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MEDITERRANEAN ACTION PLAN MED POL

Meeting on the Implementation of NAPs and the Preparation of Legally Binding Measures and Timetables required by Art. 15 of the LBS Protocol

Aix-en-Provence (France), 27-28 November 2008

Overview and assessment of priority substances globally and regionally addressed and related Emission Limit Value (ELVs)

Background document

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1. Introduction

1.1 Background

In the framework of the implementation of the Strategic Action Programme (SAP), adopted by the 12th Meeting of Contracting Parties to the Barcelona Convention (Monaco, November 2001), the Mediterranean countries prepared Sectoral Plans (SPs) and National Action Plans (NAPs) on the basis of National Diagnostic Analyses (NDAs), and the a Baseline Budgets (BBs) of emissions/releases.

The preparation of NAPs represents the operational long-term objective of the Strategic Action Programme (SAP), as it is expected to describe the pollution reduction process to be achieved by the countries making use of all the results of the individual activities of the SAP. NAPs were prepared by all countries of the region and the process of preparation was formally endorsed by the 14th Meeting of the Contracting Parties held in Slovenia in November 2005.

The 15th meeting of the CPs which was held in Almeria, Spain (January 2008) adopted the decision IG 17/8 as follows:

- 1. To continue the implementation of NAPs endorsed in 2005 to the greatest possible extent foreseeing their revision in 2011; throughout the process, the Secretariat will continue to support with capacity building activities covering technical, institutional and financial aspects.
- 2. To develop the following elements in the framework of MED POL:
 - a. Identification of priority substances and sectors during 2008-2009
 - b. Identification of a <u>differentiation mechanism</u> during 2008-2009 for the implementation of regional emission values (<u>ELVs</u>), based on BAT, and start the process of developing regional and /or sub regional-as appropriate-Environmental Quality Objectives (EQOs) for the marine environment
 - c. Identification of relevant elements and indicators arising from the implementation of the <u>ecosystem approach</u>.
- 3. To formulate by 2011 actions plans and programmes containing legally binding measures and timetables required by Art.15 of the LBS Protocol, tacking into consideration the possibility of using the elements arising from the above process for this purpose as well as for the revision of the NAPs.

1.2 Objectives and scope

The aim of this report is **to provide background information to be used for the selection of substances of priority action**, through the implementation of measures based on Emission Limit Values (ELVs)¹.

To this end, the following objectives have been established:

¹ For the purposes of this study, ELVs will be defined as 'the maximum allowable release of a substance from an industrial operation to air, water or land. It may be a concentration limit and/or a maximum load for a given period in the discharge stream'.

- (a) To identify common substances of concern for the marine environment through an <u>international comparison of lists of priority substances</u>.
- (b) To review available information on the <u>occurrence</u> of substances of concern in the Mediterranean marine environment.
- (c) To review available data on the <u>main activity sectors contributing to the emissions</u> of substances of concern.

(d) To identify <u>ELVs</u> already adopted in other international legal frameworks or regional marine conventions, to reduce pollution from substances of concern.

The document is structured in four sections each one addressing the objectives indicated above.

2. Substances of concern in the marine environment

In this section an identification of those substances of concern for the marine environment (as a consequence for example of its toxicological properties) is carried out, as well as an analysis on how these substances have been prioritised in different international and regional conventions.

2.1 Addressing substances of concern in the Mediterranean: the LBS Protocol and the SAP

The Mediterranean Action Plan (MAP) is a regional cooperative effort involving 21 countries bordering the Mediterranean Sea, as well as the European Union, which was firstly adopted in 1975. Through the MAP, these Contracting Parties to the Barcelona Convention and its Protocols are determined to meet the challenges of protecting the marine and coastal environment while boosting regional and national plans to achieve sustainable development.

The Convention for the Protection of the Mediterranean Sea against Pollution (<u>Barcelona Convention</u>) was firstly adopted in 1976, and amended in 1995. Seven Protocols addressing specific aspects of Mediterranean environmental conservation complete the MAP legal framework:

- Dumping Protocol (from ships and aircraft)
- Prevention and Emergency Protocol (pollution from ships and emergency situations)
- Land-based Sources and Activities Protocol (LBS Protocol)
- Specially Protected Areas and Biological Diversity Protocol
- Offshore Protocol (pollution from exploration and exploitation)
- Hazardous Wastes Protocol
- Protocol on Integrated Coastal Zone Management (ICZM)

The Protocol for the Protection of the Mediterranean Sea against Pollution from Land-Based Sources and Activities (**LBS Protocol**) is the main legal reference regarding the reduction of pollutants within the region. According to its general provision (art.1), the Parties "shall take all appropriate measures to prevent, abate, combat and eliminate to the fullest possible extent pollution of the Mediterranean Sea Area caused by discharges from rivers, coastal establishments or outfalls, or emanating from any other land-based sources and activities within their territories, giving priority to the phasing out of inputs of substances that are toxic, persistent and liable to bioaccumulate".

To this end, the Parties shall elaborate and implement national and regional action plans and programmes, containing measures and timetables for their implementation (art. 5). The Protocol includes in its Annex 1 some elements to be taken into account in the preparation of these plans and programmes, like sectors of activity to be primarily considered, characteristics of substances in the environment, and categories of substances to be considered.

Recently (11 May 2008) the 1996 amendments to the LBS Protocol (initially adopted in 1980) have finally entered into force. This accelerates the process for Mediterranean countries to develop short term and medium term regional action plans and programmes containing legally binding measures and timetables for their implementation, as stated in art. 15 of the Barcelona Convention. According to art.15, the plans and the programmes must be approved within one year following the entry into force of the protocol and then become legally binding.

Previously, the MED POL Programme had been preparing the ground for the preparation of the above plans and measures through a process started in 1996 that culminated in the adoption in 1997 of a Strategic Action Programme (SAP) to address pollution from land-based sources and activities and of National Action Plans, recently endorsed by the countries.

The **Strategic Action Programme (SAP)** is an action-oriented initiative identifying priority target categories of polluting substances and activities to be eliminated or controlled by the Mediterranean countries through a planned timetable (up to the year 2025) for the implementation of specific pollution reduction measures and interventions.

During 2004–2005, all Mediterranean Countries prepared **National Action Plans** (NAPs) which describe what pollution reduction measures they will implement, by when and with what funds, taking into consideration the environmental and socioeconomic issues, legislative frameworks, and the available infrastructure.

2.2 Identification of priority substances: international comparison

To undertake an international comparison, we have selected those regional marine conventions and international legal frameworks where a systematic procedure have been established to identify, prioritise and approve lists of substances of concern for the aquatic or marine environment. A brief description of these lists and procedures is provided below.

2.2.1 European Union

2.2.1.1 First initiatives protect the aquatic environment from dangerous substances

European water legislation regulating hazardous substances in the aquatic environment (see Figure 1) mainly started in the mid seventies with the approval of Directive 76/464/EEC concerning "pollution caused by certain **dangerous substances** discharged into the aquatic environment of the Community". This directive identified different water bodies according to their environmental conditions and established two lists of substances considering the degree of hazard they pose to the aquatic environment. The risk was evaluated by a criteria based on the persistence, toxicity and capacity to bioaccumulate of each compound. The first list included the considered most dangerous substances, whose main purpose was its elimination from the aquatic environment via the settlement of emission limit values and quality standards. The second list included less hazardous substances subject to a progressive reduction in the environment, for which quality objectives needed to be determined. This directive was a first attempt to reduce concentrations of several pollutants in the aquatic environment in order to ensure the chemical good status of the waters from the European region.

During the following decade, the 76/464/EEC Directive was developed by 5 different directives and their amendments, which are known as the "Daughter Directives to the 76/464/EEC". They set up limit values and quality objectives for the pollutants included in the first list of the 76/464/EEC Directive, occasionally taking into account their source sectors. Thus, Directives 82/176/EEC and 84/156/EEC established emission limit values and quality objectives for mercury discharges in the chlor-alkali electrolysis industries and other sectors. Directives 83/513/EEC and 84/149/EEC regulated cadmium and hexachlorocyclohexane discharges, respectively; and finally, Directive 86/280/EEC and its following amendments, Directives for the discharges of 14 dangerous substances included in List 1 of the 76/464/EEC Directive.

Concurrently, Directive *80/68/EEC* concerning protection of groundwater pollution against dangerous substances was adopted on 17th December 1979 with the purpose to prevent groundwater pollution by several substances also classified in two lists (Annex I and II). Similarly to Directive 76/464/EEC, its objective was to prevent the discharge into groundwater of substances included in the first list and to limit the release of substances in the second list.



Figure 1 The European legal framework to protect the aquatic environment against hazardous substances.

