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HarmoNIA

Harmonization and Networking for contaminant assessment
in the Ionian and Adriatic Seas

HarmoNIA methodological proposals.

Part I: Harmonizing monitoring of marine contaminants and sharing data Quality Control procedures

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Contents

1. Introduction

The assessment of chemical pollution and relative mitigation measures, in the Adriatic Ionian (ADRION) Region, is based on objectives defined by the EU Directives (WFD - Water Framework Directive, MSFD - Marine Strategy Framework Directive), the Barcelona Convention protocols (Dumping Protocol, LBS – Land Based Sources Protocol, Offshore Protocol, Prevention and Emergency Protocol, Hazardous Wastes Protocol) and by national level control and prevention plans. For the purposes of their implementation all these legislation and agreements, require specific monitoring programmes which are in place by EU and non-EU Countries, yet with a high level of heterogeneity among them. In this framework, the HarmoNIA project focuses on multilateral scientific and technological cooperation related to the stipulation of monitoring plans, the management of environmental contamination emergencies, to a shared approach to manage, validate and make accessible marine data, and to address existing low coherence and comparability.

The MSFD and the WFD state that countries sharing a marine region or sub-region should adopt a common approach in environmental monitoring, good environmental status definition and assessment. In the Mediterranean, the Ecosystem Approach (EcAp) of the Barcelona Convention requires harmonized and integrated approach for water quality assessment at the regional and sub-regional level. Concerning spatial scales for environmental status assessment, MSFD implementation is primarily based at regional (Mediterranean Sea) or sub-regional level (Adriatic and Ionian Sea) with the possible use of further subdivisions to be included in the Marine Reporting Units (MRU) defined by Member States. Regional or sub-regional cooperation should ultimately assure coherent monitoring programmes and assessment between Member States with agreed and common MRUs.

However, in the Adriatic – Ionian marine sub-regions, the level of coherence and consistency of several EU and regional environmental policies, particularly in the assessment of contamination from hazardous substances (Chemical Status of the WFD; Descriptor 8 of the MSFD; Ecological Objective (EO) 09 of EcAp/IMAP), needs a common implementation (Fig. 1). As a consequence, heterogeneity of monitoring procedures for environmental status assessment, as well as types of substances and matrices monitored, are still open issues in the Mediterranean Region and, in particular, in the area.

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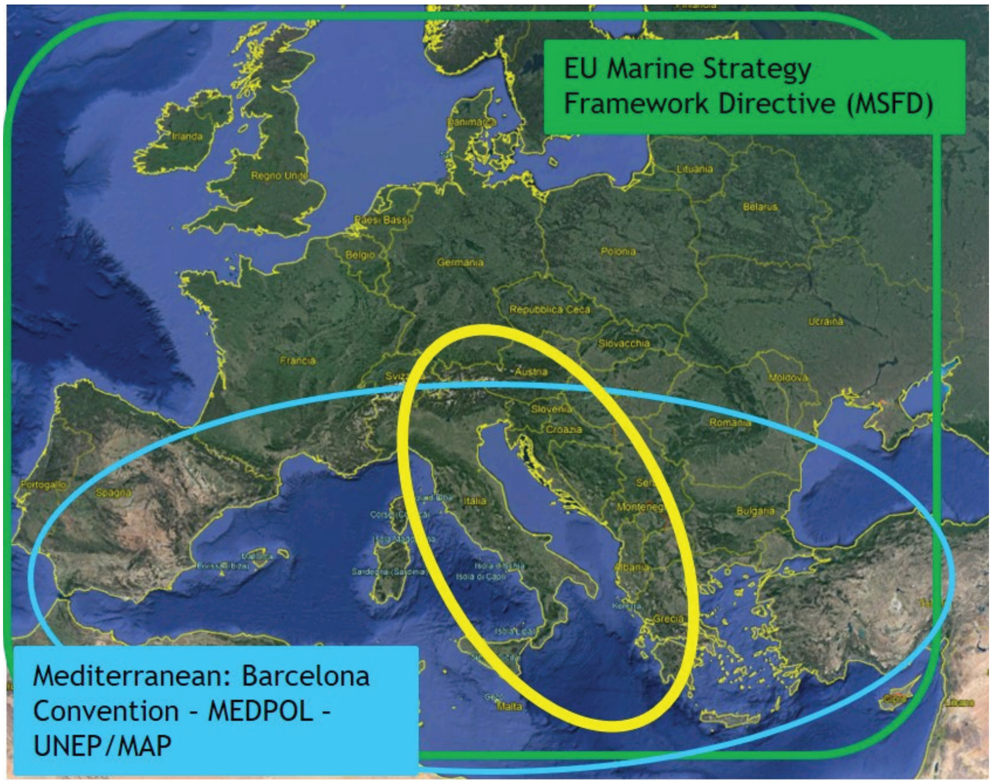


Fig. 1: Legislative tools in the Adriatic – Ionian marine sub-region

Apart from the needs for monitoring for the implementation of the EU Directives, Environmental Impact Assessment procedures (EIA), regulated according to EU/national legislation, require too, specific monitoring programmes in order to evaluate the impact of marine and coastal infrastructures including offshore activities. Although EIA procedures adopted by ADRION countries are similar, the actual monitoring programme implemented in terms of parameters, stations, temporal frequencies and analytical methods are substantially different, undermining equal conditions for economic operators in the area.

Based on these gaps, HarmoNIA project aimed to share experience and knowledge, to propose best practices, and to support the harmonized implementation of marine environmental directives in the ADRION region.

Focusing on contaminants, a review of monitoring and analytical protocols adopted by 6 countries along the Adriatic – Ionian seas was carried out. The information was compared with guidelines included in the European directives and in the documents of the UNEP/MAP (United Nations, 2019), in order to define best practices of monitoring and for data quality assurance and quality control (QA/QC) procedures.

The outcome of this review showed heterogeneity among substances and matrices measured in the different countries, in sampling and analytical methods, as well as in QA/QC procedures. This comparison provided the basis to identify the main targets towards harmonization.

2. Monitoring of contaminants in the ADRION area

Nine institutions from six countries of the ADRION region (Italy, Slovenia, Croatia, Montenegro, Albania and Greece), have contributed to the study, most of them involved in the national monitoring activities. The information gathered was related to the specific chemical substances measured, sampling and analytical protocols and QA/QC procedures.

The analysis focused on a selection of substances (Annex 1), considering contaminants that are routinely monitored for WFD and MSFD assessment objectives. Most of the available data correspond to substances significant either for EU legislation or for Barcelona convention or for both (Annex 2) (Tornero & Hanke, 2016). It is important to note that some of the substances are already considered as emerging Chemicals in the Mediterranean Sea, and included in the chemicals candidate list by the UNEP/MAP (United Nations, 2017) .

The information gathered revealed a high degree of heterogeneity among the countries and indicated a clear need of harmonization concerning monitoring procedures used for the assessment of the environmental status, in order to meet both European and Mediterranean legislation.

Of the total number of chemical substances considered in the study, only ~5% are measured by all 6 countries in sediment and biota matrices and ~14% in water matrix. However, about 60-70% are common substances for at least 4 countries, with the highest percentage in the sediment matrix (Fig. 2).

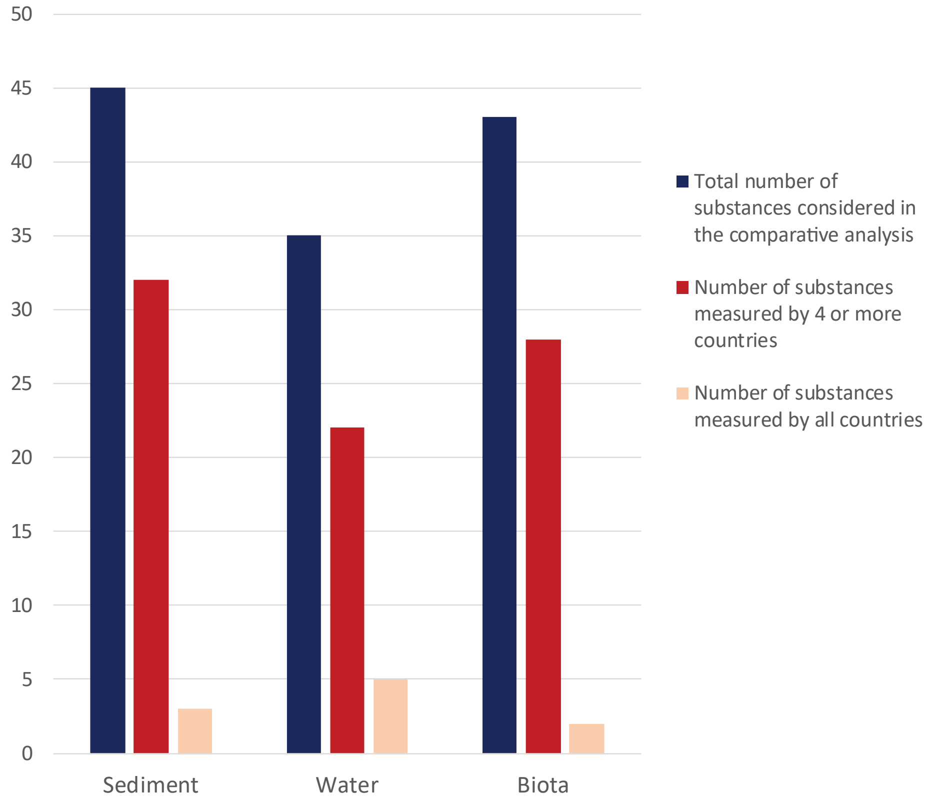


Fig. 2: Number of substances in the different matrices

2.1. Water

Hydrocarbons and heavy metals are the most common groups of substances sampled in the region (Fig. 3). However, only a subset of the substances is measured by more than 4 countries in the region (Fig. 3).

