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DEVELOPMENT OF ASSESSMENT CRITERIA FOR HAZARDOUS SUBSTANCES IN THE MEDITERRANEAN

UNEP/MAP
Athens, 2011

Development of Assessment Criteria for Hazardous substances in the Mediterranean

October 2011

PREAMBLE

The Report on the development of assessment criteria for hazardous substances in the Mediterranean presents information on the methodology to be followed for the definition of the above criteria and offers the first estimates of background concentrations for trace metals in sediments and biota, and PAHs in sediments. The Report has been prepared by Prof. Joan Albaigés (Department of Environmental Chemistry, CID-CSIC, Spain) and Prof. Barak Herut (Israel Oceanographic & Limnological Research), under the supervision of UNEP/MAP - MED POL.

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Executive summary

The assessment of monitoring data for the hazardous substances included in the MEDPOL database, namely trace metals, chlorinated pesticides and PCBs, in sediments and biota, requires relevant assessment tools in order to determine the levels that can be considered of concern and how to identify hot spots for priority action.

Following the OSPAR approach there are two concentration "thresholds" to be defined: T_0 and T_1. T_0 will be defined in sediments and biota, as the concentration of a contaminant at a "pristine" or "remote" site, where no deterioration of the environment can be expected. For a man-made compound this concentration should be taken as zero. In turn, T_1 is the concentration above which significant adverse effects to the environment or to human health are most likely to occur. Between T_0 and T_1, the levels do not pose significant risk to the environment or to human health.

The establishment of the transition points T_0 and T_1, involves the definition of a series of reference concentrations, particularly of Background Assessment Concentrations (BACs), derived from the Background Concentrations (BCs), and the Environmental Assessment Criteria (EACs). This requires specific statistical analysis of the database and additional information. For instance, the definition of T_1 for each pollutant concerned requires ecotoxicological information for the key species to be used for such a purpose.

The scope of the present report is to prepare an adapted manual for the formulation of Environmental Assessment Criteria for the Mediterranean, as part of the implementation of Mediterranean-wide environmental objectives to define GES in the framework of the ECAP. The adoption of specific Mediterranean Ecological Quality Objectives (EQOs) and Environmental Quality Standards (EQS) are essential for the risk assessment of the pollution.

The document provides background information on the methodology to be followed for the definition of the above criteria and offers the first estimates of background concentrations for trace metals in sediments and biota, and PAHs in sediments. Suggestions are given for improving the available information (e.g. dated cores) in order to improve the definitions of the EACs. Recommendations are also made for improving the MEDPOL monitoring programme in order to overcome data variability. These refer to the compulsory determination of Al content in sediments for normalization of trace metal data and the OC percentage for normalizing the PAHs and CBs concentrations.

1. Introduction

1.1 Background

The gradual application of the Ecosystem Approach for the management of human activities in the Mediterranean adopted by the contracting parties, as part of the MAP (UNEP/MAP, 2010), requires the assessment of the environmental status of marine areas using defined methodological criteria. For this purpose, 11 Ecological Objectives (EO) have been defined, including EO9 on contamination by hazardous substances. For each EO, Operational Objectives with associate indicators and targets are under development by MAP, in order to provide a tool to measure the progress made towards achievement of Good Environmental Status. Therefore, for EO9, it is necessary to establish threshold values for key contaminants to distinguish between acceptable (little or no risk or “good”) and un-acceptable (unacceptable risk) environmental conditions. In the Mediterranean region, threshold values for major hazardous contaminants, namely trace metals, chlorinated compounds (pesticides and PCBs) and PAHs, are lacking and have to be defined.

Two main conceptual approaches are used to define these values, also known as Environmental Assessment Criteria (EAC), the OSPAR and NOAA/EPA approaches.

The OSPAR approach uses an ideal derivation of environmental assessment criteria for any given substance based on its policy for achieving concentrations in the environment near background values for naturally occurring substances and close to zero for man-made synthetic substances, and based on dose-response relationships. This approach involves the adoption of a “traffic light” system in which the green/red transition level represents contaminant concentration below which no chronic effects are expected to occur in marine biota species, including the most sensitive. Thus, the transition between green to red implies a transition from a marine state which is acceptable and there is little or no risk to an unacceptable risk. These thresholds may be related to the Environmental Quality Standards (EQSs) applied to concentrations of contaminants in water under the EU Water Framework Directive (WFD).

The NOAA/EPA approach uses benchmarks, based upon a database primarily of synoptic marine sediment chemistry and sediment toxicity bioassay data. For a given contaminant, the samples which were categorized as toxic by the original data generator is selected, and that subset is then ranked by increasing contaminant concentration and the 10th (Effect Range-Low, ERL) and 50th (Effect Range-Medium, ERM) percentiles determined. The ERL is calculated as the lowest 10th percentile concentration of the available data at which effects were empirically observed.

Another approach is presented in the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life based on similar database compilation but using different calculations, Threshold Effect Levels (TELs, geometric mean of the 15th percentile) and Probable Effects Levels (PELs, geometric mean of the 50th impacted samples and the 85th of the non impacted) are calculated. The ERL is at the low ranges of levels at which effects were empirically observed and it represents the value at which toxicity may begin to be observed in sensitive species.

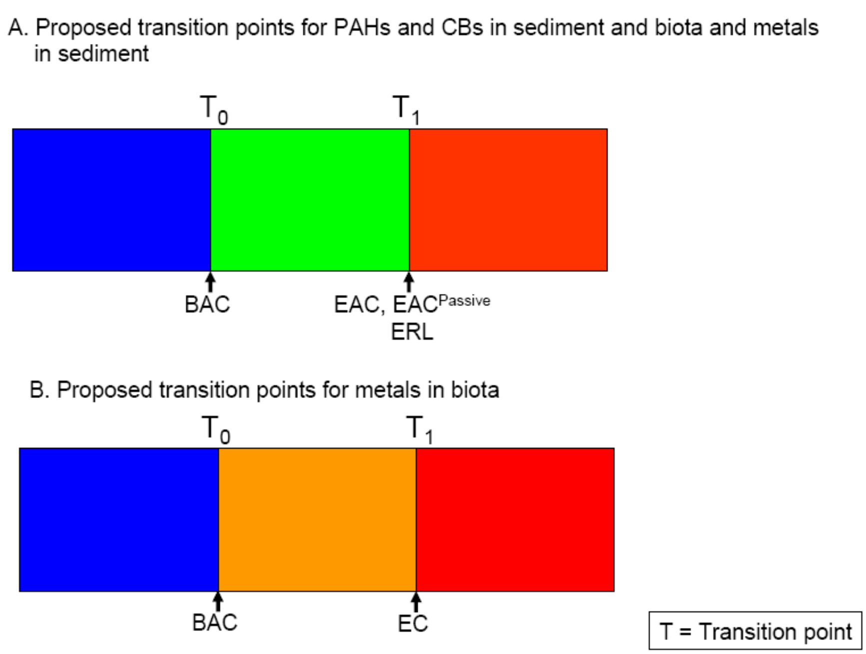
The scope of the present report is to prepare an adapted manual for the formulation of Environmental Assessment Criteria (EAC) for selected substances (trace metals, chlorinated compounds and PAHs) in Mediterranean sediments and biota, as part of the implementation of Mediterranean-wide environmental quality objectives (EQO) and standards (EQS) for different "uses" of the sea, to determine locally applicable effluent standards and input limits. The adoption of specific Mediterranean EQOs and EQSs are essential for the risk assessment of the pollution.

1.2 Conceptual framework

Following the OSPAR approach there are two concentration "thresholds" to be defined: T_0 and T_1. T_0 will be defined in sediments and biota, as the concentration of a contaminant at a "pristine" or "remote" site, where no deterioration of the environment can be expected. For a man-made compound this concentration should be taken as zero. In turn, T_1 is the concentration above which significant adverse effects to the environment or to human health are most likely to occur. Between T_0 and T_1, the levels do not pose significant risk to the environment or to human health.

The definition of these thresholds requires specific statistical analysis of the database and additional information. For instance, the definition of T_1 for each pollutant concerned requires ecotoxicological information for the key species to be used for such a purpose. The outcome of these definitions can be described by the transition in a "**traffic light scheme"** between green and red as shown in Figure 1. This is wise from a presentational perspective, as it can give the reader a clear and immediate picture of where environmental conditions are acceptable or not and prompt appropriate environmental management options.

Figure 1. Illustration of the proposed traffic light system and the relevant transition point criteria for: A. PAHs and CBs in sediment and biota and metals in sediments, and B. metals in biota. The green/red boundary corresponds to the achievement of a statutory target (in WFD terms) or a policy objective (in OSPAR terms)



A green assessment for a particular contaminant means that the environmental concentrations meet relevant statutory limits or policy objectives, and are satisfactory in that they present little or no risk. A red assessment means that the relevant limit or objective had not been met. The statistical aspects of the comparisons are on a precautionary basis.

The interpretation of the proposed blue/green/red scheme in relation to hazardous substances is summarised in Table 1, which explains what this means in the context of contaminants. Table 1 further summarises the type of management activity which may be possible for each colour:

i. Below the T_0 value, measured contaminant concentration should not give rise to any biological effects. No immediate management action would be required, the monitoring frequency could be reduced or monitoring ceased.

ii. Between the T_0 and T_1 values, biological effects are possible (e.g. biomarker response, impaired growth, reproduction). Management actions could be to identify the reasons for elevated level(s), the use of expert judgement to assess significance, check trends and variability or the introduction of additional monitoring.

iii. Above T_1, long-term biological effects are likely (e.g. impaired growth, reproduction and survival), and acute biological effects (survival) are possible. Appropriate management actions could involve additional analysis to verify findings, identification of the reason(s) for elevated level(s), re-design of monitoring strategies for specific elevated contaminants and consider resource or emission management issues.