Other legislative initiatives concerning the protection of the aquatic environment were also set up during the nineties, such as the nitrates Directive *91/676/EEC* and Directive *91/271/EEC* concerning urban waste water treatment. However, an increased dispersion in the legislative framework to protect the aquatic environment, as well as the remaining existing gaps in several other domains, led to the development of a more global and integrative legislation, by the approval of the Water Framework Directive.

2.2.1.2 The Water Framework Directive (WFD)

The Water Framework Directive (2000/60/EC) was adopted on the 23rd October 2000. It was set with the intention of providing an adequate global policy framework for the management of the Community water domain in an attempt to reach a final <u>good</u> <u>ecological status</u> for all water bodies. The WFD provides the major common principles that must prevail when adopting new policies to protect and improve the quality of the aquatic environment. Moreover, it sets the basis for future legislation, foreseeing the integration of the water sector in other policy domains (i.e. Energy, Agriculture).

For this purpose, definitions and provisions for all water bodies are laid down in this Directive, as well as the commitment to ensure the good environmental water status since the river basin level. In terms of the management of <u>hazardous substances</u>, the WFD requires "the progressive reduction of emissions of dangerous substances to water", the final objective being "the reaching of background values for naturally

occurring substances and close to zero for man-made synthetic substances". The term 'hazardous substances' is defined as "substances or groups of substances that are toxic, persistent and liable to bio-accumulate and other substances or groups of substances which give rise to an equivalent level of concern".

A combined approach for point and diffuse sources is adopted, based on <u>emission limit</u> <u>standards</u> for the control of pollution at source, as well as <u>environmental quality</u> <u>standards</u> to guarantee a good ecological water status. It also states the need to establish a list of priority substances and <u>priority hazardous substances</u> presenting a significant risk to the aquatic environment, in addition to a set of control measures. Emissions, discharges or losses of priority hazardous substances to the environment are to be eliminated or phased out, while priority substances should be subject to a progressive reduction.

The Water Framework Directive constitutes a general *corpus* for the Community action that relates all legislations concerning water management in all fields, guaranteeing consistency between directives and programmes, as well as coordination among Member States with same marine regions. Consequently, the WFD will repeal several present Directives, such as some of the formerly described. As soon as the main provisions are implemented, the WFD will take over some previous policies, mainly the framework concerning dangerous substances defined by the 76/464/EEC, and the provisions of Directive 80/68/EEC on protection of groundwater against pollution.

For example, Decision 2455/2001/EC of the European Parliament and of the Council, of 20 November 2001, established the required **list of priority and priority hazardous substances** in the field of the European water policy based on a criteria of toxicity, persistence and capacity to bioaccumulate. The list, which was set up by monitoring the state of surface waters of the Member States and by using modelling programs, became the Annex X of the Water Framework Directive (2000/60/EC). It ranked by priority a selection of <u>33 substances</u> or groups of substances that could pose a risk for the aquatic environment; 13 are nowadays considered as priority dangerous substances, even though some of these pollutants are subject to re-classification as priority or priority hazardous compounds. As determined by the Water Framework Directive, quality standards and emission control measures had to be designed at a Community level for each pollutant contained in this list.

The recent proposal of directive on <u>Environmental Quality Standards</u> to surface waters, *COM(2006)397,* is also expected to develop the WFD. It sets up quality objectives concerning the occurrence in surface waters of the substances and groups of substances previously identified as priority pollutants by the WFD (Annex X, Decision 2455/2001/EC). The proposed quality standards are concentration limits (thresholds) for each compound and different types of water bodies. They intend both to ensure the long term quality of the aquatic environment –by fixing an average concentration of pollutant over a one-year period; and to protect it against limit peaks of pollution –by setting a maximum allowable concentration for each compound. This proposal will repeal and integrate the re-Directives of 76/464/EEC, Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC and 86/280/EEC, with effect from 22 December 2012.

In 2006 other policies were adopted in accordance with the WFD. Directive 2006/118/EC on groundwater against pollution and deterioration, is meant to fill the gap left by the repeal of Directive 80/68/EEC in 2013. Similarly, the new Directive 2006/11/EC on "Pollution caused by certain dangerous substances discharged in the aquatic environment of the Community" has updated and replaced the Hazardous Substances Directive 76/464/EEC and will remain until its repeal by the WFD in 2013.

As most of the contemporary EU environmental policies, the WFD directive was set up in compliance with the Precautionary Principle, which states the need to anticipate damage before it occurs. In this sense, management of hazardous substances under WFD is strongly related to several directives applying the same principle and concerning chemical dangerous compounds, such as the Directive 96/61/EC on Integrated Pollution Prevention and Control (IPPC), the Regulation EC/850/2004 on POPs and the Regulation EC/1907/2006 on the control of chemicals (REACH). The IPPC Directive aims to prevent or reduce pollutant releases to the atmosphere, water and soil by fixing minimum requirements in the authorisation of industrial and agricultural activities. Likewise, the Regulation EC/850/2004 seeks to limit pollution by persistent organic pollutants (POPs), including the compounds regulated under the Stockholm Convention. Finally, the new European Regulation on Chemicals EC 1907/2006 (REACH Regulation) aims to improve the protection of human health and environment. It calls for the better and earlier identification of the intrinsic properties of chemical substances and requires for the progressive substitution of the most dangerous chemicals when suitable alternatives have been identified.

2.2.1.3 The Marine Strategy Framework Directive

The need to establish a legislative framework for the protection of the marine environment rose from the evidence of the deterioration of seas and oceans and the lack of relevant and precise legal instruments allowing enhancing marine protection. Most sectoral measures do exist, contributing partially to the protection of marine areas, but are not designed specifically for the marine environment. On the other hand, there is a need to work in cooperation with other international fora which also contribute to the protection of regional seas in order to achieve the agreed objectives.

Decision 1600/2002/EC of the European Parliament and of the Council laid down the Sixth Environment Action Programme and required the development of seven thematic strategies, including the marine environment protection among them. Therefore, since 2002 several directive proposals have lead to the recent adoption of the Directive 2008/56/EC of 17 June 2008, in the field of marine environmental policy (the **Marine Strategy Framework Directive**), which is in accordance with WFD. It constitutes the legislative framework for the management of marine environment and provides with the common principles allowing adopting the corresponding programmes and measures. Moreover, it also ensures coordination between other European policies and sectors, such as the common fisheries policy or the upcoming European maritime policy.

The Marine Strategy aims at promoting the sustainable use of the seas and at restoring marine ecosystems in order to achieve a good environmental status by 2020 at the latest. The following marine regions are defined: the Baltic Sea area, the North-East Atlantic Ocean, the Mediterranean Sea and the Black Sea, including different subregions. The directive states that each Member State must develop its own specific marine strategy in order to give response to the different threats affecting its own regional sea. In this sense, coordination between Member States and with regional sea conventions is essential, and becomes a relevant aspect concerning the monitoring of marine regions. Member States must establish coordinated monitoring programmes for the assessment of the status of marine environment and to state the efficacy of the adopted measures.

Several annexes of the directive provide with the scientific and technical indications permitting the description of the marine environment status and its physical, chemical and biological characteristics. Concerning pollution by hazardous substances, Annex V specifies general groups of synthetic and non-synthetic substances that are considered

as harmful to the marine environment, even though they are subject to future amendments and updates.

2.2.2 OSPAR

In 1974, the 1972 Oslo Convention – also called the Convention for the Prevention of Marine Pollution by Dumping from Ships and Airplanes – entered into force. The Convention regulated dumping operations involving industrial waste, dredged material and sewage sludge. The Paris convention – or Convention for the Prevention of Marine Pollution from Land-Based Sources – was established in 1974 and came into force in 1978. Its principal aim was to prevent, reduce and, if necessary, eliminate pollution of the Convention area from land-based sources, which are discharges from rivers, pipelines, the coast, but also offshore installations and the atmosphere.

The tasks set forth in both Conventions were originally handled by two individual commissions, the Oslo commission and Paris commissions. In 1978, both commissions established a Joint Monitoring Programme, the JMP, obliging contracting parties to initiate monitoring activities for a number of parameters in their water bodies.

In the eighties, the policy of the Oslo and Paris Commissions evolved with the general evolution of environmental policy in Western Europe, voiced at the Ministerial Conferences for the Protection of the North Sea. It was soon recognised that the existing Oslo and Paris Conventions did not adequately control some of the many sources of pollution, and that a revision was warranted (Roose and Brinkman, 2005). This resulted, not in a revision of the initial conventions, but more importantly, in the merger of both commissions into a new convention, the Convention for the Protection of the Marine Environment of the North-East Atlantic or OSPAR², opened for signature in September 1992.