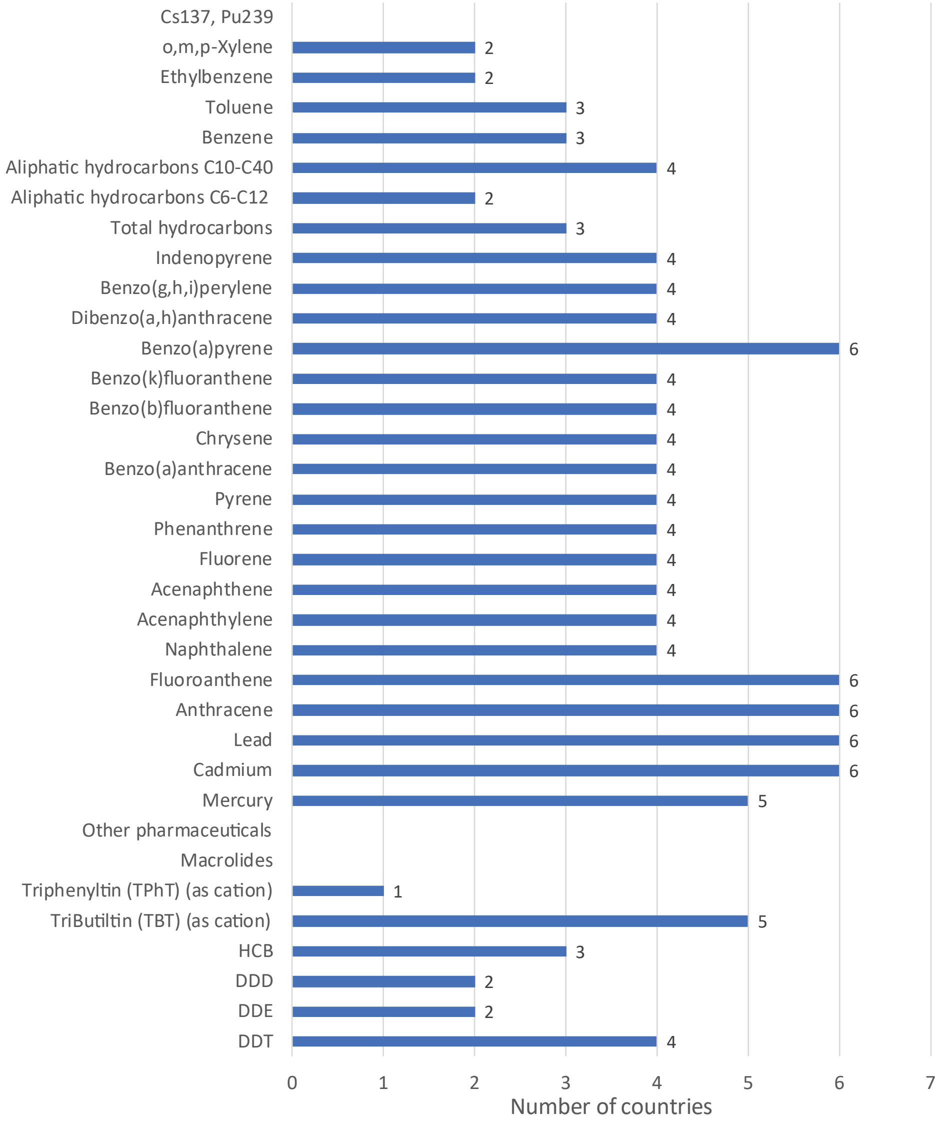


Fig. 3: Main substances measured in water in the ADRION sub-region

Concerning parameters such as sample type (filtered, unfiltered), sampling, storage and analytical methods, limits of detection and quantification, the use of reference materials and intercalibration exercises, it appears that monitoring of waters is more homogeneous than for sediments. For example, the sampling types and methods show a certain degree of harmonization; all institutions use the unfiltered sample for pesticides and biocides, antifoulants and hydrocarbons, and filtered sample (0.45 μm) for heavy metals.

2.2. Sediment

With regard to sediment, the major groups of contaminants that are more commonly measured in the area are hydrocarbons, heavy metals, pesticides, biocides and antifoulants. A detailed list of the chemical substances measured in the ADRION countries is given in figure 4.

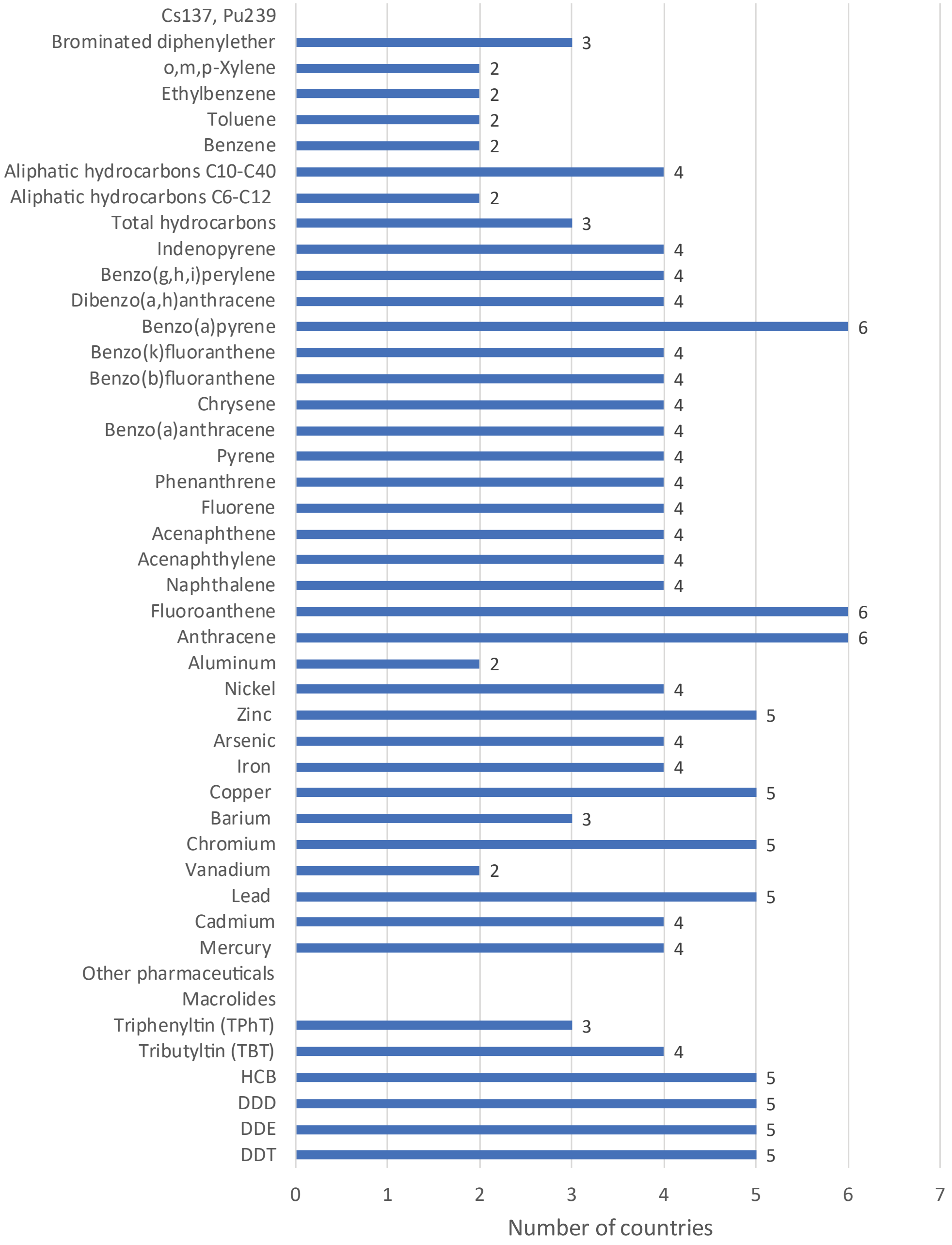


Fig. 4: Main chemical substances measured in sediment in the ADRION sub-region

There is a high heterogeneity regarding the grain size of the sampled sediment as illustrated in Fig. 5, which summarizes the variable grain sizes analyzed per groups of substances among countries. Even within the same country, there are differences between different institutions.

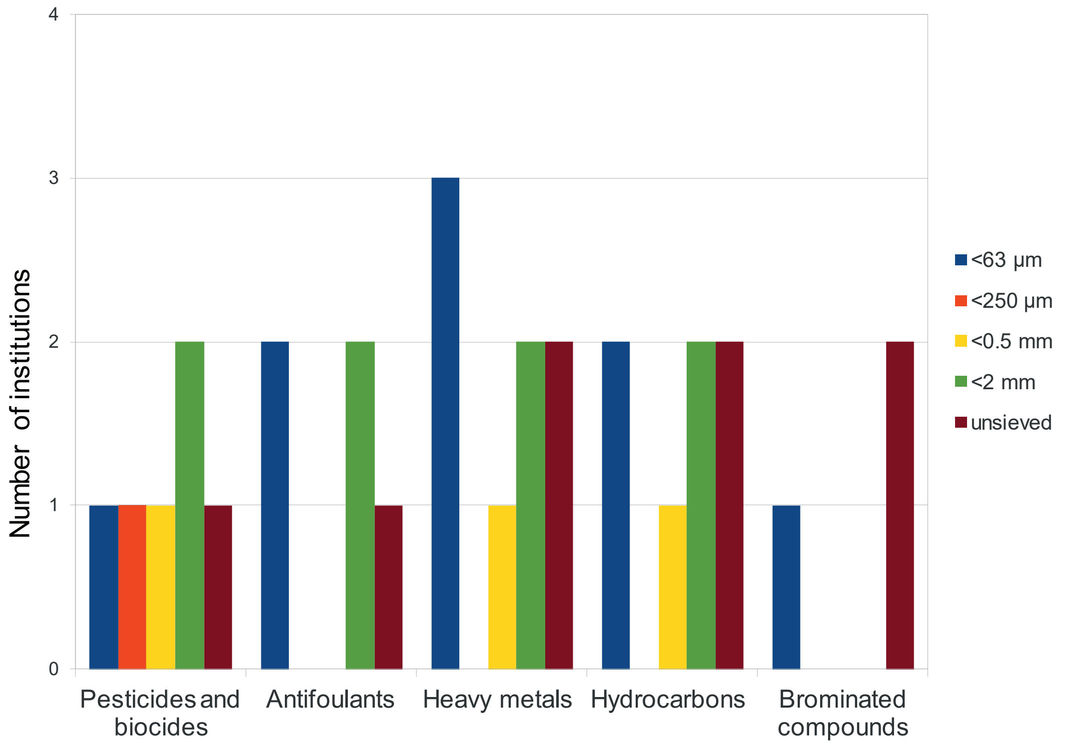
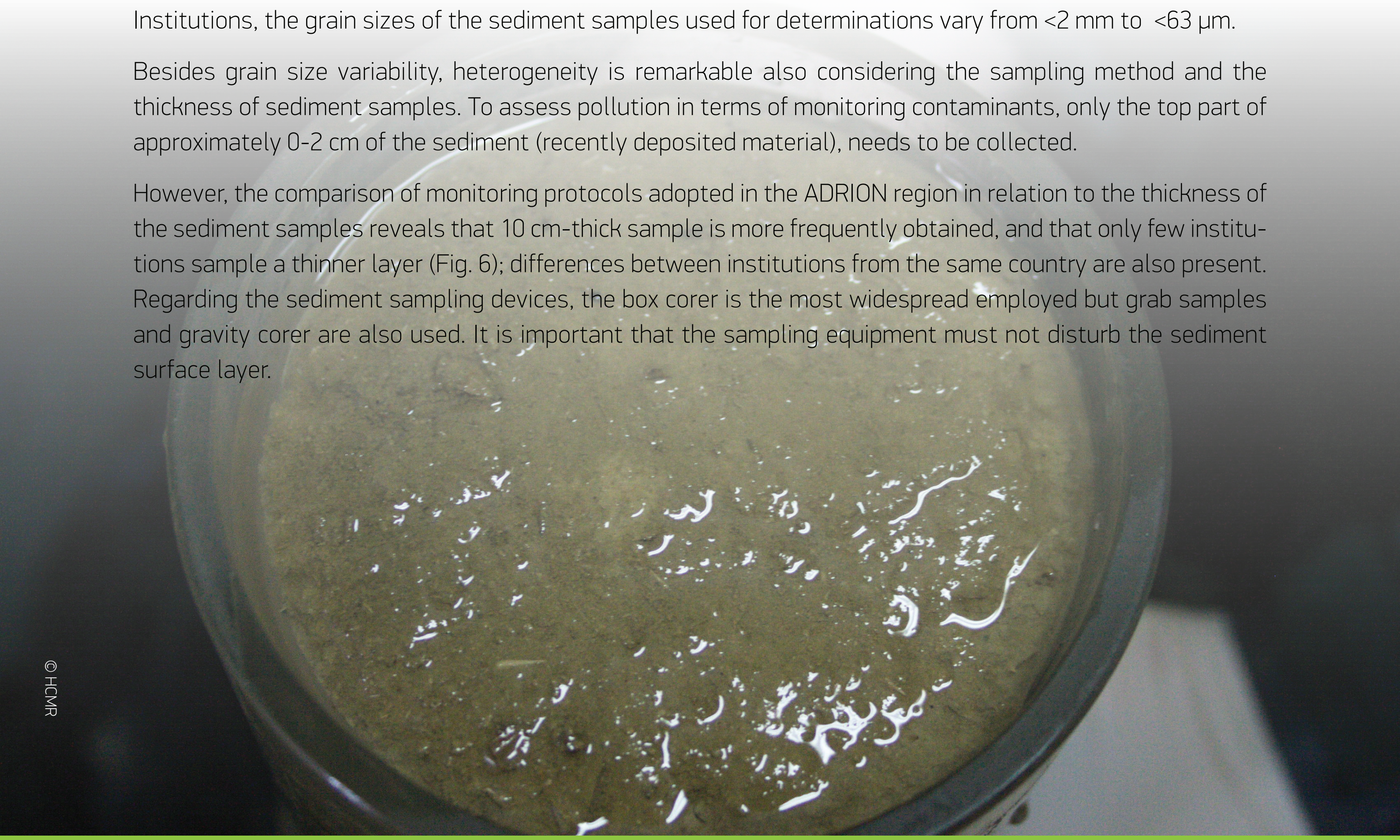


Fig. 5: Sediment grain size

Additionally, within the groups of contaminants, and considering only the substances measured by 5 or more Institutions, the grain sizes of the sediment samples used for determinations vary from <2 mm to <63 µm.