Table 1. Descriptors for a red, green, blue "traffic light" system.

Traffic light colour	**Understanding of what the traffic light colours mean**		**Possible types of management activity**
RED	Status is unacceptable. Concentrations of contaminants are at levels where a risk to the environment and its living resources at the population or community level should be assumed. Potential for significant adverse effects to the environment, or to human health.		Measures in place or under consideration to address the cause. Regular monitoring to determine status and trends.
GREEN	Status is acceptable. Concentrations of contaminants are at levels where it can be assumed that little or no risks are posed to the environment and its living resource at the population or community level. No significant risk of adverse effects to the environment, or to human health.		Measures generally are not necessary to improve status, but may be required if there is a trend towards a deterioration in status. Appropriate monitoring regime to ensure that there is no deterioration.
BLUE	Status is acceptable. Concentrations are close to background or zero, i.e. the ultimate aim of the OSPAR Strategy for Hazardous Substances has been achieved.		Measures not required. Appropriate monitoring regime to ensure that there is no deterioration.
AMBER	Concentrations are lower than EC dietary limits for fish and shellfish and above background but the extent of risks of pollution effects is uncertain		

The establishment of the transition points T_0 and T_1, requires the definition of a series of reference concentrations, particularly of Background Assessment Concentrations (BACs), derived from the Background Concentrations (BCs), and the Environmental Assessment Criteria (EACs).

2. Definitions

2.1 Background concentration (BC)

"Background concentrations" (BCs) are assessment tools intended to represent the concentrations of certain hazardous substances that would be expected in "pristine" or "remote" sites, based on contemporary or historical data. The Background Concentration for man-made substances (e.g. chlorinated pesticides) should be regarded as zero.

The BCs in Annex I have been recommended for use throughout the OSPAR maritime area.

It is recognised that natural processes such as geological variability or upwelling of oceanic waters near the coast may lead to significant variations in background concentrations of contaminants, for example trace metals. The natural variability of background concentrations should be taken into account in the interpretation of data, and local conditions should be taken into account when assessing the significance of any exceedance. This needs to be explained where it is a relevant factor in data interpretation.

In order to facilitate precautionary assessments of data against BCs, OSPAR has developed Background Assessment Concentrations (BACs).

2.2 Background assessment concentration (BAC)

"Background assessment concentrations" (BACs) are statistical tools defined in relation to the background concentrations (BCs), which enable statistical testing of whether observed concentrations can be considered to be near background concentrations. Observed concentrations are said to be 'near background' if the mean concentration is statistically significantly below the corresponding BAC (OSPAR Publication 2008/379).

BACs are calculated according to the method set out in Section 4 of the CEMP Assessment Manual. The outcome of this method is that, on the basis of what is known about variability in observations, there is a 90% probability that the observed mean concentration will be below the BAC when the true mean concentration is at the BC. Where this is the case, the true concentrations can be regarded as "near background" (for naturally occurring substances) or "close to zero" (for man-made substances).

The BAC value for a particular contaminant will depend, for PAHs and metals, on the BC and the residual variance in temporal trend series at the BC (OSPAR Publication 2008/379). The BC for man-made substances is zero, and in this case the variance used to derive BACs is the variance at a low concentration that is small but detectable by common analytical methods.

2.3 Environmental Assessment Criteria (EAC)

"Environmental Assessment Criteria" (EAC) are assessment tools intended to represent the contaminant concentration in sediment and biota below which no chronic effects are expected to occur in marine species, including the most sensitive species. EACs continue to be developed for use in data assessments. Concentrations below the EACs are considered to present no significant risk to the environment and to that extent EACs may be considered as being related to the EQSs applied to concentrations of contaminants in water, for example under the Water Framework Directive.

EACs use as starting point an ideal approach to derivation of environmental assessment criteria for any given substance based on dose-response relationships. The immediate consequence of the EAC definition is that a relation between exposure and its associated biological effect must be known. Also, the EAC concept relies on the assumption that not only a relation between dose (or concentration) and response (the biological effect) exists, but that this relation is strictly monotone.

The mathematical form of a dose-response relation must be expected to be specific for each contaminant × response combination, with a general distinction between continuous and binary responses. If the individual response is measured on a continuous scale (e.g. loss in weight), then responses are equal to or greater than zero with no theoretical upper limit, and the same holds for the mean within a population or a sample. If the individual response is of the binary yes/no type (e.g., an individual is diseased or not), then the dose-response relation for a population or a sample describes the proportion or the percentage of affected individuals, and this is restricted to lie in the range 0 to 1 (or 0% to 100%) (Figure 2).

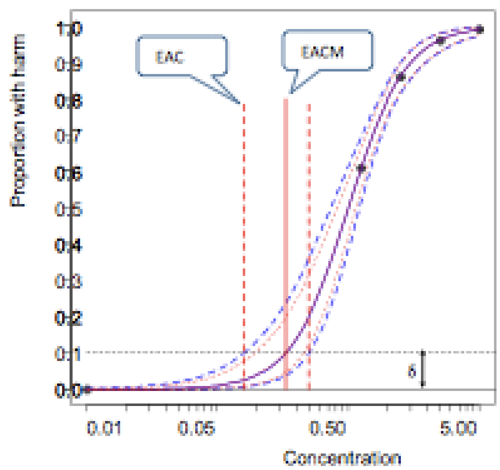


Figure 2. Typical dose-response relationship for a population of organisms.

Identify the largest dose for which the associated expected response is < δ. This initial approach is demonstrated by the EACM. The resulting uncertainty in the dose response relation is expressed by the 95% confidence band for the dose response curve. Uncertainty in the whole dose-response relation induces uncertainty in the resulting EAC value, which can be expressed by the 95% confidence interval for the EAC. In order to incorporate the sampling uncertainty into the determination of the EAC it is recommended to use the lower confidence limit of EACM as the assessment criterion.

BCs, BACs and EACs currently available for chemical contaminants are shown in Annex I. The latter have been derived on the basis of existing toxicological data.

2.4 Cautionary note on the use of EACs

EAC should be used as an assessment tool specifically for the interpretation of monitoring data and the development of monitoring strategies. However, caution should be exercised in using these generic environmental assessment criteria in specific situations. Their use does not preclude the use of common sense and expert judgement when assessing environmental effects and/or the potential for them. EAC should not be used as a trigger for source directed action without further evaluation. Furthermore, the defined environmental assessment criteria do not take into account specific long-term biological effects such as carcinogenicity, genotoxicity and reproductive disruption due to hormone imbalances, and do not include combination toxicology.

Sediments may also be a source of biomagnification and effects in higher organisms, but as yet no reliable method is available to carry out this type of assessment.

For some substances and matrices EAC have not been derived because of the limited quantity of ecotoxicological data for marine species.

3. Methodologies

3.1 Determination of Background Concentrations (BCs) for metals (Cd, Hg, Pb) and PAHs [BC for CBs is considered zero]

Sediments

Data from the analysis of pre-industrial layers of dated cores will be collected from the scientific literature and organized per geographical areas. Then the median will be calculated in each area, as well as the median of the medians. One BC will be used for the whole Mediterranean region, unless scientific evidence suggests a different BC for a specific site.

In order to normalize for sediment size variability in the metal content, metal data should be normalized to Al. Similarly, the OC percentage will be used for normalizing the PAHs concentrations in sediments.

The results of these calculations will be compared with the data in MED POL database, in order to assure that the calculated median from the scientific literature is compatible with the MED POL data in non-polluted areas.

Biota

BCs of trace metals in biota will be defined taking the median of the lower 5% of data available in the MED POL database, excluding well known polluted sites.

In order to decide if normalization to organism size (age) is required, MED POL will check if there is a significant metal concentration/size statistical dependency, using the trend analysis monitoring data.

As in the case of sediments, the results of these calculations will be compared with the scientific literature, in order to assure that the calculated median from the MED POL database is compatible with the concentrations in non-polluted areas.

3.2 Determination of Background Assessment Concentrations (BACs) for CBs, PAHs and metals (Cd, Hg, Pb)

BACs are derived from the BCs, taking into account the analytical precision of the monitoring programme. This can be calculated by considering temporal monitoring data (OSPAR, 2008) or the variability of reported data on Certified Reference Materials (sediment and biota) used by regional laboratories in proficiency testing:

- QUASIMEME database
- IAEA database
- MED POL database

Using temporal data from the OSPAR Monitoring Programme, typical levels of variability (field and analytical combined) at concentrations near background can be established. For each contaminant/matrix combination, the residual standard deviation ψ was estimated for all available time series. This was then used to calculate the % coefficient of variation (% CV) of the estimated mean concentration in the final year of a ten years time series:

$$\% \text{ CV} = 72.7\psi$$

Since residual standard deviations, or equivalently the % CVs, might be greater at lower concentrations where analytical measurements are more challenging, the relationship between variability and mean concentration was summarised by a robust LOESS smoother. The smoother was then used to estimate a "typical" % CV at the BC, and from this, the provisional BAC was calculated as:

$$\text{BAC} = \text{BC} \exp(3.18 \text{ CV})$$

Modifications were needed to deal with CBs where the BC is zero. Specifically, the BAC for individual CBs and Σ7CB was calculated as

$$\text{BAC} = 0.1 \exp(3.18 \text{ CV}) \quad \text{and} \quad \text{BAC} = 0.4 \exp(3.18 \text{ CV})$$

respectively.