The work under the convention is managed by the OSPAR Commission, made up of representatives of the Governments of 15 Contracting Parties and the European Commission, representing the European Community. The work under the Convention is guided by the Ministerial Declarations and Statements made at the adoption of the Convention and at the Ministerial Meetings of the OSPAR Commission. The work applies the ecosystem approach to the management of human activities, and it is organised under six strategies:

- Protection and Conservation of Marine Biodiversity and Ecosystems
- Eutrophication
- Hazardous Substances
- Offshore Oil and Gas Industry
- Radioactive Substances
- Monitoring and Assessment

The **Hazardous Substances Strategy** sets the objective of preventing pollution of the maritime area by continuously reducing discharges, emissions and losses of hazardous substances, with the ultimate aim of achieving concentrations in the marine

² http://www.ospar.org

environment near background values for naturally occurring substances and close to zero for man-made synthetic substances.

As its timeframe, the Hazardous Substances Strategy further declares that the Commission will implement this Strategy progressively by making every endeavour to move towards the target of the <u>cessation of discharges</u>, <u>emissions and losses of hazardous substances by the year 2020</u>. To implement this Strategy, a List of Substances of Possible Concern and a List of Chemicals for Priority Action have been established, which are described below.

To monitor environmental quality throughout the north-east Atlantic, a **Joint Assessment and Monitoring Programme (JAMP)** was established in 1995, and the first Quality Status Report was published in 2000. In 2003, a new Strategy for JAMP was adopted. This provides for the work to support and produce a series of thematic assessments, leading to a further comprehensive assessment in 2010.

2.2.3 HELCOM

The Baltic Marine Environment Protection Commission or the Helsinki Commission (HELCOM) is the governing body of the Convention on the Protection of the Marine environment of the Baltic Sea Area, signed in 1992³. HELCOM's main goal is to protect the marine environment of the Baltic Sea from all sources of pollution, and to restore and safeguard its ecological balance. The present contracting parties to HELCOM are Denmark, Estonia, the European Community, Finland, Germany, Latvia, Lithuania, Poland, Russia and Sweden.

The set-up is very similar to that of OSPAR, and many of the principles – such as the 'best environmental practices', 'best available technologies' and 'the polluter pays' – are adopted and applied by HELCOM (Roose and Brinkman, 2005). HELCOM priorities are also similar to OSPAR strategies:

- Eutrophication, especially the contribution of agriculture
- Hazardous substances
- Land transport sector
- Maritime transport sector, including carrying out the Baltic Strategy
- Environmental impacts of fishery management and practices
- Protection and conservation of marine and coastal biodiversity
- Implementation of the Joint Comprehensive Environmental Action Programme and HELCOM Recommendations

HELCOM's objective with regard to **hazardous substances** is to prevent pollution of the convention area by continuously reducing discharges, emissions and losses of hazardous substances towards the target of their cessation by the year 2020, with the ultimate aim of achieving concentrations in the environment near background values for naturally occurring substances and close to zero for man-made synthetic substances (HELCOM Recommendation 19/5, March 1998).

³ http://www.helcom.fi

The Recommendation contains a list of numerous <u>substances of concern</u>, from which HELCOM selected 42 hazardous substances for immediate priority action. These include pesticides and biocides such as lindane and pentachlorophenol, metals and metal compounds such as mercury and lead, and industrial substances including short-chained chlorinated paraffins and nonylphenol.

<u>Monitoring and assessment</u> are an integral part of the convention and according to the convention "Emissions from both point sources and diffuse sources into water and the air should be measured and calculated in a scientifically appropriate manner by the Contracting Parties". Every five years, the Commission publishes a "Periodic Assessment of the State of the Environment of the Baltic Marine Area" based on monitoring activities going on in the area.

2.2.4 The Stockholm Convention

The Stockholm Convention is a global treaty to protect human health and the environment from persistent organic pollutants (usually called UNEP POPs) that has been signed by 151 governments⁴. In implementing the Convention, which was adopted in 2001 and entered into force 2004, governments will have to take measures to <u>eliminate or reduce the release of POPs</u> into the environment.

The Stockholm Convention has identified **12 priority POPs**: aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, PCBs, polychlorinated dibenzodioxins (PCDDs), PCDFs and toxaphene. Under the Convention, any Party can submit proposals for listing new chemicals. These are considered by the POPs Review Committee, who will initiate a reviewing process, including a risk management evaluation.

The Stockholm Convention on POPs and other international agreements state that monitoring activities should be established to verify the effective implementation of the conventions and the decrease of environmental levels of persistent pollutants. Some monitoring activities are already in place but, as different methodologies are used, comparison of the data is often very difficult (Roose and Brinkman, 2005).

2.3 Criteria and procedures to identify priority substances

2.3.1 European Union

In the EU, priority substances in the aquatic environment are listed in Decision 2455/2001/EC, which integrates the previous legislation and became the Annex X of the Water Framework Directive (2000/60/EC). The basic procedure to identify these substances was the Combined Monitoring-based and Modelling-based Priority Setting (COMMPS) procedure (Klein et al., 1999; European commission 2001).

During the initial step of the COMMPS procedure, priority substances were again selected from among the list of hazardous substances, based on evidence regarding the intrinsic hazard, widespread environmental contamination and other proven factors which may indicate the possibility of widespread contamination such as production or use volume. Next, exposure indices – based both on surface water monitoring and on modelling data – and effect indices were calculated, which finally led to a risk-based priority index, essentially by multiplying both previous indices. The list was checked

⁴ http://www.pops.int

against the OSPAR list, other lists from EC regulations and lists resulting from international agreements, e.g. the Stockholm Convention on POPs.

For the final assignment of a priority substance, "additional considerations" were considered to confirm or reject the status of the substance. The "additional considerations" included other relevant Community legislation or relevant international agreements, the production and use of the substance, the socio-economic impacts of a cessation or phase-out and the suspected endocrine disrupting potential of the substance.

The overall procedure is shown in Figure 2. At each stage, a checking with different reference lists is carried out, which is and the different steps are summarized below:

- <u>Check 1</u>: Selection of priority substances in accordance to Article 16(2) of the Water Framework Directive as the basic list for which the identification will be applied.
- <u>Check 2</u>: Identification of inclusion of priority substances in the up-dated "OSPAR List of Chemicals for Priority Action" as adopted at OSPAR 2000 and the OSPAR "Draft List of Substances of Possible Concern" including the identification of the "Selection Criteria" for the substances.
- <u>Check 3</u>: Identification of priority substances for labelling as "dangerous to the environment" <u>or</u> carcinogenic, mutagenic or toxic to reproduction.
- <u>Check 4</u>: Identification of priority substances where agreements for phase-out on international level exist, in particular UN-ECE, UNEP, OSPAR and IMO.
- <u>Check 5</u>: Identification of priority substances for which a final conclusion has been drawn that there is a risk to or via the aquatic environment under (EEC) No. 793/93 or 91/414/EEC.
- <u>Check 6</u>: Identification of priority substances which are regulated under Council Directive 76/464/EEC as List I Substances.
- <u>Check 7</u>: Additional Considerations.

In the application of the COMMPS procedure about 820000 monitoring data from waters and sediments from all Member States were evaluated and data for more than 310 substances on production, use and distribution in the environment were used for modelling if the available monitoring information was insufficient⁵.

The procedure resulted in a list of **33 priority hazardous (groups of) substances** and an additional 10 priority (groups of) substances (Table 1). The difference between these groups is such that for priority hazardous substances emissions, discharges and losses should be ceased not later than in 20 years, and that for priority substances the discharges should progressively reduced.

⁵ http://ec.europa.eu/environment/water/water-framework/preparation_priority_list.htm



Figure 2 Modified Procedure for the identification of priority hazardous substances in accordance with the Water Framework Directive. Source: EC, 2001.