Besides grain size variability, heterogeneity is remarkable also considering the sampling method and the thickness of sediment samples. To assess pollution in terms of monitoring contaminants, only the top part of approximately 0-2 cm of the sediment (recently deposited material), needs to be collected.

However, the comparison of monitoring protocols adopted in the ADRION region in relation to the thickness of the sediment samples reveals that 10 cm-thick sample is more frequently obtained, and that only few institutions sample a thinner layer (Fig. 6); differences between institutions from the same country are also present. Regarding the sediment sampling devices, the box corer is the most widespread employed but grab samples and gravity corer are also used. It is important that the sampling equipment must not disturb the sediment surface layer.



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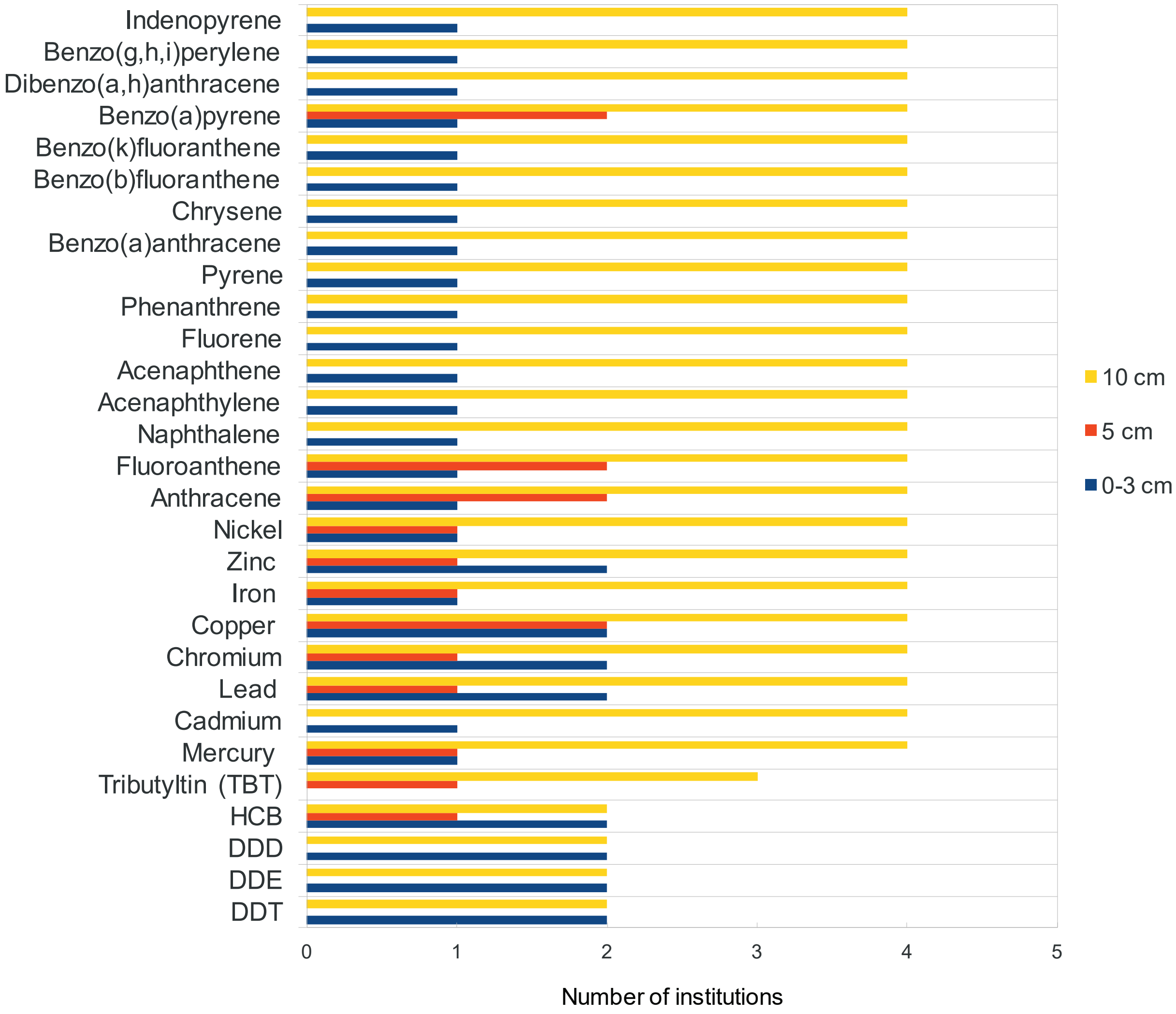

Fig. 6: Sample thickness for the substances measured by 5 or more institutions

Additional aspects considered were: storage, method of analysis, limit of detection and quantification, the use of reference materials, intercalibration exercises. Results from the comparisons among institutions indicate an overall lack of harmonisation that leads to low comparability of the final data.

2.3. Biota

Pesticides, heavy metals and hydrocarbons are more commonly determined in biota. However, only a subset of the substances is measured by more than 4 countries in the region (Fig. 7).

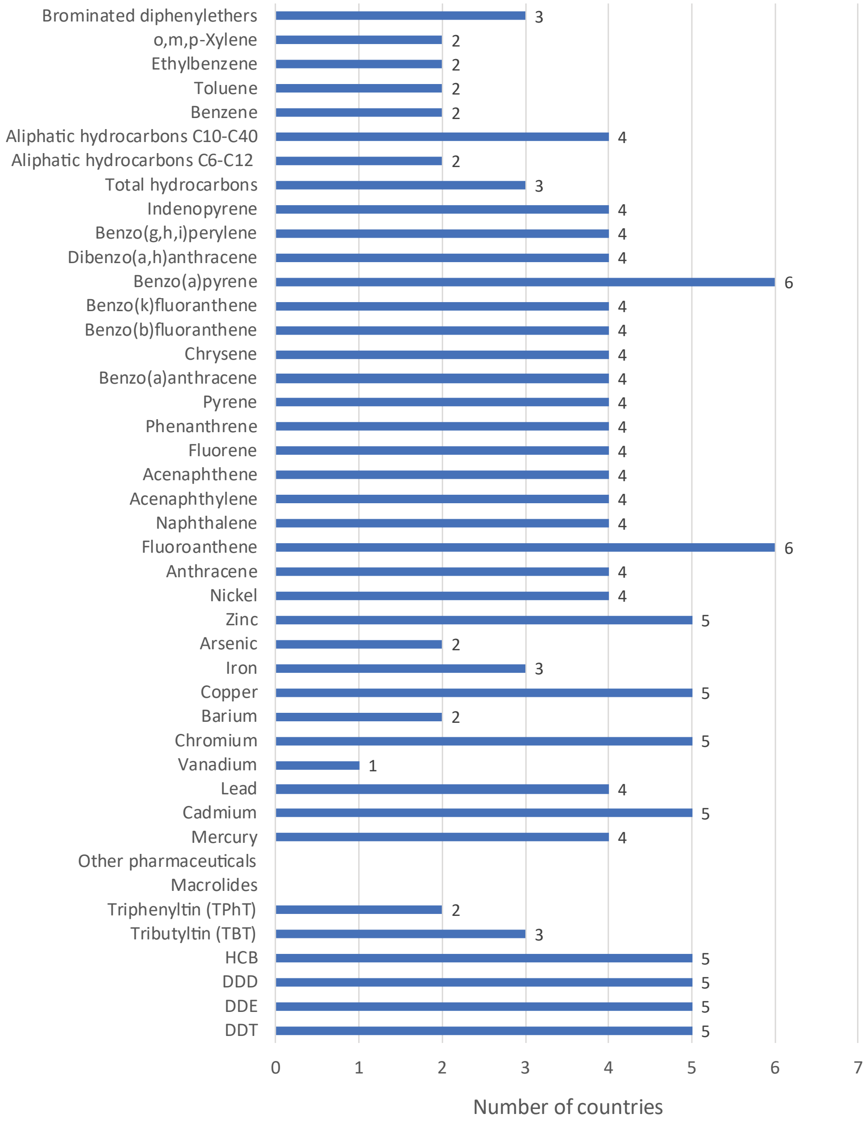

Fig. 7: Main substances measured in biota in the ADRION sub-region

In addition to the observed differences in the substances measured in biota, further inconsistencies were revealed regarding the measurement weight basis (wet or dry), the tissue analyzed, the number of replicates, storage, methods of analysis and limits of detection and quantification, reference materials and exercises of intercalibration.

The use of wet weight basis is more frequent than the dry weight one, except for heavy metals, for which dry weight basis is more frequently used for reporting than the wet weight one. This is expected due to the Environmental Quality Standard Directive, EQSD, and the commission regulation setting maximum levels for certain contaminants in foodstuffs (R.1881/2006) which require that the results on biota measurements are expressed per wet weight of tissue. Differences within some countries are observed, i.e. institutions from same country use different measurement weight basis.

