Authors	Year	Radionuclides	SAR method	Metals	Method	Derivation of Background values	Determination method
Degetto et. al.	2005	^{210}Pb, ^{137}Cs, ^{7}Be	C.R.S. model (Goldberg, 1973; Appleby and Oldfield, 1978).	Pb, Zn, Cd, Ni, Cr, Hg, As, Cu	Energy Dispersive Polarized X-ray Fluorescence spectrometer (EDPXRF): SPECTROX-LAB2000 (SN DK 949196).	YES	Metal concentration in the sediment core layers, dated around the end of the 19th century.
Bernardello et. al.	2006	NO	n.a.	Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Zn	HF, HNO$_3$, HCl; Thermo Jarrell Ash Iris/AP ICP-OE spectrometer.	YES	metal concentrations in the deepest strata of radio dated cores (pre-industrial values); from reference values (Pavoni et. al., 1992).
Apitz et. al.	2009	^{210}Pb, ^{137}Cs	n.a.	Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Br, Rb, Sr, Y, Zr, Nb, Cd, Sn, Sb, I, Cs, Ba, La, Ce, Nd, Hg, Pb, Th, U	Energy Dispersive Polarized X-ray Fluorescence spectrometer (EDPXRF): SPECTROX-LAB2000 (SN DK 949196).	YES	Statistical analysis of the concentration in different sediment layers.

Authors	Year	Radionuclides	SAR method	Metals	Method	Derivation of Background values	Determination method
MAV-CVN, Zonta et. al.	2011	^{210}Pb, ^{137}Cs	n.a.	n.a.	n.a.	n.a.	n.a.
Zonta et. al.	2018	^{210}Pb, ^{137}Cs	Constant flux (CF); Constant initial Activity (CA); Constant sedimentation rate (CFCS.)	Al, As, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Zn	HNO$_3$ (8N); plasma atomic emission spectrometry (ICP-AES - Optima 2100DV, Perkin Elmer, USA); Mercury analysis was carried out by cold vapor atomic absorption spectrometry (AAS - Analyst 100, Perkin Elmer, USA).	NO	n.a.

Table AP2. Descriptive statistics of the data from the selected radio-dated cores (sRDC dataset) and the background concentrations available in the literature (lBV dataset) presented in Figure 3.2.1.

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	
	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	
sRDC dataset	12,7	0,4	31,6	12,4	0,6	30,6	22,6	75,3	Mean
	12,0	0,5	28,5	11,8	0,6	31,0	23,3	71,9	Median
	2,6	0,2	10,3	5,3	0,4	2,6	5,6	16,0	Std.dev
	7,9	0,1	18,5	3,1	0,0	24,7	13,1	52,2	Min
	17,8	0,7	52,0	23,2	1,5	35,0	32,8	111,9	Max
	0,4	0,0	1,4	0,7	0,1	0,4	0,8	2,1	Std.err
	0,8	0,0	2,7	1,4	0,1	0,8	1,5	4,2	95% conf
	1,0	0,1	3,6	1,9	0,2	1,0	2,0	5,5	99% conf
	48,0	55,0	57,0	54,0	54,0	47,0	54,0	59,0	Size
lBV dataset	11,2	0,6	39,4	17,9	0,2	38,4	36,9	51,7	Mean
	10,9	0,7	44,5	17,2	0,1	38,2	25,0	60,0	Median
	8,3	0,4	20,1	9,3	0,2	15,9	23,9	29,6	Std.dev
	4,3	0,1	4,0	2,0	0,0	12,5	5,0	13,7	Min
	35,0	1,2	80,0	40,0	0,7	66,9	97,4	130,0	Max
	2,4	0,1	3,4	1,4	0,1	2,6	3,4	4,2	Std.err
	5,3	0,2	7,0	2,7	0,1	5,3	6,8	8,4	95% conf
	7,4	0,3	9,4	3,7	0,1	7,1	9,0	11,2	99% conf
	12,0	16,0	34,0	47,0	19,0	37,0	50,0	50,0	Size