Table	1	List	of	priority	substances	in	the	field	of	EU	water	policy	(*)	_	Decision
2455/2	00)1/EC).											_	

	Name of priority substance	Identified as priority hazardous substance
(1)	Alachlor	
(2)	Anthracene	(X) (***)
(3)	Atrazine	(X) (***)
(4)	Benzene	
(5)	Brominated diphenylethers (**)	X (****)
(6)	Cadmium and its compounds	Х
(7)	C ₁₀₋₁₃ -chloroalkanes (**)	Х
(8)	Chlorfenvinphos	
(9)	Chlorpyrifos	(X) (***)
(10)	1,2-Dichloroethane	
(11)	Dichloromethane	
(12)	Di(2-ethylhexyl)phthalate (DEHP)	(X) (***)
(13)	Diuron	(X) (***)
(14)	Endosulfan	(X) (***)
	(alpha-endosulfan)	
(15)	Fluoranthene (*****)	

	Name of priority substance	Identified as priority
	Name of priority substance	hazardous
		substance
(16)	Hexachlorobenzene	X
(17)	Hexachlorobutadiene	X
(18)	Hexachlorocyclohexane	Х
	(gamma-isomer, Lindane)	
(19)	Isoproturon	(X) (***)
(20)	Lead and its compounds	(X) (***)
(21)	Mercury and its compounds	Х
(22)	Naphthalene	(X) (***)
(23)	Nickel and its compounds	
(24)	Nonylphenols	Х
	(4-(para)-nonylphenol)	
(25)	Octylphenols	(X) (***)
	(para-tert-octylphenol)	
(26)	Pentachlorobenzene	Х
(27)	Pentachlorophenol	(X) (***)
(28)	Polyaromatic hydrocarbons	Х
	(Benzo(a)pyrene),	
	(Benzo(b)fluoranthene),	
	(Benzo(g,h,i)perylene),	
	(Benzo(k)fluoranthene),	
	(Indeno(1,2,3-cd)pyrene)	
(29)	Simazine	(X) (***)
(30)	Tributyltin compounds	Х
	(Tributyltin-cation)	
(31)	Trichlorobenzenes	(X) (***)
	(1,2,4-Trichlorobenzene)	
(32)	Trichloromethane (Chloroform)	
(33)	Trifluralin	(X) (***)

(*) Where groups of substances have been selected, typical individual representatives are listed as indicative parameters (in brackets and without number). The establishment of controls will be targeted to these individual substances, without prejudicing the inclusion of other individual representatives, where appropriate.

(**) These groups of substances normally include a considerable number of individual compounds. At present, appropriate indicative parameters cannot be given.

(***) This priority substance is subject to a review for identification as possible "priority hazardous substance". The Commission will make a proposal to the European Parliament and Council for its final classification not later than 12 months after adoption of this list. The timetable laid down in Article 16 of Directive 2000/60/EC for the Commission's proposals of controls is not affected by this review.

(****) Only Pentabromobiphenylether (CAS-number 32534-81-9).

(*****) Fluoranthene is on the list as an indicator of other, more dangerous Polyaromatic Hydrocarbons.

2.3.2 OSPAR

In the 90s, some initial lists of potentially hazardous substances and priority substances were established within the framework of the International Conference on the Protection of the North Sea (Roose and Brinkman, 2005). Later, the OSPAR Commission developed a dynamic selection and prioritisation mechanism, <u>DYNAMEC</u>, to select priority substances (OSPAR, 2006).

The Dynamic Selection and Prioritisation Mechanism for Hazardous Substances (DYNAMEC) was established, following the adoption at the OSPAR Ministerial Meeting in 1998 of the Hazardous Substances Strategy, as a tool to enable the OSPAR Commission to select those hazardous substances that need to be addressed under the Hazardous Substances Strategy and to identify the substances which should be given priority in OSPAR's work. The selection and prioritisation mechanism consisted initially of 3 basic steps (see Figure 3):

step 1: an initial selection step which by a worst case screening procedure identifies certain hazardous substances on the basis of their intrinsic hazardous properties of persistence, liability to bioaccumulate and toxicity (P, B and T, see Table 2). These have been placed on the "List of Substances of Possible Concern" (see Annex A) because they could adversely affect marine ecosystems. A number of substances which do not meet the full P, B and T criteria have already been added to the List of Substances of Possible Concern because it has been recognised that they give rise to a similar level of concern (for example, endocrine disruptors, or shown to be widely spread in the marine environment by monitoring) (OSPAR, 2002);

Criteria		Cut-Off Values
Persistency (P)		Half-life (T½) of 50 days ⁶ and
Liability Bioaccumulate (B)	to	log K _{ow} >=4 or BCF>=500 and
Toxicity (T)		Taq: acute L(E)C50=<1 mg/l, long-term NOEC=<0,1 mg/l or Tmammalian: CMR or chronic toxicity

Table 2 Cut-Off Values for the Selection Criteria of the OSPAR Dynamic Selection andPrioritisation Mechanism for Hazardous Substances. Source: OSPAR, 2005.

- **step 2**: a step which ranks these substances of possible concern according to their actual occurrence and effects in the marine environment. Data on direct and indirect effects and production volumes and use are also taken into account.
- **step 3**: a step which selects those substances from the ranked list judged to require priority action by OSPAR. An initial list of 15 priority substances has been progressively updated until the current <u>OSPAR List of Chemicals for Priority Action</u> (OSPAR, 2007), which includes about 50 substances or groups of substances (see Table 3).

Having concluded the initial selection and prioritisation work, OSPAR initiated in 2003 a study process on the selection and prioritisation of hazardous substances, in the light of similar work going on in the European Community. This study process resulted in the

⁶ In the absence of data on half-lives, alternative approaches have been agreed, as described in Appendix 1, which allow the use of different types of available information on the biodegradability of a substance.

conclusion in 2004 that OSPAR should not, for the time being, carry out a further systematic review of chemical substances in order to select and prioritise chemicals for priority action. In particular, there should, for the time being, be no re-run of DYNAMEC (OSPAR, 2006).



2. OSPAR will not, for the time being, take any new initiatives for prioritisation and ranking.

Figure 3 The OSPAR DYNAMEC mechanism. Source: OSPAR, 2006.

Table 3 OSPAR List of Chemicals for Priority	y Action (l	Jpdate 2007).
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Туре	Group of substances / substances
A: CHEMICALS WHERE A BACKGR	OUND DOCUMENT HAS BEEN OR IS BEING

Туре	Group of substances / substances
PREPARED	
Metallic Compound	cadmium
	lead and organic lead compounds
Metal / Organometallic Compound	mercury and organic mercury compounds
Organometallic Compound	organic tin compounds
Organic Ester	neodecanoic acid, ethenvl ester
	perfluorooctanyl sulphonic acid and its salts
	(PFOS)
	tetrabromobisphenol A (TBBP-A)
	1 2 3-trichlorobenzene
	124-trichlorobenzene
Organohalogens	1.3.5-trichlorobenzene
organonalogeno	brominated flame retardants
	polychlorinated hinhenyls (PCBs)
	polychlorinated dipenzodioxins (PCDDs)
	polychlorinated dibenzofurans (PCDEs)
	short chained chlorinated paraffins (SCCP)
Organia Nitragan Compound	4 (dimethylbutylamina)dinbonylamin (SCCP)
Organic Millogen Compound	
	endosulphan
Pesticides/Biocides/Organohalogens	nexachiorocycionexane isomers (HCH)
	methoxychlor
Pharmaceutical	
	2,4,6-tri-tert-butyipnenoi
Phenols	Nonylphenol/ethoxylates (NP/NPEs) and related
	substances
	Octylphenol
Phthalate Ester	certain phthalates: dibutyiphthalate (DBP),
	diethylhexylphthalate (DEHP)
Polycyclic aromatic compounds	polyaromatic hydrocarbons (PAHs)
Synthetic Musk	musk xylene
B. CHEMICALS WHERE NO BACKG	ROUND DOCUMENT IS BEING PREPARED
BECAUSE THEY ARE INTERMEDIA	TES IN CLOSED SYSTEMS
Aliphatic hydrocarbon	1,5,9 cyclododecatriene
	cyclododecane
C: CHEMICALS WHERE NO BACKG	ROUND DOCUMENT IS BEING PREPARED
BECAUSE THERE IS NO CURRENT	PRODUCTION OR USE INTEREST
Organohalogens	2-propenoic acid, (pentabromo)methyl ester
	2,4,6-bromophenyl 1-2(2,3-dibromo-2-
	methylpropyl)
	pentabromoethylbenzene
	pentacnioroanisole
	polychlorinated naphthalenes
	trichloronaphthalene
	tetrachloronaphthalene
	pentachloronaphthalene
	hexachloronaphthalene
	heptachloronaphthalene

Туре	Group of substances / substances		
	octachloronaphthalene		
	naphthalene, chloro derivs.		
Organic Nitrogon Compound	3,3'-(ureylenedimethylene)bis(3,5,5-		
	trimethylcyclohexyl) diisocyanate		
	ethyl O-(p-nitrophenyl) phenyl phosphonothionate		
	(EPN)		
Pesticides/Biocides	flucythrinate		
	isodrin		
	tetrasul		
Pharmaceutical	diosgenin		

2.3.3 HELCOM

The HELCOM Convention signed in 1992 already included in its Annex I a list of intrinsic chemical properties and characteristics allowing identifying hazardous substances, as well as a preliminary list of harmful compounds. Thus, Part I of Annex I established that the identification and evaluation of compounds should be based on the Persistency, on the Toxicity and other noxious properties, and on the Tendency to bio-accumulation. Part II and III of Annex I set up two lists of harmful compounds, based on the described properties. Part II concerned banned substances, which should be partially banned or prohibited (i.e. DDT and derivatives, PCBs and PCTs); and part III involved pesticides and biocides that should be minimised or whenever possible banned, such as the Drins, Hexachlorobenzene or some metal compounds.