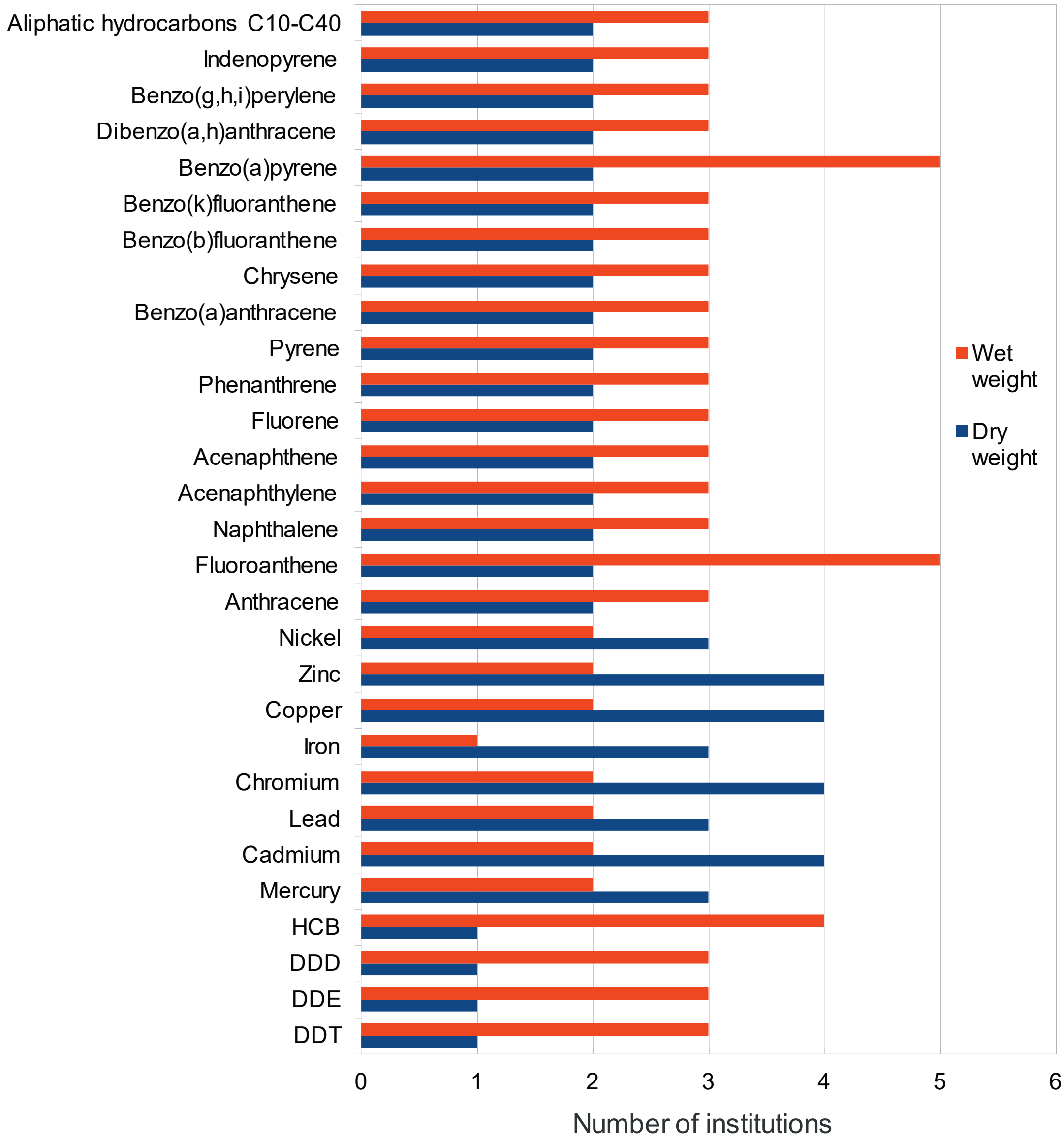

Fig. 8: Measurement weight basis for biota analysis

Mytilus galloprovincialis is the most widespread species used by all the institutions. There is more differentiation on the choice of the analyzed tissue (muscle vs whole body), though the majority of the substances refer to mussel whole tissue (Fig. 9). Differences between institutions of the same country are again present.

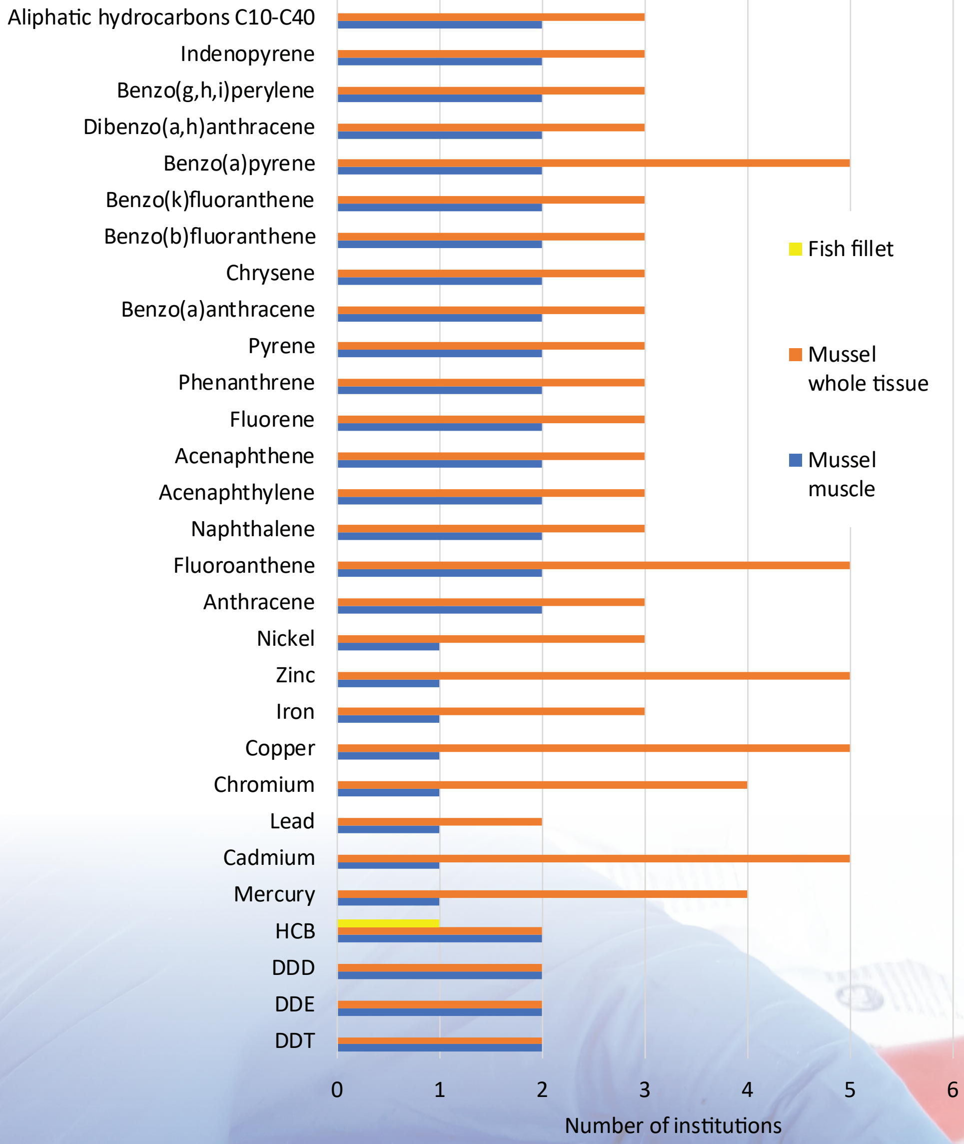

Fig. 9: Species and tissues analyzed

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3. Gaps and needs

Due to the large heterogeneity identified in the ADRION region, a coherent assessment is yet to be achieved concerning the Good Environmental Status (GES) required by the MSFD, the IMAP, and the implementation of the EcAp.

Both the MSFD and the EcAp require harmonized and integrated approaches for environmental status assessment at the regional and sub-regional level. Up to now, threshold values regarding Descriptor 8 (Contaminants) of the MSFD rely mainly on the WFD threshold values which are mostly related to inland waters (EQSD) and EcAp process has just started with the IMAP indicator development, which still has to be completed. As a consequence, the harmonization of the monitoring procedures for the GES assessment is still an open issue in the Mediterranean Region and, in particular, in the Adriatic and Ionian sub-region.

In general, the main gaps and needs identified to allow a coherent assessment of the GES, regarding contaminants, are:

- ☐ The lack of threshold values for sediment, for which, reference values (e.g. Med BACs, US-ERL, TEL, etc.) are commonly used
- ☐ The lack of common thresholds relevant to the MSFD i.e. coastal and open marine waters
- ☐ The absence of common procedures for basin level assessment in UNEP/MAP
- ☐ The absence of inter-calibration exercises in the Common Implementation Strategy (CIS) of MSFD (DG-ENV, 2017)
- ☐ The absence of monitoring of emerging pollutants e.g. pharmaceuticals

In light of the results of the exercise on the comparability of the monitoring protocols used in the ADRION region, there is a clear need:

- ☐ For a common protocol regarding the analytical procedures
- ☐ For monitoring additional pollutants, e.g. radionuclides and pharmaceutical products
- ☐ For harmonization, at sub-regional level, of the list of measured chemical substances
- ☐ For improving the possibility to compare data: i) by increasing the available information (metadata) on sampling - analytical methods/normalization procedures, and/or ii) by harmonization of the protocols. In particular, aspects that need to be harmonized are:
    - Grain size fraction of sediment analyzed
    - Thickness of the sediment layer sampled
    - Measurement weight basis for biota (i.e. have the water content of the soft tissue in order to be able to convert WW to DW)
    - Lastly, more information is needed for the metadata in relation to:
        - ✗ accuracy and reproducibility
        - ✗ use of appropriate limits of detection and quantification in order to assess contamination based on established EQS or background values
        - ✗ reference materials used
        - ✗ inter-calibration exercises

4. Proposed methodologies

Monitoring programmes for the assessment of contaminants in the ADRION Region are planned taking into consideration objectives defined by EU Directives (WFD and MSFD), the Barcelona Convention protocols (Dumping Protocol, LBS – Land Based Sources Protocol, Offshore Protocol, Prevention and Emergency Protocol, Hazardous Wastes Protocol) and national level control and prevention plans. For each of the Barcelona Convention Protocols specific monitoring programmes have been defined by EU and non-EU countries with a high level of heterogeneity between them, with many activities overlapping with those required by WFD and MSFD.

In this framework, the HarmoNIA project focuses on multilateral scientific and technological cooperation related to the stipulation of monitoring plans, the management of environmental contamination emergencies and to a shared approach to manage, validate and make marine data accessible, in order to address existing low coherence and comparability. The following proposed methodologies aim to address monitoring strategies, analytical methodologies and data quality control.

4.1. Sampling and analysis

With the aim to define a methodological proposal for monitoring strategies and analytical methodologies, priority is given to the following main targets of harmonization:

1. Matrix characteristics
2. Measurement units
3. Sampling procedures
4. Indications on sample storage and methods of analysis
5. Indications on LOQ

The proposed methodologies that follow are based on the information collected at ADRION scale and on the references listed at the end of the document.

The proposed methodologies concerning 1 – 4 and LOQ proposals are presented in Annex 3.

As general recommendations, HarmoNIA proposes to perform all activities, from sampling to chemical analyses, according to quality assurance procedures following international standards ISO 9001 and ISO/IEC 17025. The traceability of each step of the process can improve the harmonization of the procedures and favor the comparability among different laboratories, even if it does not ensure, a priori, a better analytical performance.

The use of certified reference materials is recommended for all compounds, in order to achieve the best methodological accuracy and data comparability. However, given the difficulty to provide certified reference materials for water matrix, it is suggested that all laboratories should attend an intercalibration round (e.g. QUASIMEME, Aquacheck, IAEA etc.) for all the considered compounds, also in order to improve the analytical accuracy and reproducibility.

According to WFD and the relative amendments and implementing decrees, the chemical status of a water body is defined considering chemical compounds in waters and biota only. With this background, one of Harmonia's goals is to improve the knowledge in relation to the threshold values for sediment contamination, considering the legislation of participating partners. According to HarmoNIA analysis, in the Adriatic – Ionian region there are no national threshold values for sediment, except for Italy (Italian Legislative Decree 172/2015).

Concerning indications on LOQ for marine waters, QA/QC procedures set in European directives (LOQ, method of analysis, etc.) are proposed, when possible. The values of EQS reported in the 2013/39/EU Directive (annual average values – AA-EQS for "other surface waters" column for waters) are used as the basis for the proposal of LOQ for marine waters. In this context, the proposed LOQ values should be equal or below 30% of the EQS values (according to 2009/90/EC Directive, Art. 4) reported in the 2013/39/EU Directive. For compounds not included in the legislative references, LOQ values were proposed on the basis of information exchanged between HarmoNIA partner through the questionnaires submitted. The choice was based on the lowest values in order to promote the best method performance using a precautionary approach.