The factors 0.1 and 0.4 were adopted as twice the QUASIMEME constant error in estimating CBs (expressed as µg kg^{-1}) and thus represent lowest concentrations that should be measurable.

As detailed above CEMP data can be assessed to evaluate the precision of the monitoring program (OSPAR, 2008). Provisional BACs can then be set to give a high probability of concluding that concentrations are near background when [c] = BC. This was considered by CEMP using the temporal monitoring data from the UK National Marine Monitoring Program. Table 3 gives the precision of the programme *summarised* by contaminant group and matrix.

Table 3: Precision of OSPAR Monitoring Programme

	Sediment	Shellfish	Fish	Water
Metals	11%	14%	21%	11%
CBs	32%	30%	36%	
PAHs	21%	27%		

Figure 3 shows the corresponding probability (power) of concluding that concentrations are near background when [c] = BC as the BAC increases relative to the BC. Thus, for metals, setting the BAC to be twice the BC would give at least 90% power of concluding that concentrations are near background when [c] = BC. Different multipliers could be used for contaminant group / matrix combination, or for each contaminant / matrix combination, if appropriate.

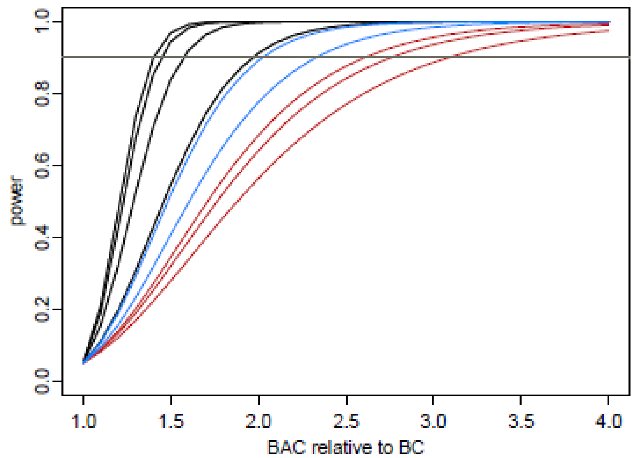


Figure 3. The power of concluding that concentrations are near background when [c] = BC for different values of BAC based on UK monitoring data. Running from left to right, the black lines are for metals in sediment, water, shellfish and fish; the blue lines are for PAHs in sediment and shellfish; and the red lines are for CBs in shellfish, sediment and fish.

At this stage a statistical test as described above on the MEDPOL monitoring programs is not yet available. Therefore we could use the above relationships between BC and BAC for metals in sediments, fish and shellfish to assess the BACs levels. Thus, for sediments and shellfish BAC=1.5xBC, for fish BAC=2xBC. It is recommended to perform a statistical test to evaluate the precision of MEDPOL monitoring programs (per country), in order to define relationships between BC and BAC for fish and shellfish in the Mediterranean. Regarding the CBs, the data availability is very limited, therefore we have been unable to determine corresponding BACs.

3.3 Determination of Environmental Assessment Criteria (EAC) for CBs, PAHs and trace metals (Cd, Hg, Pb)

The development of Mediterranean EACs is a difficult task because it requires together with concentrations in biota and sediments of the priority subtsances, ecotoxicological data for autochthonous marine species, which is largely lacking. To this end, Mediterranean and international data should be used to:

- Find out the most appropriate key sensitive species in the Mediterranean that can serve as a proxy for assessment, and
- Propose ecotoxicological studies to fill the gaps.

Although it is biologically inappropriate to evaluate absolute BC, BAC and EAC metal levels in one species from the parallel levels of even a close relative species, however, as a first approach, we can use information deriving from the work of OSPAR, assuming that the EACs defined for one species in the OSPAR region can be used in the Mediterranean. Specifically:

Mytilus edulis (OSPAR) vs *Mytilus galloprovincialis* (MAP)
A benthic fish (OSPAR) vs *Mullus barbatus* (MAP)

A summary of the adaptation of the OSPAR Environmental Assessment Criteria to the Mediterranean is presented in section 7.

4. Definition of Background Concentrations (BC) for trace metals in Mediterranean sediments

The BCs were estimated based on published historical data (sediment cores) in the Mediterranean basin. For each data set the bottom values were taken (usually median concentration if more than one value was available) as shown in Table 4. If anoxic conditions and derived diagenetic processes or anthropogenic influences were suspected the data was excluded. Only on few data sets it was possible to normalize the metal concentrations to Al.

Table 4. Estimated background concentrations of Hg, Pb and Cd based on available data in sediment cores in the Mediterranean.

Location	n Cores	Core Depth / Sections (cm)	Dated	Sedimentation rate	Core bottom date	Hg Surficial conc. (ng/g dw)	Hg Bottom conc. (ng/g dw)	Pb normalised to 5% Al (ug/g dw)	Pb Bottom conc. (ug/g dw)	Cd normalised to 5% Al (ug/g dw)	Cd Bottom conc. (ng/g dw)	Reference	Comments
Ionian Sea	1	10 / 1 cm intervals	No			40.32	16-40					Ogrinc et al., 2007	Sampling 2003
Levantine basin	1	10 / 1 cm intervals	No			43.53	10-40					Ogrinc et al., 2007	Sampling 2003
Strait of Otranto	1	10 / 1 cm intervals	No			77.03	16-40					Ogrinc et al., 2007	Sampling 2003
Western basin south	1	10 / 1 cm intervals	No			40.32	16-40					Ogrinc et al., 2007	Sampling 2003
Alboran Sea	1	10 / 1 cm intervals	No			55.96	16-40					Ogrinc et al., 2007	Sampling 2003
Western basin north	1	10 / 1 cm intervals	No			60.38	16-40					Ogrinc et al., 2007	Sampling 2003
Eastern Mediterranean basin						8-40						Cossa and Coquery, 2005	
Western Mediterranean basin						78-90						Cossa and Coquery, 2005	
Northwestern Mediterranean, Llobregat cont.	3	50 / 3 or 5 cm intervals	yes till 1840	0.15-0.29 cm yr-1	1840 - 1860			36	29-30			Palanques et al., 2008	Sampling 1997?; cores CN-
Eastern Mediterranean, Thermaikos Gulf	3	35 / 0.5or1or 5 cm intervals	~1850 (IP-30)	0.087 - 0.751 cm yr-1	~1850 (IP-30)			30	17-34			Karageorgis et al., 2005	Sampling 2001; cores IP-17, IP-30,
Ligurian Sea	2	40 / 0.5 or 1 cm intervals	1860		~1900				15-18			Martin et al., 2009	normalization to Ti
Soline bay, Croatia	2	24-26 / 2 cm intervals							28.5-29.9			Kljakovic-Gaspic et al., 2009	
	1	35 / 0.5 or 2 cm intervals	yes	0.5 cm yr-1	1840				75			Garcia-Orellana et al., 2011	
Lebanese coast, eastern Mediterranean	3	30 / 1 or 3 cm intervals	no				10-20					Abi-Ghaneam et al., 2011	sampling 2006
Western Basin, deep sea sediment	2	37 / 0.5 or 1 or 2 cm intervals							14.1-23.5		67-107	Angelidis et al., 2011	sampling 2001
Eastern Basin, deep sea sediment	2	37 / 0.5 or 1 or 2 cm intervals		0.006-0.017 cm yr-1					11.2-18.9		84-301	Angelidis et al., 2011	sampling 2001
Eastern Basin, Israeli coast	3	25 / 1 cm intervals	yes		1900			7-8.5	7.4-10.2	~100	<110	Almogi-Labin, Herut, unpublished	sampling 2007
Eastern Basin, Israeli coast	2		yes		7600/8500			9	6-7	~100	200	Mor-Federman T. (MSc Thesis, in press)	
Eastern Basin, Israeli coast	3	25 / 1 cm intervals	no			130	9-20					Herut et al., 1996; Bareket M (MSc Thesis in process)	sampling 2009
Eastern Basin, Israeli coast	1	29 / 1 cm intervals	no					7.5	7-10	~100	100-300	Hyams-Kaphzan, Herut, Almogi-Labin unpublished	sampling 2003
Estimated median as BC							***30***	***20***		***100***	***100***		

Total mercury (Hg)

In Ogrnic et al. (2007) the concentrations of Hg (total) ranged from 12 to 447 ng g^{-1} dw. In most sediment cores concentrations decreased from surface and at a depth of 10 cm varied between 16 and 40 ng g^{-1} dw within the range values of the Earth's crust. This range of concentrations is in agreement with total Hg concentrations observed in deep sea cores collected in the Eastern and Western Mediterranean basins (Cossa and Coquery, 2005): at surface sediments between 78 and 90 ng g^{-1} dw and 8 and 40 ng g^{-1} dw in the Western and eastern Basins, respectively. The decrease of Hg with depth may be attributed also to diagenetic processes (Fe-related remobilization). At the continental shelf off the Lebanese coast and off Israel, similar but somewhat lower values were recorded at the bottom of the sediment cores, 9-20 ng Hg g^{-1} dw.

Lead (Pb) and Cadmium (Cd)

Few cores with data were available and only in part normalization to Al was possible (see Table 4). Generally, Pb showed a correlation with Al while no such relationships were observed for Cd. Pb value for cores normalised to Al were between 7 and 36 ug g^{-1} dw.