In the subsequent years, HELCOM Recommendations 12/18 and 14/18 also concerned pollution control and survey of certain dangerous substances that needed to be restricted and monitored.

The HELCOM Recommendation 19/5 with regard to Hazardous Substances from 1998 integrated and further developed the previous guidelines in the field of management of dangerous compounds. It set up a list of criteria allowing identifying hazardous compounds representing a risk to the marine environment. Thus, in accordance with Helsinki Convention, dangerous compounds are substances or groups of substances which fall into one of the following categories:

- substances or groups of substances that are <u>toxic</u>, <u>persistent</u> and <u>liable to</u> <u>bioaccumulate</u>;
- other substances or groups of substances, agreed by the Commission, requiring a similar approach as the substances referred to in the first category, even if they do not meet all the criteria for toxicity, persistence and bioaccumulation, but which also <u>give grounds for concern</u>; this second category includes both substances which work synergistically with other substances to generate such concern as well as substances which do not themselves justify inclusion but which degrade or transform into substances referred to the first group.

The properties of toxicity, persistence and tendency to bio-accumulation are also described in the Appendix I of the Hazardous Substances Recommendation. *"Toxicity"* is defined as the capacity of a substance to cause toxic effects to organisms or their progeny such as reduction in survival, growth and reproduction; carcinogenicity, mutagenicity or teratogenicity; and adverse effects resulting from endocrine disruption. Depending on the exposure time and life cycle of the target organism, toxicity is classified as:

- <u>acute toxicity</u>: lethal and/or sublethal toxicity resulting from intermittent or continuous exposure to a substance or mixture of substances for a period substantially shorter than the life cycle of the organism in question (e.g. 96 h LC₅₀ for a fish with a life cycle measured in months or years);
- <u>subchronic toxicity</u>: sublethal (and possibly also lethal) toxicity resulting from intermittent or continuous exposure to a substance or mixture of substances for a period which is a substantial proportion of the life cycle of the organism in question (e.g. 21 day reproductive NOEC for a crustacean with a life cycle measured in weeks or months);
- <u>chronic toxicity</u>: sublethal toxicity resulting from intermittent or continuous exposure to a substance or mixture of substances for a period not less than the life cycle of the organism in question (e.g. lifecycle reproductive NOEC for a fish which includes measurements of the F1 generation).

On the other hand, a substance is defined to be "*persistent*" if its conversion or the conversion of its degradation products is slow enough to permit long-term occurrence and widespread distribution in the marine environment. Finally "*bioaccumulation*" is defined as the enrichment of a substance in an organism. It includes "bioconcentration" from environmental concentrations and additional uptake via the food chain; bioaccumulation includes all routes, i.e. via the air, water, soil and food.

Taking into account these properties, the HELCOM Commission considered the work already undertaken in other international organisms (such as OSPAR, the EU, The North Sea Conferences) and the previous HELCOM regulations concerning hazardous substances to draw up a list of potential substances of possible concern (HELCOM Recommendation 19/5, Appendix 2). The list included about 300 substances meeting the former criteria, candidates for selection, assessment and prioritisation according to the strategy to implement HELCOM Recommendation 19/5.

The Commission developed a <u>dynamic selection and prioritization mechanism</u> in order to rank the listed substances by their degree of concern, taking into consideration the specific conditions in the Baltic Sea. The criteria used in these selection and prioritisation mechanisms also include several considerations, whose application should both reflect the hazardous characteristics of substances and groups of substances and give priority to their actual or potential occurrence and effects in the Convention Area. These considerations involved substances or groups of substances:

- being a general threat to the aquatic environment due to their hazardous properties;
- showing indications of risks for the marine environment;
- being able to endanger human health via consumption of food directly or indirectly from the marine environment;
- being found in one or more compartments of the Convention Area;
- being able to reach, or likely to reach, the marine environment, for instance from a diversity of sources through various pathways.

Special reference should be paid to endocrine disrupters when developing the mechanisms of selection and prioritization of compounds. Because of the growing international research effort (especially in OSPAR, EU and OECD) HELCOM will take the results of such investigations into account, and conduct surveys of the Convention

Area to estimate the spatial extent of their occurrence and distribution and of any adverse effects.

The application of the mechanism resulted in a <u>list of 42 selected compounds for</u> <u>immediate priority action</u> (HELCOM Recommendation 19/5, Appendix 3), which is shown in Table 4. However, HELCOM will keep the selection and prioritization mechanisms under review to ensure that it remains effective to identify all aspects of hazard and risk which should give rise to reasonable grounds of concern about substances taking account of developments in OSPAR, the Intergovernmental Forum on Chemical Safety, and the LRTAP (Convention on Long-Range Transboundary Air Pollution).

Concerning hazardous substances identified by the Commission for immediate priority action, such action generally includes the initial identification of their sources and pathways to the marine environment (using information from monitoring and research) as well as the assessing of the caused risks in order to determine relevant measures to minimize pollution.

CAS No	Name
	Alkanes
85535848	Chlorinated paraffins, short chained
67663	Chloroform
	Phenols
9016459	Nonylphenolethoxylate and the degradation/transformation products
104405	Nonylphenol, 4-
	<u>Xylenes</u>
81152	Musk xylene
	Organic oxygen compounds
117817	Diethylhexylphthalate
84742	Dibutylphthalate
	Metallic compounds
7440439	Cadmium
7439921	Lead
7439976	Mercury
7782492	Selenium
	Pesticides/Biocides
106934	1,2-Dibromoethane
93765	2,4,5-T
107131	Acrylonitrile
309002	Aldrin
140578	Aramite
319857	beta-HCH
57749	Chlordane
143500	Chlordecone (Kepone)
6164983	Chlordimeform
50293	DDT
60571	Dieldrin
n.a.	Drins
72208	Endrin
7664393	Fluoroacetic acid and derivatives
608731	НСН

Table 4 HELCOM selected substances for immediate priority action (HELCOM Rec. 19/5).

76448	Heptachlor
118741	Hexachlorobenzene
297789	Isobenzane
465736	Isodrin
4234791	Kelevan
143500	Kepone (Chlordecone)
58899	Lindane
2385855	Mirex
4636833	Morfamquat
1836755	Nitrophen
87865	Pentachlorophenol
82688	Quintozene
8001352	Toxaphene
n.a.	Organotin Compounds
	Polycyclic halogenated aromatic compounds
36355018	Hexabromobiphenyl
1336363	PCB
617883388	PCT (mixtures)
1746016	TCDD, PCDD, PCDF
	Polycyclic aromatic hydrocarbons
50328	PAH

2.3.4 The Stockholm Convention

Under the Convention, any Party can submit proposals for listing new chemicals. These are considered by the POPs Review Committee (POPRC), who will initiate a reviewing process, which is outlined as follows:

1. <u>Propose a new chemical</u>. Any party may submit a proposal to the Secretariat for listing a new chemical including information specified in Annex D (Screening) of the Convention. The Secretariat forwards the proposal to the POPRC.

2. <u>Apply screening criteria</u>. The POPRC examines the proposal and applies the screening criteria in Annex D, which includes:

- Persistence
- Bio-accumulation
- Potential for long-range environmental transport
- Adverse effects to human health or the environment

3. <u>Develop a risk profile</u>. If the POPRC decides that the screening criteria have been fulfilled, the Secretariat invites all Parties and observers to provide technical comments and information specified in Annex E (Risk Profile). The POPRC develops a risk profile based on the information.

4. <u>Develop a risk management evaluation</u>. If the POPRC decides on the basis of the risk profile that the proposal shall proceed, the Secretariat invites all Parties and observers to provide technical comments and socio-economic information specified in Annex F (Risk Management Evaluation). The POPRC develops a risk management evaluation based on the information.

5. <u>List the chemical in Annex A, B, and/or C</u>. The Conference of the Parties decides whether to list the chemical and specifies its related control measures in Annex A (Elimination), B (Restriction), and/or C (Unintentional Production).

Currently (August 08), the listing of new chemicals is as follows:

Status	Chemicals	Proposed by	
	Pentabromodiphenyl ether	Norway	
Chemicals with	Chlordecone	EU	
completed risk	Hexabromobiphenyl	EU	
management evaluations	Lindane	Mexico	
	PFOS	Sweden	
Chemicals with completed risk profiles or with risk profiles under development	Octabromodiphenyl ether	EU	
	(commercial)	EU	
	Pentachlorobenzene	EU	
	Alpha-hexachlorocyclohexane	Mexico	
	Beta-hexachlorocyclohexane	Mexico	
	Short-chained chlorinated paraffins		
	(draft)	LU	
New proposals:	Endosulfan	EU	
	Hexabromocyclododecane (HBCDD)	Norway	

2.3.5 Summary and comparison with the LBS Protocol criteria

Despite the fact that only a general review of criteria and procedures to prioritise substances has been presented above, some common criteria can be identified throughout the different approaches:

- Persistence
- Liability to bioaccumulate
- Toxicological risk (towards humans and/or the environment)
- Potential for long range transport
- Widespread occurrence
- Production volume and current use

In general both monitoring and modelling data are taken into account. In the prioritisation, regional marine conventions like OSPAR and HELCOM, as expected, seems to be more influenced by the actual occurrence of substance in the marine environment, while in the WFD and UNEP POPs a strong emphasis is put on the current production and use and the risk analysis.