Sediment monitoring generally addresses the top layer of the sediment because this layer indicates the recently deposited material and the actual status of pollution. The main criterion for choosing the correct sediment sampling depth (the thickness of the sediment layer sampled) in a specific area is the knowledge of the deposition rate of the sampling site. In theory, the lower the deposition rate, the thinner the layer that one might be interested to sample. With the aim to improve data comparability, it is recommended to sample the top part of the sediment layer, from 0 to 2 cm depth (or preferably 0-1 cm) and taking into consideration the deposition rate in the area, in order to appreciate the recent temporal trends. The measurement of the sedimentation rate would allow to select the most appropriate sampling thickness, possibly even thinner than 2 cm. Even though selection of sampling devices is out of this scope, box corer is suggested as the most suitable tool for soft sediment sampling, as it is designed to minimize sample disturbance.

To improve the comparability, it is better to consider the grain size fraction <2 mm because in sandy sediments the < 63 μm would represent a negligible fraction not representative of the bulk sediments.

For LOQ values in sediment, results obtained by HarmoNIA questionnaires were used. The choice was based on the lowest values in order to promote the best method performance using a precautionary approach.

For the assessment of the sediment contamination the following values were considered, as a reference: Mediterranean Background Assessment Concentrations, BACs (United Nations, 2016) , US Effects Range Low (ERL), Threshold Effect Level (TEL) (Environment Canada, 2007). In addition, the recent review carried out at EU scale (Tornero et al., 2019) was taken in consideration.

Concerning biota, in order to improve the comparability of chemical data, it is suggested to indicate the biometric measurements of the organisms used for chemical analyses. Additionally, it would be advisable to perform isotopic analysis aimed at the definition of the trophic level, as indicated in the Common Implementation Strategy (CIS) (European Commission, 2010) for the WFD.

Additionally, in order to evaluate bioaccumulation in the trophic web, other organisms should be monitored, besides *Mytilus galloprovincialis*. To allow comparability among different areas, general criteria to select target species should be agreed in order to evaluate bioaccumulation in the same trophic level. However, the choice of specific taxa may vary in different sea areas, according to the food web structure and the taxonomic composition of the specific region.

Regarding the LOQ proposed for biota it must be considered that the EQS-biota values reported in the 2013/39/EU Directive are relative to fish species. The exceptions are dioxins and dioxin-like compounds where EQS refers to fish, crustaceans and mollusks, while for fluoranthene and PAH the EQS values refer to mollusks and crustaceans. LOQ values for biota were proposed considering also other reference values as: OSPAR BAC, OSPAR EAC, MED BAC and values from Reg. 2006/1881/EC and its amendment 2008/629/EC.

4.2. Data Quality Control

The ‘data quality’ management process is without a doubt the most important component of the overall data management system structure to ensure the quality of data. While data Quality Assurance (QA) is the responsibility of the analytical laboratories, common guidelines to evaluate the quality of data at database level are of key importance to guarantee the long-term usability and comparability of data. This is particularly important for data managed by large marine data infrastructures (eg. SeaDataNet, EMODnet), that foresee the suitable instruments and tools to format and check data and metadata.

The Quality Control (QC) procedures proposed involve:

- An overall dataset format check for all matrices (seawater, biota and sediment), that includes metadata completeness and additional data needs
- Application of detailed QC methods for a selection of trace metals and of polycyclic aromatic hydrocarbons (PAHs) measured in the sediment. Due to the complexity of data on contaminants, the QC has been restricted to a case study with a limited number of substances in the sediment.

Once data are quality checked, Quality Flags (QF) are assigned, adopting the standard coding (Annex 4) proposed in the framework of the Pan-European marine data infrastructure SeaDataNet (https://www.seadatanet.org)

4.3. Dataset format check

The format of the collection is an “extended-ODV” spreadsheet file, that contains data plus almost all associated metadata.

Dataset format check includes:

1. Meta-data quality check: especially check the correctness of latitude and longitude.
2. Units check: Consistency with adopted units in relation to the matrix, e.g. µg/kg dry weight for sediments. In case of unrealistic measurement units, parameter and matrix should be checked to understand the origin of the suspected error. A wrong attribution of a parameter (substance) to the standard vocabulary (P01 SeaDataNet vocabulary) which combines substance + matrix, may be responsible for the mismatch between unit and matrix.
3. Parameters harmonization: The harmonization of comparable parameters allows to join them inside the collection in order to have coherent collections without duplicates in the parameters list.
4. Coherence of parameters: All parameters within a collection must be coherent in relation to the matrix.
5. Station control: It is important to check that all the stations contain data to avoid stations without data related to contaminants.

4.4. Metadata completeness and additional data needs

All the collections must contain 100% of data from the “primary variable”, which is time for time series and depth for profiles. The lack of data in the primary variable makes data completely un-useful.

Additionally, following metadata additional variables are needed in the datasets:

For contaminants in seawater:

- ☐ Station bottom depth
- ☐ Sampled depth

For contaminants in biota:

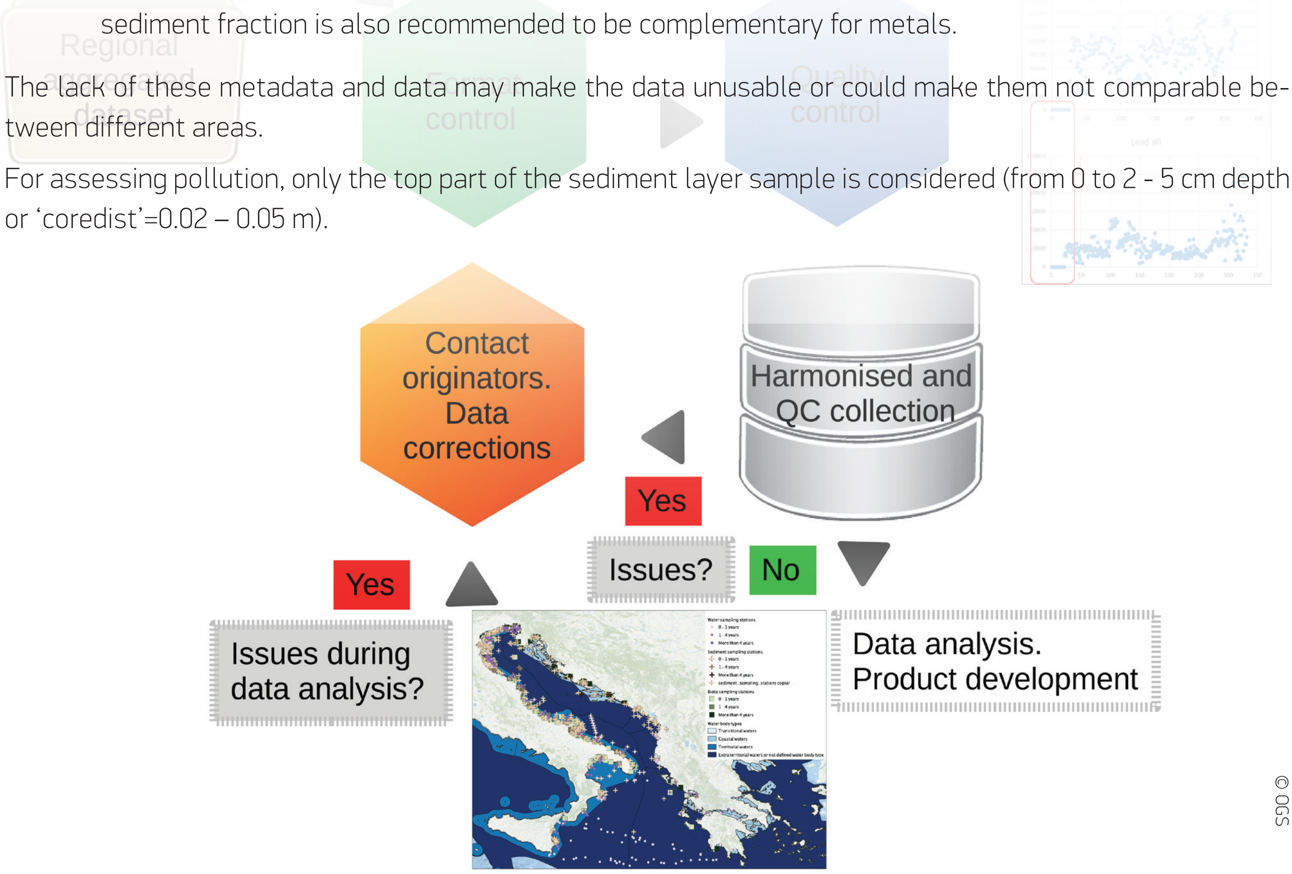
- ☐ Lipid content required for normalization and reporting purposes.
- ☐ Soft tissue wet weight/dry weight ratio required for normalization and reporting purposes.
- ☐ Biometrics (size/length)
- ☐ Biological parameters such as condition index (mussels) and condition factor (fish) according to established protocols and scientific knowledge.

For contaminants in sediment:

- ☐ Grain size of the analyzed sediment fraction
- ☐ Station bottom depth
- ☐ Sampled depth and sampling thickness or minimum and maximum sample depth from the sediment to water interface
- ☐ Information about sediment granulometric fractions (percentage sand, silt, clay)
- ☐ Aluminium (Al), Total Organic Carbon (TOC) in the < 2mm particle size fraction required for normalization and reporting purposes for trace metals and organic contaminants respectively. The < 63µm sediment fraction is also recommended to be complementary for metals.

The lack of these metadata and data may make the data unusable or could make them not comparable between different areas.

For assessing pollution, only the top part of the sediment layer sample is considered (from 0 to 2 - 5 cm depth or ‘coredist’=0.02 – 0.05 m).



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4.5. Data QC on selected trace metals and PAHs in sediment of coastal and offshore areas

The procedure is based on the following steps:

1 - Geographical check: Only data for coastal and offshore sediments can be checked with this approach. Transitional environments as lagoons and inner rivers mouths are out of scope.

2 - Range check: Check if values fall within a defined range of expected variability.

Regional ranges for QC were established on the basis of existing data published in the scientific literature for the Eastern Mediterranean Sea, following the approach used for chemical oceanographic data (UNESCO, 2010).

Criteria for the range definition are:

- The value should be equal or higher than the minimum value of regional background concentration (RBCmin) and Regional Minimum Concentration for Offshore sediments (RMinCO) for the Eastern Mediterranean based on all relevant background concentrations reported in the scientific literature.
- The value should be equal or lower than the maximum value of Regional coastal maximum concentration (RMaxC), regional maximum Offshore concentration (RMaxCO) and Regional maximum Background Concentration (RBCmax) derived for Eastern Mediterranean area.
- Data with "zero" value are not acceptable: in these cases "0" value should be substituted with the appropriate LOD or LOQ value, when possible, and they should be labeled with the SeaDataNet QF 6 "value below detection limit" or Q "value below limit of quantification".

The ranges proposed for QC of trace metals in sediments in the Eastern Mediterranean (EMed) and comparison with ranges in Western Mediterranean (WMed) coastal sediments are indicated in table 1.