The core values were compared to the lowest concentrations obtained from the surface sediments of MEDPOL database. With the exception of Egypt, Israel and Italy (Figure 4), it was not possible to normalise the concentrations to Al (or other normaliser). Therefore, the whole MEDPOL surface sediments dataset was considered. For each metal, the lower 5% percentile was taken as a probable lowest concentration in surface sediments, as shown in Table 5, and then the median of the 5% and 10% percentile was calculated (Table 5 and Figure 4).

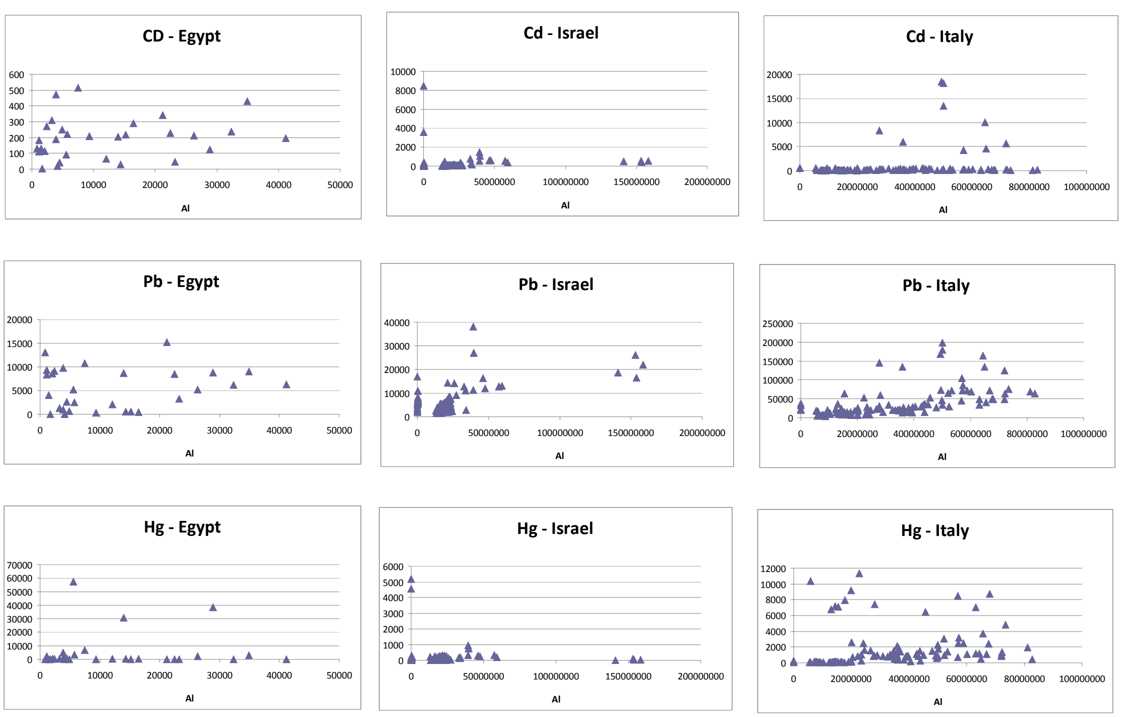


Figure 4. Hg, Cd and Pb versus Al concentrations in surficial sediments in the Mediterranean (MEDPOL dataset).

Table 5. Calculated Hg, Cd and Pb median concentrations of the 5% percentile for surficial sediments in the Mediterranean (MEDPOL dataset).

Element	*Country_Determ*	*Rec N*	*N/40=*	*ng/g dw. median 5% percentile*	*Comment*
Cd	Croatia_CD	24	0.6	**60.86**	
	Egypt_CD	30	0.8	**3.8**	
	France_CD	13	0.3	**50**	constant value
	Greece_CD	197	4.9	**0.09**	
	Israel_CD	143	3.6	**20.48**	
	Italy_CD	113	2.8	**20**	
	Morocco_CD	5	0.1	**0; 230**	zero values
	Syria_CD	8	0.2	**1190**	
	Tunisia_CD	13	0.3	**0.2**	
	Turkey_CD	219	5.5	**19**	
Hg	Croatia_HGT	20	0.5	**55.7**	
	Egypt_HGT	30	0.8	**22**	
	France_HGT	13	0.3	**10**	
	Greece_HGT	149	3.7	**0.12**	
	Israel_HGT	152	3.8	**1.74**	
	Italy_HGT	555	13.9	**6**	"0" values in 59 cells
	Tunisia_HGT	13	0.3	**0.06**	
	Turkey_HGT	233	5.8	**25.54**	
Pb	Croatia_PB	24	0.6	**10455.2**	
	Egypt_PB	30	0.8	**0; 25**	zero values
	France_PB	13	0.3	**6000**	
	Greece_PB	189	4.7	**12.5**	
	Israel_PB	144	3.6	**1865.4**	
	Italy_PB	555	13.9	**620**	
	Morocco_PB	12	0.3	**2310**	
	Syria_PB	8	0.2	**4060**	
	Tunisia_PB	13	0.3	**12.76**	
	Turkey_PB	135	3.4	**3420**	

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Rec N is the number of records in the dataset,
N/40 gives the medians of the 5% percentile (which is N/20).

For all metals, the 5% or even 10% percentile are close to, and sometimes even lower than the proposed BC value. A summary of the Hg, Cd and Pb concentrations of the 5% and 10% percentile in surface sediments in the Mediterranean from the MEDPOL dataset is shown in Figure 5.

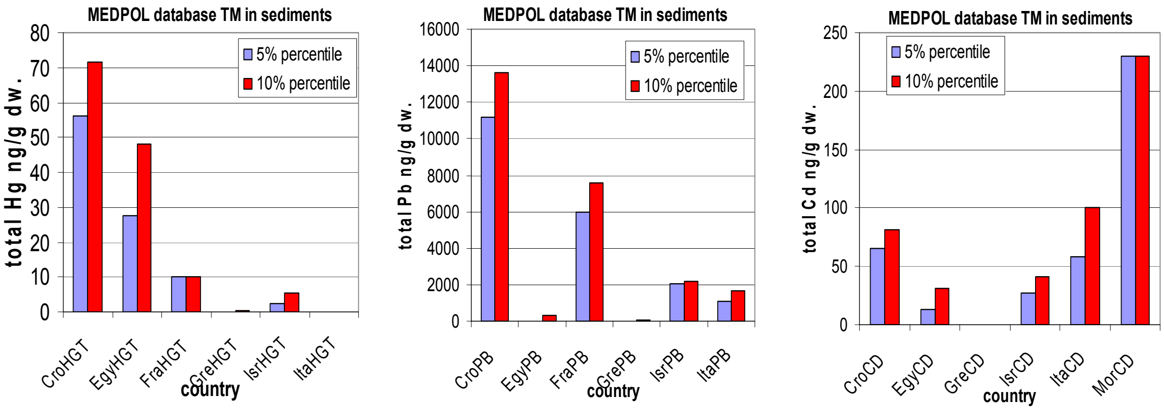

Figure 5. Hg, Cd and Pb concentrations of the 5% and 10% percentile in surface sediments in the Mediterranean (MEDPOL dataset).

The BC values obtained for the Mediterranean area are also compared to the background concentrations estimated by OSPAR and ICES database. Table 6 gives the suggested normalised BC values for all regions of the OSPAR area. It also presents the lower values of the current concentrations in surface sediments, using results collated from the ICES OSPAR Commission, 2008: database. As it was not possible to normalise those data, only sediments from the fine fraction (20–90 µm) were taken into consideration. For each metal, the lower 5% percentile was taken as a probable lowest concentration in surface sediments. As shown in Table 6, for all metals, the 5% percentile of ICES data is close to, and often even lower than, the proposed BC value. Comparing BCs with the lower 5% percentile concentrations in the ICES database, it can be seen that Hg and Pb concentrations in current surface sediments are generally well above the suggested background concentration, whereas the other elements are close to or below the suggested background concentration. The table includes also the global average for shale after recalculating them to 50 g kg^{-1} Al, and the content in the earth's crust (not normalised).

Table 6: Estimated background concentrations (mg/kg dw.) and corresponding former BRCs, earth crust values, data held in the ICES database, and OSPAR EACs.

Table 3.1 Estimated background concentrations and corresponding former BRCs, earth crust values, data held in the ICES database, and OSPAR EACs.

Element		As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Suggested BC[1)]		15[2)]	0.2	60	20	0.05	45[2)]	25	90
1996 BRC (lower) [3)]		12	0.04	52	13	0.02	26	8	51
1996 BRC (upper) [3)]		26	0.17	116	33	0.04	53	23	104
1996 BRC (shale)		6	0.08	51	25	0.02	38	9	65
Earth Crust[4)]		5.5	0.15	51	23		35	11.5	92
ICES[5)]	5% Percent.	11	0.11	51	14	0.07	18	31	95
Database	Median	33	0.50	92	28	0.25	38	94	200
(20–90 µm)	(n)	(1304)	(1754)	(1656)	(1858)	(1764)	(1472)	(2162)	(1866)
EAC (low)		1	0.1	10	5	0.05	5	5	50
EAC (high)		10	1	100	50	5	50	50	500

[1]The suggested normalised BC values are valid for all regions of the OSPAR Area.

[2]For these elements, the core data from Region II and the Baltic area suggest that a lower value could be applied for this region.

[3]The Me/Al ratios were recalculated to a sample composition of 50 g kg^{-1} Al.

[4]Data for earth crust not normalised.