It must be noted that the above <u>common criteria are very similar to those considered in</u> <u>the LBS Protocol</u> (Annex I-B; see below). In fact, in its Annex I, the LBS Protocol states that in preparing action plans, programmes and measures, the Parties will give priority to substances that are toxic, persistent and liable to bioaccumulate, in particular to persistent organic pollutants (POPs).

LBS Protocol / Annex I – B: Characteristics of Substances in the Environment:

"For the preparation of action plans, programmes and measures, the Parties should take into account the characteristics listed below:"

- a) Persistence;
- b) Toxicity or other noxious properties (e.g. carcinogenicity, mutagenicity, teratogenicity);
- c) Bioaccumulation;
- d) Radioactivity;
- e) The ratio between observed concentrations and no observed effect concentrations (NOEC);
- f) The risk of eutrophication of anthropogenic origin;
- g) Health effects and risks;
- h) Transboundary significance;
- i) The risk of undesirable changes in the marine ecosystem and irreversibility or durability of effects;
- j) Interference with the sustainable exploitation of living resources or with other legitimate uses of the sea;
- k) Effects on the taste and/or smell of marine products for human consumption;
- I) Effects on the smell, colour, transparency or other characteristics of seawater;
- m) Distribution pattern (i.e. quantities involved, use patterns and probability of reaching the marine environment).

This is of key relevance, as the resulting <u>international lists of substances of concern</u> and priority substances can be used as a basic reference to identify priority substances in the Mediterranean region, to be refined with regionally specific circumstances and data on occurrence of pollutants in the Mediterranean Sea, use and emissions of substances, etc.

2.4 Comparing the lists

2.4.1 Common priority substances

As it can be observed from the lists presented above, chemical compounds can be classified in different groups depending on the selected criteria: chemical nature, functional use of the substance (e.g. biocides, pharmaceuticals), effects on the environment (e.g. endocrine disruptors), etc. In order to compare both lists of substance of concern (Annex 1) and priority substances, chemical compounds have been grouped into a common classification, which is always a difficult task. To this end, very general categories have been established, combining the nature of substances and its use, following as far as possible the categories suggested in Annex 1-C of the LBS Protocol and the SAP. As a result, the following general categories have been used:

- Metals and related compounds
- Hydrocarbons
- Organohalogen compounds
- Organohalogenated pesticides/biocides
- Other organic compounds

According to this general categories and its subcategories, a comparison has been first carried out between the two identified lists of substances of concern for the marine environment (OSPAR and HELCOM), which is shown in Annex 1. Each individual list includes about 300 different substances or groups of substances, and the combination of both lists results in about **530** different substances of concern.

A comparison of the **lists of priority substances** presented above (EU-WFD, OSPAR, HELCOM and the Stockholm Convention) is shown in **Table 5**. The combination of these lists results in about <u>110 different priority substances</u> or groups of substances. As it can be observed, several overlaps can be identified between the different lists, due to the fact that most of them are mutually influenced. However, some significant differences can also be appreciated.

As indicated by Roose and Brinkman (2005), the "old organochlorines" (e.g. PCBs, some pesticides like DDT, aldrin, or dieldrin, PCDD/Fs, etc.) are mostly considered by the UNEP POP list, and they are also priority substances in OSPAR and HELCOM, but not in the WFD list (with the exception of HCB and HCH). Although the initial COMMPS selection procedure included most of them, they were not considered as priority substances because of the fact that there is no current production or usage, or use is strictly regulated or forbidden. Exclusion is therefore not based on toxicological properties and/or presence in the environment. On the other side, the WFD list includes exclusively other substances probably due to the importance of its current production and usage criteria, as for example benzene, dichloromethane or 1,2-dichloroethane.

Metals and its related compounds are also commonly identified as priority substances, specially cadmium, lead, mercury and organotin. They are not included in the UNEP POPs list as it is restricted to organic pollutants, and organometals are often not considered there. However, PAHs are commonly recognised as priority pollutants, but are not included in the UNEP POPs list.

'Modern' or 'emerging' contaminants, like some pesticides or pharmaceuticals, tend to be more considered in the OSPAR and WFD lists. For example, some 'modern' pesticides like alachlor, atrazine, diuron or isoproturon are only included in the WFD list. Other pesticides like acrylonitrile or aramite are only considered in the HELCOM list, as a consequence of region specific circumstances (Roose and Brinkman, 2005).

Some of the 'emerging' contaminants that are commonly considered are Brominated Flame Retardants (except in OSPAR) and short-chained chlorinated paraffins (SCCP). Alkylphenols have also received increasing attention in recent years, as well as Diethylhexylphthalate (DEHP), which appears in all lists except in UNEP POPs.

In summary, the substances or groups of substances that have been identified as priority substances in all (4) or almost all (3) the selected lists are indicated below:

- Metals and related compounds:
 - Cadmium (3)
 - Lead (3)
 - Mercury (3)
 - Organic tin compounds (3)
 - Organic mercury compounds (3)
 - Organic lead compounds (3)
- Hydrocarbons:
 - Polycyclic aromatic hydrocarbons (3)
 - Organohalogen compounds:
 - Short chained chlorinated paraffins (4)
 - Polychlorinated Biphenyls (PCBs) (3)
 - Polychlorinated dibenzodioxins (PCDDs) (3)

- Polychlorinated dibenzofurans (PCDFs) (3)
- Organohalogenated pesticides/biocides:
 - Endosulphan (3)
 - Hexachlorocyclohexane (4)
 - Hexachlorobenzene (3)
- Other organic compounds:
 - o diethylhexylphthalate (DEHP) (3)

Finally, it is also worth to mention that some categories and subcategories of compounds considered in the lists of substances of possible concern (Annex 1), are not included in any of the priority lists of substances, as a result of implementing the prioritisation mechanisms of OSPAR and HELCOM. For example, some halogenated alkenes (e.g. trichloroethylene or tetrachloroethylene) and organophosphates.

Table 5 Comparison of lists of priority substances.

CHEMICAL COMPOUNDS	UNPOPs	OSPAR	HELCOM	WFD	Included in SAP?		
METALS AND RELATED COMPOUNDS							
Metals							
Cadmium		Х	Х	Xc	Yes		
Lead		Х	Х	Xc	Yes		
Mercury		Х	Х	Xc	Yes		
Selenium			Х				
Nickel				Х	Yes		
Metallic Compounds							
Organic tin compounds		Х	Х		Yes		
Tributyltin compounds				Xc	Yes		
TributyItin-cation				Х			
Cadmium compounds			Х	Xc			
Nickel compounds				Х			
Organic Mercury compounds		Х	Х	Xc	Yes		
Organic Lead compounds		Х	Х	Xc	Yes		
Selenium compounds	<u>.</u>	<u>.</u>	Х		.		
HYDROCARBONS							
Aliphatic HC							
cyclododecane		xb					
1,5,9-cyclododecatriene		xb					
Aromatic HC							
Benzene				Х			
Polycyclic Aromatic		Х	Х	Xc	Yes		
Hydrocarbons							
Anthracene				Xc			
Napthalene				Xc			
Fluoranthene				Х	Yes		
Benzo(a)pyrene				Х	Yes		
Benzo(b)fluoranthene				Х	Yes		
Benzo(g,h,i)perylene				Х	Yes		
Benzo(k)fluoranthene				Х	Yes		
Indeno(1,2,3-cd)pyrene				Х	Yes		
Synthetic musk							