Table 1. Ranges of trace metals in Mediterranean sediments

Element	Units		EMed			WMed[2]	
			Min	Max		Min	Max
As	mg kg^{-1} dw	RMinCO	1	18,2	RMaxC	na	na
Cd	mg kg^{-1} dw	RMinCO	0,06	18,2	RMaxC	<0.1	3,6
Co	mg kg^{-1} dw	RMinCO	10	28,2	RMaxCO[1]	na	na
Cr	mg kg^{-1} dw	RMinC	19,4	276	RMaxCO	na	na
Cu	mg kg^{-1} dw	RMinCO	2	101	RMaxC	2,5	208
Hg	mg kg^{-1} dw	RMinCO	0,013	6,18	RMaxC	0,01	4,9
Ni	mg kg^{-1} dw	RBCmin	16,9	323	RMaxCO	na	na
Pb	mg kg^{-1} dw	RMinCO	5	230	RMaxC	9,5	321
V	mg kg^{-1} dw	RMinCO	4	175	RMaxC	na	na
Zn	mg kg^{-1} dw	RMinCO	34	339	RMaxC	21	741

na: data not available [1] no data available for coastal sediments [2] RNO, 1998

The ranges proposed for QC of PAHs in sediments in the EMed and comparison with ranges in WMed coastal sediments are indicated in table 2.

Table 2. Ranges of PAHs in Mediterranean sediments

Compound	Unit		EMed			WMed[1]	
			Min	Max		Min	Max
Acenaphthene	µg kg^{-1} dw	RMinC	0,1	256	RMaxC	-	-
Acenaphtylene	µg kg^{-1} dw	RMinC	0,1	69,6	RMaxC	-	-
Anthracene	µg kg^{-1} dw	RMinCO	0	765	RMaxC	-	-
Benzo[a]anthracene	µg kg^{-1} dw	RMinC	0,1	1888	RMaxC	-	-
Benzo[a]pyrene	µg kg^{-1} dw	RMinC	0,1	2756	RMaxC	<1	2340
Benzo[b]fluoranthene	µg kg^{-1} dw	RMinC	0,1	3807	RMaxC	<1	2790
Benzo[ghi]perylene	µg kg^{-1} dw	RMinC	0,1	1924	RMaxC	<1	2525
Benzo[k]fluoranthene	µg kg^{-1} dw	RMinC	0,1	-		<1	1320
Chrysene	µg kg^{-1} dw	RMinCO	0	2327	RMaxC	-	-
Dibenzo[ah]anthracene	µg kg^{-1} dw	RMinCO	0	1379	RMaxC	-	-
Dibenzothiophene	µg kg^{-1} dw	RMinCO	0	93,4	RMaxC	-	-
Fluoranthene	µg kg^{-1} dw	RMinC	0,1	3089	RMaxC	4,5	8200
Fluorene	µg kg^{-1} dw	RMinC	0,1	172	RMaxC	-	-
Indeno[1,2,3-cd] pyrene	µg kg^{-1} dw	RMinC	0,1	1944	RMaxC	<1	1900
Naphthalene	µg kg^{-1} dw	RMinCO	0	76,3	RMaxC	-	-
Perylene	µg kg^{-1} dw	RMinCO	0	678	RMaxC	-	-
Phenanthrene	µg kg^{-1} dw	RMinC	0,2	1571	RMaxC	-	-
Pyrene	µg kg^{-1}dw	RMinC	0,1	2427	RMaxC	-	-

[1] RNO, 1998 Med: Mediterranean

These ranges can be used for QC. It has to be considered that an error of 10% can be associated with the determination of trace metals and of 15% can be associated with the determination of organic contaminants, therefore the ranges must be adapted accordingly.

The detailed description of the method is available in HarmoNIA Deliverable T1.1.3, Methodological proposal for data Quality Control procedures.

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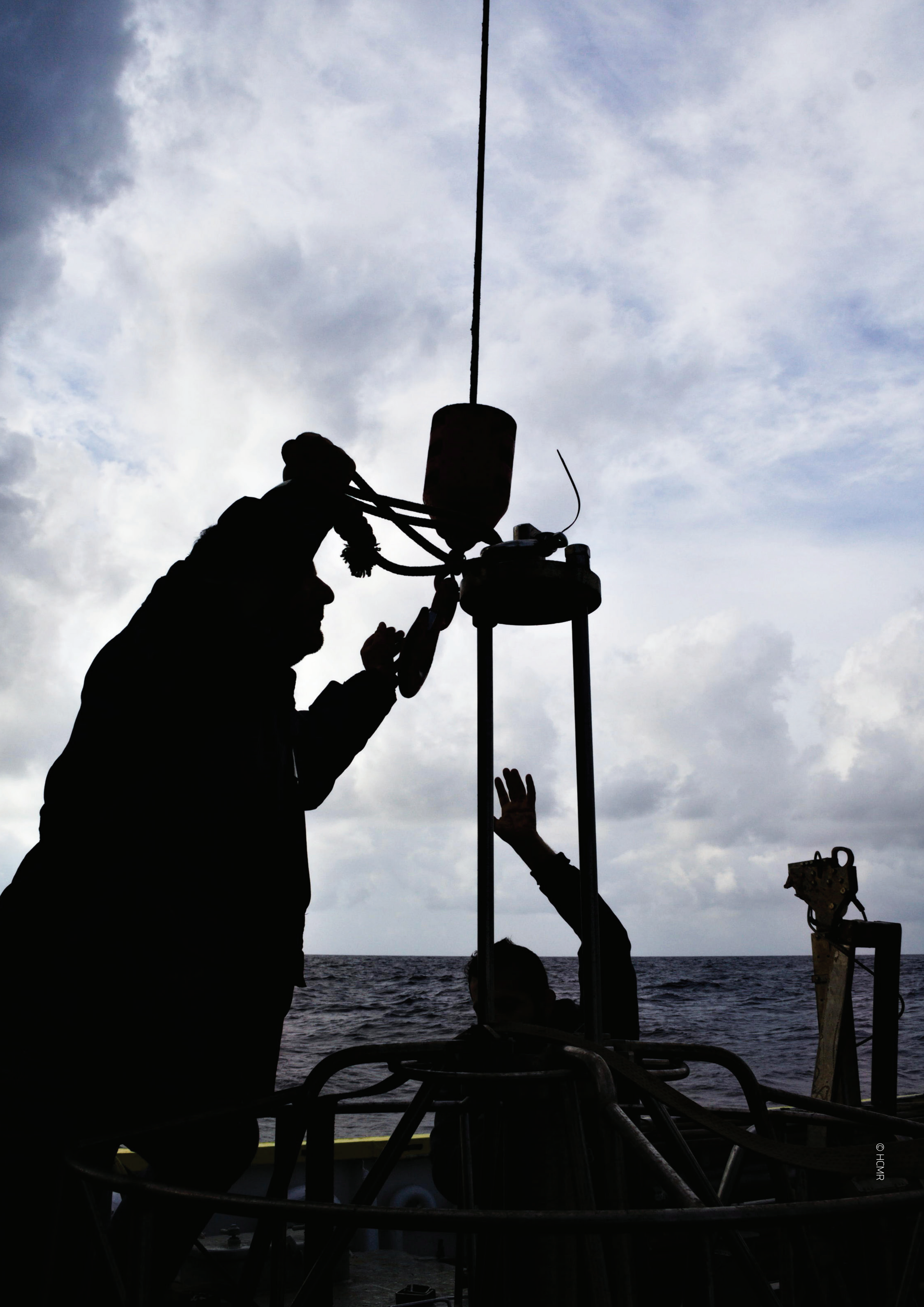

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Annexes

Annex 1: List of substances considered for the analysis of monitoring protocols

Group	Substances
Pesticides and biocides	DDT
	DDE
	DDD
	HCB
Antifoulants	Tributyltin (TBT)
	Triphenyltin (TPhT)
Pharmaceuticals	Macrolides
	other
Heavy metals	Mercury
	Cadmium
	Lead
	Vanadium
	Chromium
	Barium
	Copper
	Iron
	Arsenic
	Zinc
	Nickel
	Aluminum
Hydrocarbons	Anthracene
	Fluoroanthene
	Naphthalene
	Acenaphthylene
	Acenaphthene
	Fluorene
	Phenanthrene
	Pyrene
	Benzo(a)anthracene
	Chrysene
	Benzo(b)fluoranthene
	Benzo(k)fluoranthene
	Benzo(a)pyrene
	Dibenzo(a,h)anthracene
	Benzo(g,h,i)perylene
	Indenopyrene
	Total hydrocarbons
	Aliphatic hydrocarbons C6-C12
	Aliphatic hydrocarbons C10-C40
	Benzene
	Toluene
	Ethylbenzene
	o,m,p-Xylene
Brominated compounds	Brominated diphenylether
Radionuclides	Cs137, Pu239

Annex 2: List of substances measured in the area and considered under relevant EU legislation and Barcelona Convention

Name of substance	UNEP_considered	UE_legislation	Harmo-NIA area	JRC sea_ based
137Cs				X
Acenaphtene			X	X
Acenaphtylene			X	X
Aldrin	UNEP/MAP MEDPOl monitoring program, LBS protocol	WFD other pollutants	X	
Aluminium			X	X
Anthracene		WFD PS, WFD PHS	X	X
Arsenic	Candidate chemical for Barcelona Convention		X	X
Barium	Candidate chemical for Barcelona Convention		X	X
Benz(a)anthracene			X	X
Benzo(a)pyrene (marker of all PAH)		WFD PS, WFD PHS		X
Benzo(b)fluoranthene		WFD PS, WFD PHS	X	X
Benzo(g,h,i)-perylene		WFD PS, WFD PHS	X	X
Benzo(k)fluoranthene		WFD PS, WFD PHS	X	X
Brominated diphenylethers (sum of the concentrations of congener numbers 28, 47, 99, 100, 153 and 154) (PBDE)	LBS protocol	WFD PS, WFD PHS	X	X
Cadmium and its compounds (depending on water hardness classes)7	UNEP/MAP MEDPOl monitoring program, LBS protocol	WFD PS, WFD PHS	X	X
Chrysene			X	X
Cobalt			X	X
Copper	LBS protocol	BPD	X	X
Cromium	LBS protocol		X	X
DDT total	UNEP/MAP MEDPOl monitoring program, LBS protocol	WFD other pollutants	X	X
Dibenzo(a,h)anthracene			X	X
Dibutyltin (DBT)			X	X
Dieldrin	UNEP/MAP MEDPOl monitoring program, LBS protocol	WFD otherpollutants	X	
Dioxins and dioxin-like compounds		WFD PS, WFD PHS	X	X

Name of substance	UNEP_considered	UE_legislation	Harmo-NIA area	JRC sea_ based
Ethylbenzene			X	X
Fluoranthene		WFD PS	X	X
Fluorene			X	X
Hexachloro-benzene	UNEP/MAP MEDPOl monitoring program, LBS protocol	WFD PS, WFD PHS	X	X
HCH (isomers)	Candidate chemical for Barcelona Convention	WFD PS	X	
Gamma-HCH (lindane)	UNEP/MAP MEDPOl monitoring program, LBS protocol			
Indeno(1,2,3-cd)-pyrene		WFD PS, WFD PHS	X	X
Iron	Candidate chemical for Barcelona Convention		X	X
Lead and its compounds (bioavailable concentrations)	UNEP/MAP MEDPOl monitoring program, LBS protocol	WFD PS	X	X
Manganese	Candidate chemical for Barcelona Convention		X	X
Mercury and its compounds	UNEP/MAP MEDPOl monitoring program, LBS protocol	WFD PS, WFD PHS	X	X
Methoxychlor	Candidate chemical for Barcelona Convention			
Naphthalene		WFD PS	X	X
Nickel and its compounds (bioavailable concentrations)	Candidate chemical for Barcelona Convention		X	X
Para-para-DDD			X	X
Para-para-DDE			X	X
para-para-DDT		WFD otherpol-lutants	X	X
PCB101	UNEP/MAP MEDPOl monitoring program		X	X
PCB105	UNEP/MAP MEDPOl monitoring program		X	X
PCB118	UNEP/MAP MEDPOl monitoring program		X	X
PCB138	UNEP/MAP MEDPOl monitoring program		X	X
PCB153	UNEP/MAP MEDPOl monitoring program		X	X
PCB180	UNEP/MAP MEDPOl monitoring program		X	X
PCB28	UNEP/MAP MEDPOl monitoring program		X	X