[5]All sieved data from the ICES database were taken into account, and the lower 5% percentile value and median value were taken as a guideline for the content in surface sediments, with the number of data given parentheses.

In summary, estimated median values of BCs for trace metals in sediments in the Mediterranean are suggested in Table 7, which in addition presents the OSPAR BCs and BACs normalised to 5% aluminium for trace metals. While in the sediment cores similar values were obtained for the Mediterranean and OSPAR areas, the calculated values for the median of the 5% percentile medians in the MEDPOL dataset show much lower levels. This is probably attributed to the fact that no normalization could be done for grain size variability and probably much coarser sediments are analysed. The maximal values of the 5% percentile, however, show values somewhat closer to the OSPAR BC levels.

Table 7. Estimated median Mediterranean BCs (µg/kg dry weight) for Hg, Cd and Pb in sediments.

Element	Sediment cores estimated median Mediterranean BC	Median of 5% percentile medians MEDPOL dataset	Maximal median of 5% percentile MEDPOL dataset	OSPAR BC normalised to 5% Al	OSPAR BAC normalised to 5% Al (T_0)
Hg	**30** (10-40)	10	56	50	70
Cd	**100** (100-200)	20	61	200	310
Pb	**20,000** (9,000-30,000)	2310	10455	25,000	38,000

5. Background Assessment Concentrations (BACs) of trace metals in sediments and biota of the Mediterranean

5.1. Sediments

Using the above approach on MEDPOL dataset (median values of the 5% percentile median as BCs), the calculated BACs for the sediments are shown in Table 8. The table shows also the calculated BACs based on the sediment cores BCs estimates. The calculated BACs, based on the 5% percentile median are lower than the values adopted by OSPAR or the sediment core estimates. The suggested reasons for the large differences (under-estimates) using the MEDPOL dataset are presented in section 4. It should be however emphasized that no normalisation procedure can be applied in the MEDPOL dataset and that it contains errors that needs further consideration.

Table 8. Calculated BACs for the Mediterranean (BACs=BCsx1.5) using the estimated sediment cores BCs or the median value of the 5% percentile medians of the MEDPOL dataset. Both estimates are compared to OSPAR BACs.

	Hg	Cd	Pb
5% percentile median of medians (MEDPOL dataset)			
BACs calc. med 5%	***15***	***30***	***3465***
Sediment cores			
BACs calc. med	**45**	**150**	**30000**
OSPAR BACs	***70***	***310***	***38000***

5.2. Biota

OSPAR working group on monitoring (MON) recommend the following pragmatic approach towards estimating BACs:

i. construct the empirical distribution of the upper 95% confidence limit on the fitted concentration in the final monitoring year;
ii. take the lower 5 percentile of this distribution to be the BAC.

MON 2007 reviewed the work undertaken since 2004 to establish Background Concentrations (and related Background Assessment Concentrations) for metals in fish and shellfish. The table below (Table 9) shows BAC values estimated using the proxy method proposed by MON 2007, compared with the BC and BAC values used by MON 2005 and MON 2006

Table 9. BAC values estimated using the proxy method proposed by MON 2007, compared with the BC and BAC values used by MON 2005 and MON 2006 (OSPAR documents).

		2005		2006		2007
		BC	**BAC**	**BC**	**BAC**	**BAC**
shellfish[1]	cadmium		550	1200	1940	450
	mercury		50	80	140	65
	lead		950	900	1520	340
	copper		5500	5300	7570	6000
	zinc		150000	275000	426000	63000
fish[2]	cadmium					26
	mercury		70 or 50[3]		70 or 50[3]	35
	lead					26
	copper					3900
	zinc					22000

[1] µg kg^{-1} dw

[2] µg kg^{-1} ww in muscle (mercury) and liver (others)

[3] flat fish or cod / whiting respectively

In the MEDPOL database the median of the lower 5% of data available was calculated as proxy for the trace metals BACs. However, a more comprehensive examination is needed to decide if normalization to organism size (age) is required.

The following table (Table 10) presents the calculated median values of the 5% percentile of mercury, cadmium and lead in fish (*Mullus barbatus* – MB) and shellfish (*Mytilus galloprovincialis* - MG) in MEDPOL database. For some countries the database contains errors that need further examination.

Table 10. Calculated Hg, Cd and Pb median concentrations of the 5% percentile for *Mullus barbatus* and *Mytillus galoprovincialis* in the Mediterranean (MEDPOL dataset).

Element	Country_Det_Sp	Rec N	N/40	Value
	Fish: Mullus barbatus			
Hg	Cyprus_HGT_MB	51	1.3	**30**
	Greece_HGT_MB	11	0.3	**0.5**
	Israel_HGT_MB	453	11.3	**3.32**
	Turkey_HGT_MB	263	6.6	**11.29**
Cd	Cyprus_CD_MB	35	0.9	**5**
	Greece_CD_MB	76	1.9	**0.0001**
	Israel_CD_MB	40	1	**22.55**
	Syria_CD_MB	6	0.2	**340**
	Turkey_CD_MB	263	6.6	**8.03**
Pb	Cyprus_PB_MB	30	0.8	**10**
	Greece_PB_MB	17	0.4	**0.07**
	Syria_PB_MB	6	0.2	**140**
	Bivalve: Mytillus galoprivincialis			
Hg	Albania_HGT_MG	41	1	**0.29**
	Croatia_HGT_MG	172	4.3	**68**
	France_HGT_MG	512	12.8	**0.04**
	Greece_HGT_MG	53	1.3	**0.2**
	Italy_HGT_MG	474	11.9	**0.05**
	Morocco_HGT_MG	43	1.1	**10**
	Slovenia_HGT_MG	84	2.1	**63**
	Spain_HGT_MG	343	8.6	**11.33**
	Tunisia_HGT_MG	21	0.5	**3**
	Turkey_HGT_MG	89	2.2	**9.69**
Cd	Albania_CD_MG	41	1	**0.28**
	Croatia_CD_MG	212	5.3	**290.5**
	France_CD_MG	512	12.8	**0.27**
	Greece_CD_MG	70	1.8	**0.33**
	Italy_CD_MG	508	12.7	**0.224**
	Morocco_CD_MG	51	1.3	**26**
	Slovenia_CD_MG	80	2	**560**
	Spain_CD_MG	356	8.9	**58.7**
	Tunisia_CD_MG	20	0.5	**92**
	Turkey_CD_MG	89	2.2	**59.25**
Pb	Albania_PB_MG	41	1	**3.19**
	Croatia_PB_MG	212	5.3	**282.6**
	France_PB_MG	512	12.8	**0.2**
	Greece_PB_MG	56	1.4	**0.12**
	Italy_PB_MG	503	12.6	**0.55**
	Morocco_PB_MG	49	1.2	**10**
	Spain_PB_MG	356	8.9	**211**
	Tunisia_PB_MG	20	0.5	**210**
	Turkey_PB_MG	38	1	**910**

Rec N is the number of records in the dataset, n/40 gives the medians of the 5% percentile (which is N/20).

A graphical representation is shown in Figures 6 and 7.

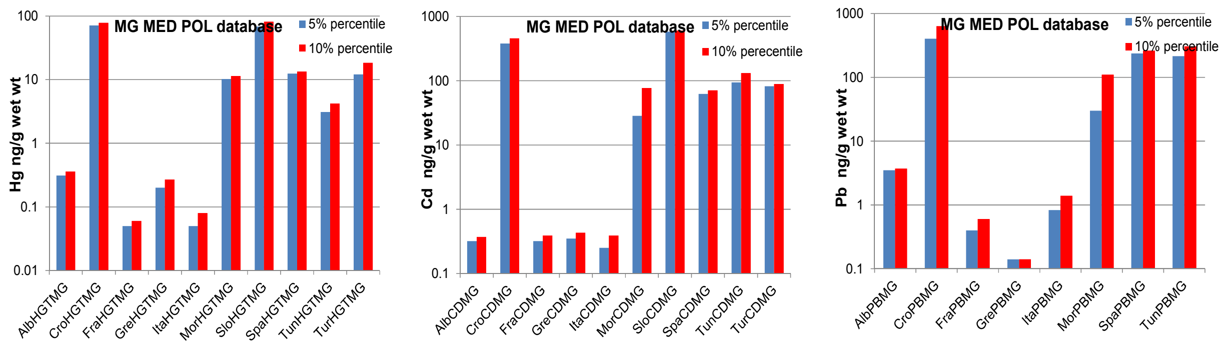

Figure 6. Hg, Cd and Pb concentrations of the 5% percentile and 10% percentile in *Mytillus galoprovincialis* in the Mediterranean (MEDPOL dataset).

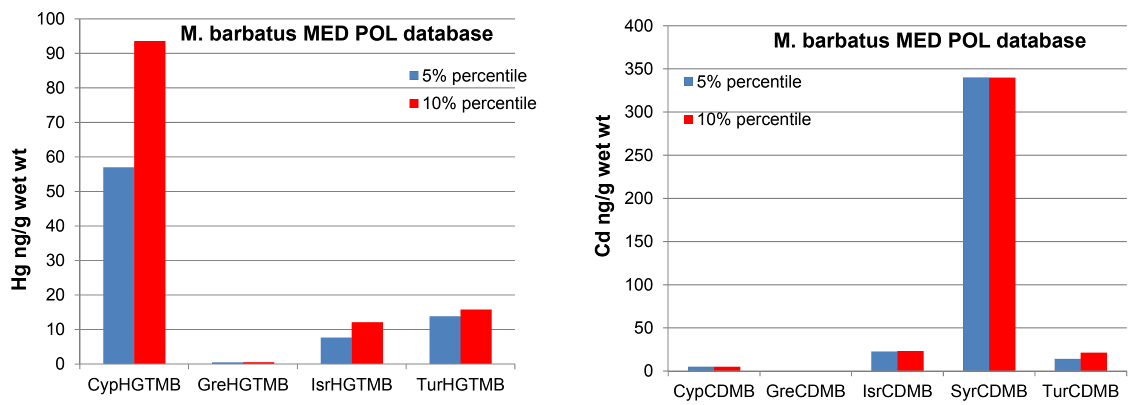

Figure 7. Hg and Cd concentrations of the 5% percentile and 10% percentile in *Mullus barbatus* in the Mediterranean (MEDPOL dataset).