ORGANOHALOGEN COMPOUNDSHalogenated Aliphatic HCChlorinated paraffins, shortYeschained (SCCP)x ^a XXChloroform (Trichloromethane)XXYesDichloromethaneXYes1,2-DichloroethaneXYes1,2-DichloroethaneXYesPFOs (PerfluorooctaneX ^a Xsulfonate)x ^a XHexabromocyclododecanex ^a X(HBCDD)x ^a X ^a
Halogenated Aliphatic HCChlorinated paraffins, short chained (SCCP)Xaa XYesChloroform (Trichloromethane)XXYesDichloromethaneXYes1,2-DichloroethaneXYesHexachlorobutadieneX°YesPFOs (Perfluorooctane sulfonate)xaa XXHexabromocyclododecane (HBCDD)xaaX
Chlorinated paraffins, short chained (SCCP)YesxaXXXChloroform (Trichloromethane)XXDichloromethaneXYes1,2-DichloroethaneXYes1,2-DichloroethaneXYesHexachlorobutadieneX ^c PFOs (Perfluorooctane sulfonate)x ^a XHexabromocyclododecane (HBCDD)x ^a X
chained (SCCP)xaXXXcChloroform (Trichloromethane)XXYesDichloromethaneXYes1,2-DichloroethaneXYesHexachlorobutadieneXcYesPFOs (Perfluorooctane sulfonate)xaXHexabromocyclododecane (HBCDD)xaX
Chloroform (Trichloromethane)XXYesDichloromethaneXYes1,2-DichloroethaneXYesHexachlorobutadieneX'YesPFOs (Perfluorooctane sulfonate)xaXHexabromocyclododecane (HBCDD)xaX
DichloromethaneXYes1,2-DichloroethaneXYesHexachlorobutadieneX ^c PFOs (Perfluorooctane sulfonate)x ^a XHexabromocyclododecane (HBCDD)x ^a
1,2-DichloroethaneXYesHexachlorobutadieneX°PFOs (Perfluorooctane sulfonate)xªXHexabromocyclododecane (HBCDD)xªX
HexachlorobutadieneX ^c PFOs (Perfluorooctane sulfonate)x ^a Kabromocyclododecane (HBCDD)x ^a
PFOs (Perfluorooctane sulfonate) x ^a Hexabromocyclododecane (HBCDD) x ^a
sulfonate)xaXHexabromocyclododecane(HBCDD)xa
Hexabromocyclododecane (HBCDD) x ^a
(HBCDD) x ^a
Halogenated Aromatic HC
Chlorobenzenes
Trichlorobenzenes X ^c Yes
1,2,3-trichlorobenzene X
1,2,4-trichlorobenzene X X
1,3,5-trichlorobenzene X
Pentachlorobenzene x ^a X ^c
Brominated Flame Retardands
Brominated diphenylethers X ^c Yes
PBDEs
Pentabrominated diphenyl x ^a Yes
ether
Polybrominated biphenyles Yes
(PBBs)
Hexabromobiphenyl x ^a X Yes
Octabromobiphenyl x ^a
Polychlorinated Biphenyls X X X Yes
(PCBs)
Polychlorinated dibenzodioxins X X X Yes
(PCDDs)
Polychlorinated dibenzofurans X X X Yes
(PCDFS)
2,4,6-bromopnenyl 1-2(2,3- X ²
Dentebrameethylbenzene
Pentachioronorbomene x ^b
Pentachioroanisole x ^a
res res
totrophlorenenthelene x ^b
bevechlerenenbthelene X
henteehlerenenhthelene x ^b
neptachioronaphthalana X [*]
octachioronaphthalene X [*]
naphinalene, chloro derivs. X [*] Chloringtod Phonelia X [*]
Chiorinated Phenolic Yes
methylethylidene)bis[2.6-

dibromo- / tetrabromobisphenol					
A (TBBP-A)					
ORGANOHALOGENATED PESTI	CIDES/E	BIOCIDES			
Alachlor				Х	
Atrazine				Xc	
1,2-Dibromoethane			Х		
Chlorophenoxyacids					Yes
2,4,5-T			Х		Yes
Acrylonitrile			Х		
Aldrin	Х		Х		Yes
Aramite			Х		
Chlordane	Х		Х		Yes
Chlordecone (Kepone)	x ^a		Х		Yes
Chlordimeform			Х		
Chlorfenvinphos				Х	
Chlorpyrifos				Xc	
Dicofol		Х			
DDTs	Х		Х		Yes
Diuron				Xc	
Dieldrin	X		X	~	Yes
Endosulphan (alpha-endosulfan)	v ^a	X	Χ	Xc	100
	X	Λ	X	Λ	Ves
Ethyl O (n nitronbenyl) nhenyl	Λ	vb	Λ		163
phosphonothionate (EPN)		Χ.			
Eluoroacotic acid and dorivator			V		
		, b	^		
		<u>x</u>	V		Vaa
		~	~		res
<u>HCH</u> (gamma isomor Lindano)	va		v	VC	Voc
	<u>x</u>		^	^	Vec
	<u>x</u>				Vec
	X		<u> </u>		Yee
Heptachior	<u>X</u>		<u>X</u>	NC	Yes
Hexachiorobenzene	X		<u>X</u>	X	res
Isobenzane		h	<u>X</u>		
Isodrin		X	X		
Isoproturon				X°	
Kelevan			X		
Methoxychlor		Х			
Mirex	Х		Х		Yes
Morfamquat			Х		
Nitrophen			Х		
Pentachlorophenol			Х	Xc	Yes
Quintozene			Х		
Simazine				Xc	
Tetrasul		xb			
Trifluralin		Х		Xc	
Toxaphene	X		Х		Yes
OTHER ORGANIC COMPOUNDS					
Phenols					
2,4,6-tri-tert-butylphenol		Х			
Nonylphenol/ethoxylates		Х	Х		
(NP/NPEs)					

Nonylphenols			Xc	
Nonylphenol, 4-		Х	Х	
Octylphenols	Х		Xc	
(para-tert-octylphenol)			Х	
Organic Nitrogen Compounds				
4-	Х			
(dimethylbutylamino)diphenylamin				
_(6PPD)				
3,3'-	x ^b			
(ureylenedimethylene)bis(3,5,5-				
trimethylcyclohexyl) diisocyanate				
Organic Oxigen Compounds				
neodecanoic acid, ethenyl ester	Х			
2-propenoic acid,	x ^b			
(pentabromo)methyl ester				
Dibutylphthalate (DBP)	Х	Х		
Diethylhexylphthalate (DEHP)	Х	Х	Xc	
Pharmaceuticals				
Clotrimazole	X			
Diosgenin	Xp			

UNPOPs: Stockholm Convention on Persistent Organic Pollutants. (X: 12 approved POPs; \mathbf{x}^{a} : proposed substance)

OSPAR: OSPAR List of Chemicals for Priority Action (update 2007) (X: priority chemicals where a background document has been or is being prepared; \mathbf{x}^{b} : priority chemicals where no background document is being prepared because they are intermediates in closed systems or there is no current production or use interest)

HELCOM: List of Selected Substances for Immediate Priority Action (Recom. 19/5)

WFD: List of priority substances in the Water Framework Directive (Decision 2455/2001/EC) (X: priority substance; X^c : identified or being identified as possible "priority hazardous substance").

2.4.2 Comparison with SAP

As indicated above, in 1997 the Contracting Parties adopted the <u>Strategic Action</u> <u>Programme (SAP)</u> to address pollution from land-based sources and activities. This is an action-oriented initiative which identifies <u>priority target categories of polluting</u> <u>substances</u> and activities to be eliminated or controlled by the Mediterranean countries through a planned timetable (up to the year 2025).

In Table 5 it has also been indicated those substances that are included in the SAP, i.e., those priority target categories, substances with specific targets, or substances that are mentioned under priority target categories.

As it can be observed, most of the common priority substances in other international lists are already considered in the SAP. Main differences with other lists are related to some pesticides (the SAP is focused on the 'old' organochlorines), and with the group of 'other organic compounds', as the SAP do not include nonyl and octyl phenols, phthalates or pharmaceuticals.

Finally, it must be taken into account that the scope of the SAP is broader than the lists of priority substances presented above. These lists are rather oriented to implement the hazardous substances strategies in the respective regions, while the SAP provides the basis to address a broader group of land-based pollutants and activities (from both

urban environment and industrial development). Accordingly, besides the common priority substances of concern (e.g. substances that are toxic, persistent and liable to bioaccumulate; other heavy metals; organohalogen compounds), the SAP also includes the following priority target categories:

- Radioactive substances
- Nutrients and suspended solids (BOD, nutrients, SS)
- Hazardous wastes

3. Occurrence of substances of concern in the Mediterranean marine environment

3.1 Sources of data

The occurrence of pollutants in the Mediterranean marine environment has been monitored since some decades in the Mediterranean by regional programmes (MED POL), national programmes (e.g. RNO in France, or SIDIMAR in Italy), or by specific research works. The MAP Technical report series are also a source of information, as well as regional assessments for specific substances (like for Persistent and Toxic Substances (UNEP/GEF, 2002)). Relevant information can also be obtained from the scientific literature and outcomes of specific projects.

3.1.1 MED POL

The MED POL monitoring and assessment program started in the mid-1970s and has been implemented in different phases. MED POL has recently finished its Phase III, which started in 1996 and lasted until 2005. From 2005 until 2013, a new phase of MED POL has come into operation.