Name of substance	UNEP_considered	UE_legislation	Harmo-NIA area	JRC sea_ based
PCB52	UNEP/MAP MEDPOl monitoring program		X	X
PCBs	UNEP/MAP MEDPOl monitoring program		X	X
PCDDs	LBS protocol	WFD PS	X	X
PCDFs	LBS protocol	WFD PS	X	X
Pentachlorophenol	Candidate chemical for Barcelona Convention	WFD PS	X	
phenanthrene			X	X
Phenol			X	X
Polyaromatic hydrocarbons (PAH)	UNEP/MAP MEDPOl monitoring program, LBS protocol	WFD PS	X	X
Pyrene			X	X
Selenium			X	X
Toluene			X	X
TPT			X	X
Tributyltin compounds (Tributyltin-cation)		WFD PS, WFD PHS, BPD	X	X
Vanadium	Candidate chemical for Barcelona Convention		X	X
Zinc			X	X

Annex 3: Detailed protocols

Seawater

Group	Examples	Units	Sampling methods	Storage (ex: methods, temperature, addition of preservative etc..)	Method of Analysis	LOQ proposal (30% EQS) Dir.2009/90/EC (Art. 4)	LOQ proposal on the basis of Questionnaires	AA-EQS Dir. 2013/39/EU	AA-EQS Italian Legislative Decree 172/2015, where different from Dir. 2013/39/EU	AA-EQS Greek Decree 1909/8-12-2010, where different from Dir. 2013/39/EU
Pesticides and biocides	DDT	µg/l	no filtration	4 degree, dark	GC-MS	0.0075		0.025		
	DDE	µg/l	no filtration	4 degree, dark	GC-MS		0.001			
	DDD	µg/l	no filtration	4 degree, dark	GC-MS		0.001			
	HCB	µg/l	no filtration	4 degree, dark	GC-MS		0.001		0.002	
Antifoulants	TriButiltin (TBT)	µg/l (as cation)	no filtration	acidification, 4 degree, dark	GC-MS	0.00006		0.0002		
	Triphenyltin (TPhT)	µg/l (as cation)	no filtration	acidification, 4 degree, dark	GC-MS		0.003		0.0002	
Pharmaceuticals	Macrolides	µg/l	no filtration	-20°C	SPE-LC-MS-MS	0.019*				
	other (amoxicillin, ciprofloxacin)	µg/l	no filtration	-20°C	SPE-LC-MS-MS					
Heavy metals	Mercury	µg/l	filtration 0,45 µm	acidification, 4 degree	CV-AAS	0.021		0.07 (MAC-EQS)		
	Cadmium	µg/l	filtration 0,45 µm	acidification HNO3 followed by an SPE preconcentration step	voltammetry-ICP/MS	0.06		0.2		
	Lead	µg/l	filtration 0,45 µm	acidification HNO3 followed by an SPE preconcentration step	voltammetry-ICP/MS	0.39		1.3		
Hydrocarbons	Anthracene	µg/l	no filtration	extraction with n-hexane onboard / 4°C without preservative, dark condition	GC-MS / HPLC-FLD	0.03		0.1		
	Fluoroanthene	µg/l	no filtration	extraction with n-hexane onboard / 4°C without preservative, dark condition	GC-MS / HPLC-FLD	0.0019		0.0063		
	Naphthalene	µg/l	no filtration	extraction with n-hexane onboard / 4°C without preservative, dark condition	GC-MS / HPLC-FLD	0.6		2		
	Acenaphthylene	µg/l	no filtration	extraction with n-hexane onboard / 4°C without preservative, dark condition	GC-MS / HPLC-FLD		0.00002			

Group	Examples	Units	Sampling methods	Storage (ex: methods, temperature, addition of preservative etc..)	Method of Analysis	LOQ proposal (30% EQS) Dir.2009/90/EC (Art. 4)	LOQ proposal on the basis of Questionnaires	AA-EQS Dir. 2013/39/EU	AA-EQS Italian Legislative Decree 172/2015, where different from Dir. 2013/39/EU	AA-EQS Greek Decree 1909/8-12-2010, where different from Dir. 2013/39/EU
Hydrocarbons	Acenaphthene	µg/l	no filtration	extraction with n-hexane onboard / 4°C without preservative, dark condition	GC-MS / HPLC-FLD		0.00002			
	Fluorene	µg/l	no filtration	extraction with n-hexane onboard / 4°C without preservative, dark condition	GC-MS / HPLC-FLD		0.00002			
	Phenanthrene	µg/l	no filtration	extraction with n-hexane onboard / 4°C without preservative, dark condition	GC-MS / HPLC-FLD		0.00002			
	Pyrene	µg/l	no filtration	extraction with n-hexane onboard / 4°C without preservative, dark condition	GC-MS / HPLC-FLD		0.00002			
	Benzo(a)anthracene	µg/l	no filtration	extraction with n-hexane onboard / 4°C without preservative, dark condition	GC-MS / HPLC-FLD		0.00002			
	Chrysene	µg/l	no filtration	extraction with n-hexane onboard / 4°C without preservative, dark condition	GC-MS / HPLC-FLD		0.00002			
	Benzo(b)fluoranthene	µg/l	no filtration	extraction with n-hexane onboard / 4°C without preservative, dark condition	GC-MS / HPLC-FLD	0.00005		0.00017		
	Benzo(k)fluoranthene	µg/l	no filtration	extraction with n-hexane onboard / 4°C without preservative, dark condition	GC-MS / HPLC-FLD	0.00005		0.00017		
	Benzo(a)pyrene	µg/l	no filtration	extraction with n-hexane onboard / 4°C without preservative, dark condition	GC-MS / HPLC-FLD	0.00005		0.00017		
	Dibenzo(a,h) anthracene	µg/l	no filtration	extraction with n-hexane onboard / 4°C without preservative, dark condition	GC-MS / HPLC-FLD		0.00002			

Group	Examples	Units	Sampling methods	Storage (ex: methods, temperature, addition of preservative etc..)	Method of Analysis	LOQ proposal (30% EQS) Dir.2009/90/EC (Art. 4)	LOQ proposal on the basis of Questionnaires	AA-EQS Dir. 2013/39/EU	AA-EQS Italian Legislative Decree 172/2015, where different from Dir. 2013/39/EU	AA-EQS Greek Decree 1909/8-12-2010, where different from Dir. 2013/39/EU
Hydrocarbons	Benzo(g,h,i)perylene	µg/l	no filtration	extraction with n-hexane onboard / 4°C without preservative, dark condition	GC-MS / HPLC-FLD	0.00005		0.00017		
	Indenopyrene	µg/l	no filtration	extraction with n-hexane onboard / 4°C without preservative, dark condition	GC-MS / HPLC-FLD	0.00005		0.00017		
	Total hydrocarbons	µg/l	no filtration	extraction with n-hexane onboard / 4°C without preservative, dark condition	GC-FID		110			
	Aliphatic hydrocarbons C6-C12	µg/l	no filtration	4°C with ammonium bisolphate adding	GC-MS		0.02			
	Aliphatic hydrocarbons C10-C40 (Specify range)	µg/l	no filtration	extraction with n-hexane onboard /4°C without preservative, dark condition	GC-FID		100			
	Benzene	µg/l	no filtration	4°C with ammonium bisolphate adding	GC-MS	2.4		8		
	Toluene	µg/l	no filtration	4°C with ammonium bisolphate adding	GC-MS		0.1		1	10
	Ethylbenzene	µg/l	no filtration	4°C with ammonium bisolphate adding	GC-MS		0.01			10
	o,m,p-Xylene	µg/l	no filtration	4°C with ammonium bisolphate adding	GC-MS		0.02		1	10
Radionuclides	Cs137, Pu239	Bq/l	no data	no data	no data			no data		
Physical parameters	Dissolved Oxygen	%	CTD probe-in situ measurement	in situ measurements	CTD probe					
	Salinity	PSU	CTD probe-in situ measurement	in situ measurements	CTD probe					
	Temperature	°C	CTD probe-in situ measurement	in situ measurements	CTD probe					
	Transmittance	%	CTD probe-in situ measurement	in situ measurements	CTD probe					
	Fluorescence	mg/m3	CTD probe-in situ measurement	in situ measurements	CTD probe					

* Maximum acceptable method detection limit of Commision Implementing Decision 2018/840/EU

Biota

Group	Examples	Units	Tissue (ex: muscle, liver, etc...)	Dry weight or wet weight (specify)	Number of replicates (1,2,3)	Storage (ex: methods, temperature, etc..)	Method of Analysis	LOQ proposal (30% EQS) Dir.2009/90/ EC (Art. 4) and Questionnaire	EQS Dir. 2013/39/EU and Italian Legislative Decree 172/2015	OSPAR BAC	OSPAR EAC	MED-BAC	Reg. 2006/1881/ EC and Reg. 2008/629/EC
Pesticides and biocides	DDT	µg/kg	total sample#	wet weight	3	Frozen at -20°C	GC-ECD	15*	50*				
	DDE	µg/kg	total sample	wet weight	3	Frozen at -20°C	GC-ECD	0.03					
	DDD	µg/kg	total sample	wet weight	3	Frozen at -20°C	GC-ECD	0.03					
	HCB	µg/kg	total sample#	wet weight	3	Frozen at -20°C	GC-ECD	3*	10*	0.63∞			
Antifoulants	Tributyltin (TBT)	µg/kg (as cation)	total sample	wet weight	3	Frozen at -20°C	GC-MS	0.59			12∞		
	Triphenyltin (TPhT)	µg/kg (as cation)	total sample	wet weight	3	Frozen at -20°C	GC-MS	3					
Pharmaceuticals	Macrolides	µg/kg	total sample	wet weight	3	Frozen at -20°C	-	-					
	other	µg/kg	total sample	wet weight	3	Frozen at -20°C	-	-					
Heavy metals	Mercury	mg/kg	total sample#	wet weight	3	Frozen at -20°C	CV-AAS	0.006*	0.02*	0.035*/0.090∞		0.101*/0.173∞	0.5-1*/0.5
	Cadmium	mg/kg	total sample	wet weight	3	Frozen at -20°C	ICP-OES / ICP-MS	0.001∞		0.026*/0.96∞		0.016*/1.095∞	0.05-0.30*/1
	Lead	mg/kg	total sample	wet weight	3	Frozen at -20°C	ICP-OES / ICP-MS	0.05∞		0.026*/1.3∞		0.040*/2.313∞	0.3*/1.5
	Vanadium	mg/kg	total sample	wet weight	3	Frozen at -20°C	ICP-OES / ICP-MS	0.1					
	Chromium	mg/kg	total sample	wet weight	3	Frozen at -20°C	ICP-OES / ICP-MS	0.01 ∞					
	Barium	mg/kg	total sample	wet weight	3	Frozen at -20°C	ICP-OES / ICP-MS	0.01 ∞					
	Copper	mg/kg	total sample	wet weight	3	Frozen at -20°C	ICP-OES / ICP-MS	0.01 ∞		6∞			
	Iron	mg/kg	total sample	wet weight	3	Frozen at -20°C	ICP-OES / ICP-MS	1 ∞					
	Arsenic	mg/kg	total sample	wet weight	3	Frozen at -20°C	ICP-OES / ICP-MS	0.001 ∞					
	Zinc	mg/kg	total sample	wet weight	3	Frozen at -20°C	ICP-OES / ICP-MS	0.1 ∞					
	Nickel	mg/kg	total sample	wet weight	3	Frozen at -20°C	ICP-OES / ICP-MS	0.01 ∞					
Hydrocarbons	Anthracene	µg/kg	total sample	wet weight	3	Frozen at -20°C	GC-MS	0.6			290∞	1.2∞	
	Fluoroanthene	µg/kg	total sample	wet weight	3	Frozen at -20°C	GC-MS	9	30	12.2∞	110∞	7.4∞	
	Naphthalene	µg/kg	total sample	wet weight	3	Frozen at -20°C	GC-MS	0.6			340∞	6.0∞	
	Acenaphthylene	µg/kg	total sample	wet weight	3	Frozen at -20°C	GC-MS	0.6				1.4∞	
	Acenaphthene	µg/kg	total sample	wet weight	3	Frozen at -20°C	GC-MS	0.6				1.4∞	