The MEDPOL database contains large variations between countries in its BCs assessment based on the distribution of the trace metals in fish and molluscs. However, in order to provide a first approximation, in Table 11 are presented draft Mediterranean BACs calculated using the median of the median values of country BCs, according to the MED POL database. Certainly further examination of the database should be performed in order to derive more reliable values.

For OSPAR, the MCWG could not recommend BCs or LCs for trace metals in fish, due to the limited dataset. Therefore, a statistical approach was used to derive proxy BACs (MON 2007 Summary Record), presented in the table in Annex I. Regarding metals in mussels, the MCWG 2008 reviewed information on the concentrations of metals in mussels from pristine areas in Spain, Greenland, Shetland/Faroe, Norway and Ireland. LCs proposed by MCWG (median of regional medians) are shown in Annex I.

Table 11. Calculated BACs for the Mediterranean using the estimated biota BCs based on the medians of the 5% percentile medians of the MEDPOL biota dataset. Both estimates are compared to OSPAR BACs.

MEDPOL dataset	**Hg**	**Cd**	**Pb**
Fish – Mullus barbatus (muscle) ng/g wet wt.			
Calulate median of medians 5% percentile median	8	8	10
Calc. BACs = BCmed x 2	***16***	***16***	***20***
OSPAR BACs	***35***	***26 (liver)***	***26 (liver)***
Bivalve – Mytillus galoprovincialis			
Calulate median of medians 5% percentile median 5% percentile median	10	42	7
Calc. BACs = BCmed x 1.5	***15***	***63***	***11***
OSPAR BACs	***140***	***1940***	***1520***

6. Definition of Background Concentrations (BC) for PAHs in Mediterranean sediments

In order to define the background concentrations for PAHs in Mediterranean sediments, data from the analysis of pre-industrial layers of dated cores have been collected from the scientific literature.

Information on PAHs in sediment cores has been obtained from 11 different studies in the different regions, as shown in Table 12. For comparison purposes, a number of studies from others parts of the world are shown in Table 13. As it can be seen, the bottom levels range from 12 to 184 ng g^{-1} dw, which are similar to those found in the Mediterranean sediments.

In general, the ratio 3-4 ring / 5-6 ring PAHs increases with depth, as observed e.g. in:

Berto et al (2009) – Ustica Island
Frignani et al (2003) – Venice Lgoon
Hatzianestis et al (2001) – Thermaikos Gulf
Hatzianestis et al (2004) – Elefsis Bay
Heath et al (2006) – Gulf of Trieste

possibly due to:

- a decrease of the pyrogenic (5-6 ring) PAHs released during industrial time (burning of coal, oils,...)
- a higher 3-4 ring PAH contribution from wildfires and domestic wood combustion previous to industrial time.

From these studies, only those cores that have been dated and included concentrations for individual PAHs have been used to derive background concentrations. Median concentrations have been calculated for each data set, as well as mean and median of the medians, which are shown in Table 14.

The resulting profile of parent PAHs is shown in Figure 8. This profile differs significantly with that obtained from surface sediments from deep sea regions, which exhibit a more significant pyrolytic signature, according to the known downward transport of Atmospheric particulate matter along the water column (Dachs et al., 1997).

The Background concentrations of individual PAHs (in ng g^{-1} dw) for Mediterranean sediments are summarized in Table 15, as well as those calculated for the Atlantic coast of Spain and those proposed by OSPAR.

Data have not been normalized to organic carbon, but % of OC for each core (which ranges 0.3-1.9%) is also provided in Table 14.

Table 12. Review of studies including concentration data of PAHs in sediment cores in the Mediterranean.

Location	**n Cores**	**Core Depth / Sections** (cm)	**Dated?**	**Core bottom date**	**Bottom depth** (m)	**n PAHs**	**Surficial conc.** (ng/g dw)	**Bottom conc.** (ng/g dw)	**Conc. data for individual PAHs?**	**Reference**
Lake Mayrut, Alexandria, Egypt	2	40 / 5 cm intervals	No	NA	NA	39	5560 (PAH16)	215 (PAH16)	No (only graphical)	Barakat et al., 2011
							115 (PAH16)	15 (PAH16)		
Ustica Island, SW Tyrrhenian, Italy	3	9-11 / 1-2 cm intervals	Yes (^{210}Pb and ^{137}Cs)	~1954	364-372	14	22-87	8-12	Yes	Berto et al., 2009
Sicily Channel and Gulf of Tunis	2	20	No	NA	720	22	343	27	No (only graphical)	Mzoughi & Chouba, 2011
					660		106	48		
Sicilian Coast, Italy	3	12-23 (Augusta)	Yes (^{210}Pb and ^{137}Cs)	~1940	62-145	16	~50	~10-20	No	Di Leonardo et al., 2007
		21 (Palermo)		~1920	100		~20,000	~100		
Venice Lagoon, Italy	3	~35-54 / 3 cm intervals	Yes (^{210}Pb and ^{137}Cs)	~1850/1870	NA	16	315-810	~40-100	No (only graphical)	Frignani et al., 2004
	1	~50	Yes (^{210}Pb and ^{137}Cs)	~1850	NA	23	528	30	Yes	Pavoni et al., 1987; Marcomini et al., 1987
Gulf of Trieste	3	245, 320, 120 / 1 cm intervals	Yes (Hg, ^{14}C)	~9000 yr BP	NA	22	~600-900	~80-250	Yes	Heath et al., 2006
Elefsis Bay, Greece	2	32-35 / 1 cm intervals	Yes (^{210}Pb)	~1900	NA	19	1257-1626	42-75	Yes	Hatzianestis et al., 2004
Thermaikos Gulf, Greece	1	60	No	NA	NA	25	453	202	No	Hatzianestis et al., 2001
NW med French coasts	5	24-34	No	NA	NA	6	61-1371	24-851	Yes	IFREMER, 1998
Rhone & Ebro prodeltas	2	30 (Rhone)	Yes (^{210}Pb)	~1840	101	32	466	174	No (only graphical)	Tolosa et al., 1996
		22 (Ebro)		~1880	75		65	37		

Table 13. Review of studies including concentration data of PAHs in sediment cores in other regions of the world.

Location	**n Cores**	**Core Depth / Sections** (cm)	**Dated?**	**Core bottom date**	**Bottom depth** (m)	**n PAHs**	**Surficial conc.** (ng/g dw)	**Bottom conc.** (ng/g dw)	**Conc. data for individual PAHs?**	**Reference**
Black Sea	1	22 / 1-2 cm intervals	No	NA	NA	28	1250	12	Yes	Wakeham, 1996
Pettaquamscutt River, Rhode Island, USA.	7	90 / 0.5 cm intervals	^{210}Pb, ^{214}Pb, ^{137}Cs	~1820	20	15	NA	NA	No (only graphical)	Lima et al., 2003
Stora Frillingen lake, Aspvreten, Sweden	1	50 / 1 cm intervals	^{226}Ra/^{210}Pb, ^{137}Cs, and ^{14}C	~1343	NA	17	1730	184	Yes	Elmquist et al., 2007
Wuhan, Central China (urban lake)	1	52 / 2 cm intervals	^{210}Pb, ^{226}Ra, ^{137}Cs	~1910	3.8	16	~300	~35	No (only graphical)	Yang et al., 2011

Table 14. Calculated mean and median background concentrations (ng g^{-1} dw) of PAHs in sediment cores in the Mediterranean.

Location	**Core depth** (cm)	**Appr. year**	**%OC**	**Nap**	**Ace**	**Acy**	**Flu**	**Ph**	**An**	**Fl**	**Py**	**BaA**	**Ch**	**BbF**	**BkF**	**BaPy**	**DBA**	**BPer**	**IPy**	**ΣPAHs**
Ustica Island, SW Tyrrhenian, Italy	10,5	1950	0,3	4,0	0,25		1,0	2,0	0,25	1,0	1,7	0,25	0,25	0,25	0,25	0,25	0,25	0,25	0,25	12,17
Elefsis Bay, Greece	32	1900	1,9		0,5	0,5	0,8	5,3	0,8	5,6	5,0	5,3	5,4	10,1		2,6	0,5	2,3	3,2	47,55
Gulf of Trieste	118,5	NA	1	7,4	1,0	1,1	0,7	27,1	2,4	9,9	15,8	7,6	0,8	1,1	0,5	0,05	0,05	0,05	0,05	75,60
Venice Lagoon	50	1850	1.1-1.6	1,2	0,05	0,2	0,3	3,8	0,8	5,5	15,6	1,6	1,8	0,9	0,55	3,1	0,05			35,50
			Mean	4,20	0,45	0,60	0,70	9,55	1,06	5,50	9,50	3,69	2,05	3,08	0,43	1,49	0,21	0,85	1,15	44,51
			Median	4,00	0,38	0,50	0,75	4,55	0,80	5,55	10,28	3,45	1,30	1,00	0,50	1,40	0,18	0,25	0,25	35,13

Nap: naphthalene. Ace: acenaphthene. Acy: acenaphthylene. Flu: fluorene. Ph: phenanthrene. An: anthracene. Fl: fluoranthene. Py: pyrene. BaA: benzo[*a*]anthracene. Ch: chrysene. BbF and BkF: benzo[*b*] and benzo[*k*]fluoranthene. BaPy: benzo[*a*]pyrene. DBA: dibenzo[*ah*]anthracene. BPer:benzo[*ghi*]perylene. IPy: indeno[*1,2,3-cd*]pyrene.