Group	Examples	Units	Tissue (ex: muscle, liver, etc...)	Dry weight or wet weight (specify)	Number of replicates (1,2,3)	Storage (ex: methods, temperature, etc..)	Method of Analysis	LOQ proposal (30% EQS) Dir.2009/90/ EC (Art. 4) and Questionnaire	EQS Dir. 2013/39/EU and Italian Legislative Decree 172/2015	OSPAR BAC	OSPAR EAC	MED-BAC	Reg. 2006/1881/ EC and Reg. 2008/629/EC
Hydrocarbons	Fluorene	µg/kg	total sample	wet weight	3	Frozen at -20°C	GC-MS	0.6				2.5∞	
	Phenanthrene	µg/kg	total sample	wet weight	3	Frozen at -20°C	GC-MS	0.6		11∞	1700∞	17.8∞	
	Pyrene	µg/kg	total sample	wet weight	3	Frozen at -20°C	GC-MS	0.6		9∞	100∞	5∞	
	Benzo(a) anthracene	µg/kg	total sample	wet weight	3	Frozen at -20°C	GC-MS	0.6		2.5∞	80∞	1.9∞	
	Chrysene	µg/kg	total sample	wet weight	3	Frozen at -20°C	GC-MS	0.6		8.1∞		2.4∞	
	Benzo(b) fluoranthene	µg/kg	total sample	wet weight	3	Frozen at -20°C	GC-MS	1.5	5				
	Benzo(k)fluoranthene	µg/kg	total sample	wet weight	3	Frozen at -20°C	GC-MS	1.5	5		260∞	1.4∞	
	Benzo(a)pyrene	µg/kg	total sample	wet weight	3	Frozen at -20°C	GC-MS	1.5	5		600∞	1.2∞	
	Dibenzo(a,h) anthracene	µg/kg	total sample	wet weight	3	Frozen at -20°C	GC-MS	0.6				1.3∞	
	Benzo(g,h,i) perylene	µg/kg	total sample	wet weight	3	Frozen at -20°C	GC-MS	1.5	5	2.5∞	110∞	2.3∞	
	Indenopyrene	µg/kg	total sample	wet weight	3	Frozen at -20°C	GC-MS	1.5	5	2.4∞		2.9∞	
	Total hydrocarbons	µg/kg	total sample	wet weight	3	Frozen at -20°C	GC-FID	-					
	Aliphatic hydrocarbons C6-C12	µg/kg	total sample	dry weight	3	Frozen at -20°C	GC-MS	-					
	Aliphatic hydrocarbons C10-C40 (Specify range)	µg/kg	total sample	dry weight	3	Frozen at -20°C	GC-FID	-					
	Benzene	µg/kg	total sample	wet weight	3	Frozen at -20°C	GC-MS	1 ∞					
	Toluene	µg/kg	total sample	wet weight	3	Frozen at -20°C	GC-MS	1 ∞					
	Ethylbenzene	µg/kg	total sample	wet weight	3	Frozen at -20°C	GC-MS	1 ∞					
	o,m,p-Xylene	µg/kg	total sample	wet weight	3	Frozen at -20°C	GC-MS	2 ∞					
Brominated compounds	Brominated diphenylethers	µg/kg	total sample#	wet weight	3	Frozen at -20°C	GC-ICPMS	0.0026*	0.0085*				
Lipid	Lipid content	%	total sample	wet weight	3	Frozen at -20°C	gravimetric	-					
Water	Water content	%	total sample	wet weight	3	Frozen at -20°C	gravimetric	-					

\# in fish according to 2013/39/EU Directive, otherwise in molluscs

* concentrations in fish tissue, otherwise in bivalve mollusk

∞ dry weight concentrations, otherwise wet weight

Sediment

Group	Examples	Units (on dry weight)	Grain size (Unsieved; 3µm; <2mm)	Sampling method (type of sampler, ex: box corer)	Thickness of sampled sediment (cm)	Storage (Method, temperature, etc...)	Method of Analysis	LOQ proposal	Med BAC1 / OSPAR BAC2	US-ERL	AA-EQS (Italian Legislative Decree 172/2015)	TEL (Canadian Environmental Quality Standard)
Pesticides and biocides	DDT	µg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	GC-ECD	0.1			1	1.2
	DDE	µg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	GC-ECD	0.1			1.8	2.1
	DDD	µg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	GC-ECD	0.1			0.8	1.2
	HCB	µg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	GC-ECD	0.005		20	0.4	
Antifoulants	Tributyltin (TBT)	µg/kg (as cation)	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	GC-MS	1			5	
	Triphenyltin (TPhT)	µg/kg (as cation)	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	GC-MS	3				
Pharmaceuticals	Macrolides	µg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	-	-				
	other	µg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	-	-				
Heavy metals	Mercury	mg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	ICP MS	0.0005	0.0795	0.15	0.3	0.13

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Heavy metals	Cadmium	mg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	ICP MS	0.05	0.1275	1.2	0.3	0.67
	Lead	mg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	ICP MS	0.05	25.425	46.7	30	30
	Vanadium	mg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	ICP MS	0.5				
	Chromium	mg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	ICP MS	0.05		81	50	52
	Barium	mg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	ICP MS	1				
	Copper	mg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	ICP MS	0.02		34		19
	Iron	mg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	ICP MS	0.05				
	Arsenic	mg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	ICP MS	0.001		8.2	12	7.2
	Zinc	mg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	ICP MS	0.001		150		120
	Nickel	mg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	ICP MS	0.05		21		

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Heavy metals	Aluminum	mg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	ICP MS	3				
Hydrocarbons	Anthracene	µg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	GC-MS	0.1	1.8	85	24	47
	Fluoroanthene	µg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	GC-MS	0.1	14.4	600	110	110
	Naphthalene	µg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	GC-MS	1	8.0	160	35	35
	Acenaphthylene	µg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	GC-MS	1				5.9
	Acenaphthene	µg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	GC-MS	1				6.7
	Fluorene	µg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	GC-MS	1				21
	Phenanthrene	µg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	GC-MS	1	7.3	240		87
	Pyrene	µg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	GC-MS	1	11.3	665		150
	Benzo(a)anthracene	µg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	GC-MS	1	7.1	261		75

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Hydrocarbons	Chrysene	µg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	GC-MS	1	8.0	384		110
	Benzo(b)fluoranthene	µg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	GC-MS	2			40	
	Benzo(k)fluoranthene	µg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	GC-MS	2			20	
	Benzo(a)pyrene	µg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	GC-MS	0.1	8.2	430	30	89
	Dibenzo(a,h) anthracene	µg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	GC-MS	2				6.2
	Benzo(g,h,i) perylene	µg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	GC-MS	2	6.9	85	55	
	Indenopyrene	µg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	GC-MS	2	8.3	240	70	
	Total hydrocarbons	µg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	GC-FID	150				
	Aliphatic hydrocarbons C6-C12	µg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	GC-MS	50				
	Aliphatic hydrocarbons C10-C40 (Specify range)	µg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	GC-FID	150				

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Hydrocarbons	Benzene	µg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	GC-MS	0.05				
	Toluene	µg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	GC-MS	0.1				
	Ethylbenzene	µg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	GC-MS	0.03				
	o,m,p-Xylene	µg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	GC-MS	0.07				
Brominated compounds	Brominated diphenylether	µg/kg	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	GC-MS	0.1				
Radionuclides	Cs137, Pu239	Bq/kg	-	-	-	-	-	-				
Organic matter	Total organic carbon (TOC)	%	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	CHN	0.1				
	Loss on ingnition (LOI)	%	<2 mm	box corer	0-2	frozen at -20°C, freeze-dried sediment stored at 4 °C	gravimetric	0.01				
Grain size analysis	Sand	%	unsieved	box corer	0-2	stored at 4 degree	mechanical sieving					
	Silt	%	unsieved	box corer	0-2	stored at 4 degree	mechanical sieving					
	Clay	%	unsieved	box corer	0-2	stored at 4 degree	mechanical sieving					
Water	Water content	%	unsieved	box corer	0-2	stored at 4 degree	gravimetric					

[1] Med BAC for heavy metals
[2] OSPAR BAC for PAHs

Annex 4: Data QC flagging according to SeaDataNet standard

List of Quality Flags (QF) adopted according to SeaDataNet (L20 vocabulary[1])

QF Code	QF name	QF definition
0	no quality control	No quality control procedures have been applied to the data value. This is the initial status for all data values entering the working archive.
1	good value	Good quality data value that is not part of any identified malfunction and has been verified as consistent with real phenomena during the quality control process.
2	probably good value	Data value that is probably consistent with real phenomena but this is unconfirmed or data value forming part of a malfunction that is considered too small to affect the overall quality of the data object of which it is a part.
3	probably bad value	Data value recognised as unusual during quality control that forms part of a feature that is probably inconsistent with real phenomena.
4	bad value	An obviously erroneous data value.
5	changed value	Data value adjusted during quality control. Best practice strongly recommends that the value before the change be preserved in the data or its accompanying metadata.
6	value below detection	The level of the measured phenomenon was less than the limit of detection (LoD) for the method employed to measure it. The accompanying value is the detection limit for the technique or zero if that value is unknown.
7	value in excess	The level of the measured phenomenon was too large to be quantified by the technique employed to measure it. The accompanying value is the measurement limit for the technique.
8	interpolated value	This value has been derived by interpolation from other values in the data object.
9	missing value	The data value is missing. There should be no accompanying value in ODV format files. The accompanying value in SeaDataNet NetCDF data must be the absent data representation specified by the _FillValue parameter attribute and lie outside the range of data not flagged bad (4) or probably bad (3).
A	value phenomenon uncertain	There is uncertainty in the description of the measured phenomenon associated with the value such as chemical species or biological entity.
Q	value below limit of quantification	The level of the measured phenomenon was less than the limit of quantification (LoQ). The accompanying value is the limit of quantification for the analytical method or zero if that value is unknown.

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[1] http://seadatanet.maris2.nl/v_bodc_vocab_v2/browse.asp?order=conceptid&formname=search&screen=0&lib=l20&v0_0=&v1_0=conceptid%2Cpreflabel%2Caltlabel%2Cdefinition%2Cmodified&v2_0=0&v0_1=&v1_1=conceptid&v2_1=3&v0_2=&v1_2=preflabel&v2_2=3&v0_3=&v1_3=altlabel&v2_3=3&v0_4=&v1_4=modified&v2_4=9&v0_5=&v1_5=modified&v2_5=10&x=19&y=22&v1_6=&v2_6=&v1_7=&v2_7=