Shadowed: Values below detection limit, divided by 2.

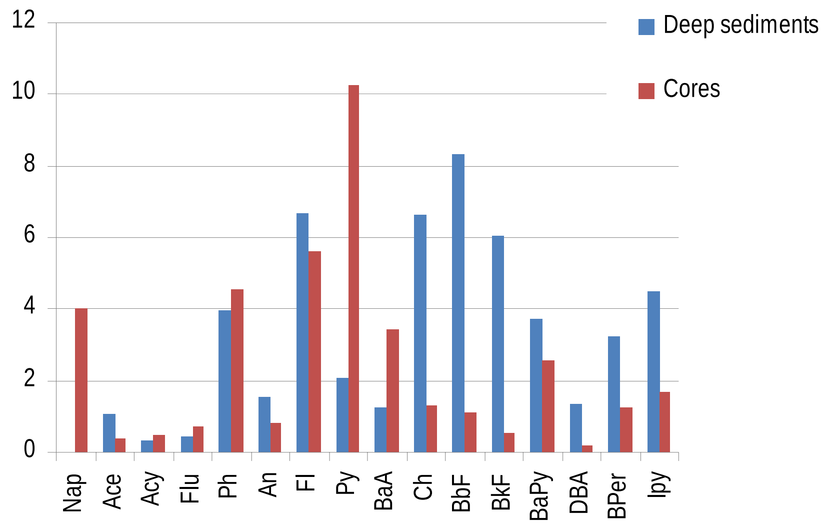

Figure 8. Sediment background concentrations (ng g^{-1} dw) calculated for individual PAHs in the Mediterranean.

Table 15. Background concentrations of individual PAHs (in ng g^{-1} dw) in Mediterranean and OSPAR sediments.

	BC calculated for Mediterranean		**BC calculated for Spain**	**BC proposed by OSPAR***
	Deep sea sed.	Cores	Atlantic coast	OSPAR
Naphtalene	-	4.00	n.a.**	5
Acenaphthene	1.05	0.38	n.a.	n.a.
Acenaphthylene	0.33	0.50	n.a.	n.a.
Fluorene	0.45	0.75	n.a.	n.a.
Phenanthrene	3.95	4.55	4.0	17
Anthracene	1.56	0.80	1.0	3
Fluoranthene	6.70	5.60	7.5	20
Pyrene	2.10	10.28	6.0	13
Benzo[a]anthracene	1.28	3.45	3.5	9
Chrysene	6.64	1.30	4.0	11
Benzo[*b*]fluoranthene	8.32	1.10	n.a.	n.a.
Benzo[*k*]fluoranthene	6.03	0.53	n.a.	n.a.
Benzo[*a*]pyrene	3.71	2.55	4.0	15
Dibenzo[*ah*]anthracene	1.37	0.18	n.a.	7
Benzo[*ghi*]perylene	3.25	1.25	3.5	45
Indeno[*1,2,3-cd*]pyrene	4.49	1.70	4.0	50

* normalised to 2.5% TOC
** not available

7. Definition of Environmental Assessment Criteria (EACs) for the Mediterranean

Based on available literature, EACs have been developed for a range of matrices and contaminants through a combination of work by OSPAR and ICES groups, as shown in Annex I. However, there are on-going discussions about the values proposed for some substances (Webster et al. 2008). Therefore, in cases where the EACs have not been recommended, alternative approaches to appropriate criteria for the assessment of data on contaminant concentrations in sediment and biota need to be considered. For the purposes of the assessment in the Mediterranean, the recently agreed assessment criteria for the OSPAR QSR 2010 (OSPAR, 2009), including EACs and alternative approaches, have been specially taken into account.

In this section we consider applying the OSPAR EACs approach to establish threshold values for key contaminants in the Mediterranean marine environment in order to assess achievement of Good Environmental Status in the framework of the gradual application of the Ecosystem Approach.

a) Trace metals - sediments

EACs are not available for metals, therefore the use of Effects Range values have been recommended by OSPAR (OSPAR, 2009). Effects Range values developed by the US EPA as sediment quality guidelines (SQGs) are used to protect against the potential for adverse biological effects on organisms (Long et al., 1995; MacDonald et al., 1996). The ER-Low (ERL) value is defined as the lower tenth percentile of the data set of concentrations in sediments which were associated with biological effects. Adverse effects on organisms are rarely observed when concentrations fall below the ERL value, and the ERL therefore has some parallels with the philosophy underlying the OSPAR EACs and WFD EQSs. The procedure by which ERL criteria are derived is very different from the methods of derivation of EACs and EQSs, and so precise equivalence between the two sets of criteria should not be expected. However, this is the current interim solution proposed at OSPAR, and therefore the ERL values are proposed as the assessment criteria for the assessment in the Mediterranean (see Table 16).

Table 16. Selected assessment criteria for TM in sediments (µg g^{-1} dw normalized to 2.5% TOC).

Parameter	ERL[a]
Cd	1.2
Pb	46.7
Hg	0.15
Zn	150
Cu	34

[a] Effects Range – Low (Long et al., 1995)

b) PAHs – sediments

EACs for PAHs in sediments are neither available, so the assessment criteria used by OSPAR were the ERL developed by the US EPA, as shown in Table 17. Mean concentrations need to be below the ERL to be classed as green (Figure 1). These values are to be used as an interim solution until EACs are available.

Table 17. Selected assessment criteria for PAHs in sediments (ng g^{-1} dw, normalized to 2.5% TOC).

Parameter	ERL
Naphtalene	160
Phenanthrene	240
Anthracene	85
Fluoranthene	600
Pyrene	665
Benzo[*a*]anthracene	261
Chrysene	384
Benzo[*a*]pyrene	430
Benzo[*ghi*]perylene	85
Indeno[*1,2,3-cd*]pyrene	240

c) PCBs – sediments

EACs are available for the seven individual congeners selected by the ICES. The recommended values to be used are shown in Table 18.

Table 18. Selected assessment criteria for CBs in sediments (ng g^{-1} dw normalized to 2.5% TOC)..

Parameter	EAC[a]
CB28	1.7
CB52	2.7
CB101	3.0
CB118	0.6
CB138	7.9
CB153	40
CB180	12

[a] OSPAR (2009)

d) Trace metals - biota

There are no recommended EACs for metals in biota and equivalents to Effects Range values are not available for fish and shellfish. The alternative approach proposed by Webster et al. (2008), which have been finally adopted for the QSR 2010 (OSPAR, 2009), is to assess the contaminant concentrations in fish and shellfish with respect to their human health risk. The Commission Regulation (EC) No 1881/2006 (and subsequent additions and amendments) sets maximum concentrations for contaminants in foodstuffs to protect public health, i.e. to ensure that contaminant concentrations are toxicologically acceptable. This regulation includes maximum levels for Pb, Hg and Cd in bivalve molluscs and fish muscle, and these are the values that can be selected for the assessment of the Mediterranean (Table 19).

Table 19. Selected assessment criteria for trace metals in biota: maximum concentrations in foodstuff – fish and bivalves (μg g^{-1} dw).

Parameter	Bivalves[a]	Fish[a]
Cd	5	0.25
Hg	2.5	5
Pb	7.5	1.5

[a] EC Commission Regulation No 1881/2006 of 19 December 2006, setting maximum levels for certain contaminants in foodstuffs. Concentrations are expressed in dw by using a factor of x5 (Webster et al. 2008).

However, as pointed out by Webster et al. (2008), standards for fish concentrations of Cd and Pb should be used with caution, as it is recognised that Cd and Pb concentrations in fish liver are naturally greater than in fish muscle. It is recognised that the use of dietary standards is not fully satisfactory in the context of an assessment addressing environmental risk, but their use is an interim solution for addressing the need for criteria until a more appropriate approach and values can be defined and agreed (OSPAR, 2009).

Regarding the MEDPOL biota database, it is biologically inappropriate to evaluate absolute EAC levels in one species from the parallel levels of even a close relative species. It is suggested here that EAC levels for the MEDPOL areas can be derived from the ratio EAC/BAC levels in the compatible OSPAR sentinel species. For example if this ratio in *M. edulis* is 5.6, the comparable level for *M. galloprovincialis* could be calculated as BAC*5.6.

e) Chlorinated pesticides in biota

As chlorinated pesticides have no longer been included in the OSPAR QSR 2010 (OSPAR, 2009), the available EACs from previous assessments have been collected (OSPAR, 2000; OSPAR, 2005; OSPAR, 2008). As it can be observed in Table 20, values are only available for DDE, dieldrin and lindane in mussels. EACs for fish are referred to fish liver; therefore these values have not been selected as the MEDPOL data is referred on a ww basis. In any case, most of the available data from the MEDPOL database is referred to mussel samples.

Table 20. Selected assessment criteria (EAC) for OCP in mussels (ng g^{-1} dw).

Parameter	EAC[a]
DDE	50
Dieldrin	50
Lindane	1.45

[a] OSPAR (2008)

f) PCBs in biota

The recommended EACs to be used in the OSPAR QSR 2010 are shown in Table 21. EACs are available for the seven individual congeners selected by the ICES. No values have been selected for fish, as the available EACs are expressed on a lipid weight basis, while MEDPOL data is available on a wet weight basis.

Table 21. Selected assessment criteria (EAC) for CBs in mussels and oysters (ng g^{-1} dw).

Parameter	EAC[a]
CB28	3.2
CB52	5.4
CB101	6.0
CB118	1.2
CB138	15.8
CB153	80
CB180	24

[a] OSPAR (2009)

8. Concluding remarks

The present report presents a methodology to develop assessment criteria for the definition of threshold limit values for contaminants, in order to assess the achievement of Good Environmental Status in the Mediterranean marine environment in relation to the Ecological Objective EO9, in the framework of the gradual application of the ecosystem approach for the management of human activities in the Mediterranean, by MAP.

The report follows a relevant methodology developed by OSPAR, which propose two threshold limits to be defined in sediments and biota: T_0 to define the threshold at “pristine” sites and T_1 to define the threshold between acceptable (GES) and non-acceptable environmental conditions.

Using Mediterranean data from the MED POL database and applying the OSPAR methodology, the report contains an evaluation of the background concentrations (BCs) and the background assessment concentrations (BACs) of trace meals (mercury, cadmium and lead) and organic contaminants (chlorinated hydrocarbons and PAHs) in sediments and biota in the Mediterranean basin.

Regarding the definition of BACs in Mediterranean sediments, it should be noted that few data was available and therefore more dated sediment cores from different areas are needed in order to increase the confidence of the proposed values. Additionally, in order to normalize for sediment particle variability, Al and OC should be considered as mandatory parameters in the new MAP integrated monitoring program.

In order to define the relationship between BC and BAC, a statistical test is required, taking into consideration the data variability of reported data on Certified Reference Materials (sediment and biota) used by Mediterranean laboratories in proficiency tests and in intercalibration exercises. At this stage a statistical test, as described in the text, on the MEDPOL monitoring program is not yet available. Therefore we could use the OSPAR defined relationships between BC and BAC for metals in sediments, fish and shellfish to assess the BACs levels. Thus, for sediments and shellfish BAC = 1.5 x BC, for fish BAC = 2 x BC. However, it is recommended to perform a statistical test to evaluate the precision of MEDPOL monitoring programs (per country).

Furthermore, considering the statistical evaluation of the MEDPOL database performed here, and the large variability in the concentration levels, it is essential to perform a quality control examination of the datasets in order to better assess BAC values

Regarding the definition Mediterranean Assessment Criteria for biota using the MED POL database, it should be underlined that it is biologically inappropriate to evaluate absolute BC, BAC and EAC metal levels in one species from the parallel levels of even a close relative species. Therefore, BCs and BACs levels were calculated / assessed generally according to OSPAR procedures. On the other hand, taking these limitations into consideration, it is possible to derive EAC levels for the MEDPOL areas from the ratio EAC/BAC levels in compatible OSPAR sentinel species. For example if this ratio in *Mytilus edulis* is 5.6, the comparable level for *Mytilus galloprovincialis* could be calculated as BAC x 5.6.

In OSPAR assessments, some EACs have not been used mainly because they are less than the OSPAR BACs. The EACs for Cd and Pb in sediment, Hg in mussels and Hg and Cd in fish are below the corresponding BACs. In addition, the BCs and BACs for trace metals in sediments are normalized to 5% aluminium whilst proposed EACs are normalised to 1% organic carbon. It has been concluded by OSPAR that EACs for PAHs or trace metals in sediment and for metals or CBs in biota cannot be used to describe the green/red (T_1)

transition. Therefore, in cases where the EACs have not been recommended, alternative approaches to appropriate criteria for the assessment of data on contaminant concentrations in sediment and biota were applied.

Table 22. Transition points for assessing contaminants in sediments and biota applied by OSPAR.

Contaminant	Transition point	Sediment	Biota
Hg, Cd, Pb	T_0	BAC	BAC
Hg, Cd, Pb	T_1	ERL	EC
PAHs	T_0	BAC	BAC
PAHs	T_1	ERL	EAC
PCBs	T_0	BAC	BAC
PCBs	T_1	EAC	EAC

For the Transition (T_0) (Blue/Green), which represent assessment that concentrations should be at, or close to, background concentrations, BACS have been used by OSPAR.

For the Transitions (T_1) (Green/Red and Amber/Red), the assessment criteria was the ERLs for PAHs and trace metals in sediment. It is a demanding task to determine real EAC levels, generally and also according to OSPAR documents. Therefore, until an appropriate approach becomes available for the assessment criteria for metals in biota, the EC maximum acceptable dietary levels (Commission Regulation (EC) No 1881/2006) were used by OSPAR (QSR 2010 assessment).

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Annex I

Background Concentrations (BCs), Background Assessment Concentrations (BACs) and Environmental Assessment Criteria (EACs) developed by OSPAR for the Atlantic

Sediment

PAHs (µg/kg dry weight normalised to 2.5% TOC)			
Assessment	BC	Blue < BAC (T_0)	Green < ERL (T_1)
Naphthalene	5	8	160
Phenanthrene	17	32	240
Anthracene	3	5	85
DBT	0.6	[a]	190
Fluoranthene	20	39	600
Pyrene	13	24	665
Benz[*a*]anthracene	9	16	261
Chrysene/ Triphenylene	11	20	384
Benzo[*a*]pyrene	15	30	430
Benzo[*ghi*]perylene	45	80	85
Indeno[*1,2,3-cd*]pyrene	50	103	240
CBs (µg/kg dry weight, normalised)			
Assessment	BC/LC	Blue < BAC (T_0)	Green < EAC (T_1)
CB28	0.0/0.05	0.22	1.7
CB52	0.0/0.05	0.12	2.7
CB101	0.0/0.05	0.14	3.0
CB118	0.0/0.05	0.17	0.6
CB138	0.0/0.05	0.15	7.9
CB153	0.0/0.05	0.19	40
CB180	0.0/0.05	0.10	12
Trace Metals (µg/kg dry weight, normalised)			
Assessment	BC	Blue < BAC (T_0)	Green < ERL (T_1)
Hg	50	70	150
Cd	200	310	1,200
Pb	25,000	38,000	47,000

Mussels and oysters

PAHs (µg/kg dry weight)			
Assessment	LC	Blue < BAC (T_0)	Green < EAC (T_1)
Naphthalene		81.2[a]	340
Phenanthrene	4.0	12.6[a]	1700
Anthracene		2.7[a]	290
Fluoranthene	5.5	11.2[a]	110
Pyrene	4.0	10.1[a]	100
Benzo[*bj*]fluoranthene	3.0	[a]	
Benzo[k]fluoranthene	1.0	[a]	260
Benz[*a*]anthracene	1.0	3.6[a]	80
Chrysene/ Triphenylene	4.0	21.8[a]	
Benzo[*a*]pyrene	0.5	2.1[a]	600
Benzo[*ghi*]perylene	1.5	7.2[a]	110
Indeno[*1,2,3-cd*]pyrene	1.0	5.5[a]	
CBs (µg/kg dry weight)			
Assessment	BC/LC	Blue < BAC (T_0)	Green < EAC (T_1)
CB28	0.0/0.25	[a]	3.2
CB52	0.0/0.25	[a]	5.4
CB101	0.0/0.25	[a]	6.0
CB118	0.0/0.25	[a]	1.2
CB138	0.0/0.25	[a]	15.8
CB153	0.0/0.25	1.1[a]	80
CB180	0.0/0.25	[a]	24
Trace Metals (µg/kg dry weight) - mussels			
Assessment	LC	Blue < BAC (T_0)	Amber< EC maximum food level (T_1)
Hg	50	140	2,500
Cd	600	1,940	5,000
Pb	800	1,520	7,500
Trace Metals (µg/kg dry weight) - oysters			
Hg	100	[b]	2,500
Cd	1,800	[b]	5,000
Pb	800	[b]	7,500

Fish

CBs (µg/kg wet weight)			
Assessment	BC/LC	Blue < BAC (T_0)	Green < $EAC^{passive}$ (µg/kg lipid weight) (T_1)
CB28	0.0/0.05	0.6	64[d]
CB52	0.0/0.05	0.2	108[d]
CB101	0.0/0.05	1.9	120[d]
CB118	0.0/0.05	1.3	24[d]
CB138	0.0/0.05	0.2	316[d]
CB153	0.0/0.05	0.2	1600[d]
CB180	0.0/0.05	0.5	480[d]
Trace Metals (µg/kg wet weight)			
Assessment	**BC**	**Blue < BAC (T_0)**	**Amber < EC maximum food level (T_1)**
Hg (muscle)	[e]	35	500
Cd (liver)	[e]	26	1000 (bivalve tissue)
Pb (liver)	[e]	26	1500 (bivalve tissue)

[a]to be defined/redefined in relation to adopted BC during Autumn 2008

[b]to be calculated by MON during Autumn 2008

[c]dry weight basis, assuming 5% dry weight lipid concentration (equivalent to 1% wet weight lipid concentration)

[d]lipid weight basis

[e]The MCWG was unable to recommend BCs for metals in fish due to the limited dataset