MED POL Phase III and IV monitoring programmes are designed to cover basically two different types of marine sites; hot spots and coastal/reference areas. Samples are collected from different environmental media. The mandatory monitoring matrices for MED POL programme are biota and sediment for hazardous substances, including trace metals (Total Hg, Cd, etc.) and organic contaminants (halogenated hydrocarbons, poly aromatic hydrocarbons etc.). Total mercury and cadmium are the only ones which are mandatory, however, most of the national programmes contain more than those as recommended. A total of 445 stations were initially included in MED POL Phase III, as shown on Figure 4.



Figure 4 MED POL Phase III Monitoring sites. Source: MED POL.

However, the overall set of data in the region has not been fully evaluated yet, since they do not allow for an accurate comparison of values over time and between regions. According to MED POL, the following qualitative distinction can be established:

Good set of data in biota:	Cadmium Lead Mercury
Old data or few data in biota:	Other metals (Selenium, copper, chromium, nickel, zinc) PAHs PCBs Chlorinated pesticides (Aldrin, DDTs, Dieldrin, Endrin, HCH, Heptachlor, Hexachlorobenzene)

The availability of indicators and coverage of data for chemical pollution is also very variable between countries.

3.1.2 National monitoring networks

National monitoring databases of the marine environment are available for France (IFREMER/RNO) and Italy (SIDIMAR).

The French National Monitoring Network $(RNO)^7$ was created in 1974 and is managed by IFREMER. Pollutants in sediments and biota are monitored since 1979, and since 2003 it also measures biological effects (imposex). The parameters include metals (Ag, Hg, Cd, Cr, Pb, Zn, Cu, V and Ni), organochlorinated compounds (DDT, DDD, DDE, YHCH (lindane), α HCH, PCBs (congeners 28, 52, 101, 105, 118, 138, 153, 156, 180) and PAHs (16). Biota is monitored annually, while sediments are sampled in a 10 years period, although with the adoption of the WFD the frequency will be every 6 years since 2007.

In Italy an initial coastal monitoring programme was undertaken in the Adriatic between 1990-1993, which was followed by a national programme (except Sicily) in 1996-2000, and since 2001 it operates at national level. Data on hazardous substances is available for sediments and biota, and parameters are similar to RNO, including some additional substances like TBTs.

⁷ http://www.ifremer.fr/envlit/surveillance/rno.htm

A summary of main parameters included in these national monitoring programs, in comparison with other regional programs is shown in Table 6.

Organization or Programme	Start of the programme	Main Parameters ¹	Sample types	Region
OSPAR	1978	HM, PCBs, PAHs, OCPs, OTINs	Biota, Sed	NE Atlantic
HELCOM	1979	HM, PCBs, PAHs, OCPs, OTINs	Biota, Sed	Baltic
MED POL	1975	HM, PCBs, OCPs	Biota, Sed	Mediterranean
RNO	1979	HM, PCBs, PAHs, OCPs	Biota, Sed	French coasts
SIDIMAR	1990	HM, PCBs, PAHs, OCPs, OTINs	Biota, Sed	Italian coasts

Table 6 Main parameters monitored in different regional and national programs.

¹Not all parameters measured during entire period and in the overall region; HM - heavy metals; PCBs - polychlorinated biphenyls; PAHs - polycyclic aromatic hydrocarbons; OCP - organochlorine pesticides; OTINs - organotins.

3.1.3 Scientific literature

In order to get an idea of the available information in the scientific literature, related with the state of the Mediterranean marine environment for the different substances of concern, an analysis of the ISI Web of Knowledge⁸ database has been carried out. To this end, a systematic analysis was developed to collect all records resulting from searching for different substances of concern and the topic 'Mediterranean Sea'. Substances or groups of substances included in this analysis were those that had been identified at least by two lists of priority substances of concern (as identified above). The topic 'Mediterranean Sea' was preferred to others such as 'Mediterranean region', as the former links more directly with the marine environment. However, it must be noted that results are only indicative, as not all the records obtained will be related with the state of the marine environment. In any case, the aim of this analysis is to observe major trends, and not to collect all the reported publications.

In this sense, in Figure 5 it can be observed that 'classical' pollutants like metals account for the majority of publications in the Mediterranean region, followed by some organohalogen (PCBs, dioxins and furans), PAHs, and some chlorinated pesticides (DDTs, HCB, HCH). On the other side, only some few records are obtained for 'emergent' pollutants (e.g. SCCP, PFOS, brominated flame retardants, nonylphenols,...), as expected.

⁸ http://www.isiwebofknowledge.com/



Figure 5 Number of records, by publication year, in the ISI Web of Knowledge database (search by 'substance' AND 'Mediterranean Sea').

Moreover, the information in the Mediterranean region is mostly limited to the last 20-30 years. In fact, only 2% of the records were published before the 80s (mainly regarding metals and DDTs), as the majority of information has been published since the 2000 (64%) and during the 90s (27%) (see Figure 6).



Figure 6 Evolution of number of records, by publication year, in the ISI Web of Knowledge database (search by 'substance' AND 'Mediterranean Sea').

According to this analysis, *potentially* there would be a good basis in the scientific literature to undertake an assessment of the state of the Mediterranean marine environment for the following substances or group of substances:

- Heavy metals (Cd, Pb, Hg)
- PAHs
- PCBs
- DDTs

The following substances or groups of substances would be partially covered in the scientific literature:

• Organotin compounds (TBT)

- Dioxins and furans
- HCH
- Hexachlorobenzene

While for the rest of substances of concern very few data in the Mediterranean region is expected to be available in the scientific literature.

3.2 Metals and related compounds

3.2.1 Heavy Metals (Cd, Pb, Hg) in sediments

Data about <u>Cadmium</u> contents in <u>marine sediments</u> is scarce in the Mediterranean Sea, and concerns mostly sediments from the Northern Mediterranean. Roussiez et al. (2006) carried out a comprehensive study of the Gulf of Lions, where they found levels ranging from 0.22 to 0.82 μ g/g dw, being 0.36 μ g/g dw the average Cd concentration. In the Southern Evoikos Gulf, in the Aegean Sea, Cd values are slightly lower and ranged from 0.10 to 0.65 ppm (Angelidis and Aloupi, 2000). Lafabrie et al. (2007) also recorded Cd in marine sediments next to the Toscanian coast and the Corsica and Sardinia islands, being 0.40 μ g/g dw, 0.03 μ g/g dw and 0.07 μ g/g dw respectively. Finally, the Strait of Sicily has registered higher Cd levels between 0.1 and 1.6 μ g/g dw, being 0.7 μ g/g dw the average concentration (Böttcher et al., 2003).

Studies on Lead levels in marine sediments have also been focused in the North Mediterranean. The Gulf of Lions (North Western Mediterranean) has registered concentrations ranging from 20.6 μ g/g dw up to 69.7 μ g/g dw with a mean concentration of 39.2 μ g/g dw (Roussiez et al., 2006). The Gulf of Taranto (Ionian Sea) recorded higher Pb values ranging between 44.7 to 74.8 μ g/g dw, although levels in sediments offshore dropped to 59.0 μ g/g dw. In the Southern Evoikos Gulf, Pb registered 13.8 to 19.4 μ g/g dw (Angelidis and Aloupi, 2000). Lafabrie et al. (2007) found 44.50 in the Toscanian coast, 4.67 μ g/g dw in sediments next to Corsica and 18.67 μ g/g dw next to Sardinia.

Data available about <u>Mercury</u> levels in Mediterranean sediments is commonly related to industrialised and densely occupied areas. Lafabrie et al. (2007) found Hg values up to 560 ng/g dw in the Toscanian coast, 20 ng/g dw in marine sediments in North-east of Corsica and 70 ng/g dw in Sardinia. Buccolieri et al. (2006) detected Hg concentrations in the Gulf of Taranto ranging from 40 to 410 ng/g dw in sediments near the coast and 70 ng/g dw in sediments offshore, in the centre of the gulf.

Concentrations of Hg in sediments offshore have also been studied. Levels in the Alboran Sea have been found to be around 56 ng/g dw. Very similar concentrations of about 44 ng/g dw Hg have been reported in the South Levantin Basin, the Ionian Sea and in the Levantin Basin (Ogrinc et al., 2007). An extensive study in the Strait of Sicily revealed that Hg levels ranged from 50 to 70 ng/g dw, with samples registering higher contents peaking up to 202 ng/g dw (Di Leonardo et al., 2007). A distribution pattern for Hg can be observed from the available data, as higher Hg concentrations occur mostly in the coastal sediments, while the offshore sediments record lower Hg contents.

It is difficult to provide <u>background levels</u> of heavy metals so as to easily assess whether sediments are polluted and their degree of contamination. Metal natural levels may fluctuate from one geographical area to another depending on the type of substrate and the physical characteristics of the soil along with other chemical properties (i.e. amount of organic matter, carbonates) (Boughriet et al., 2007; Choi et al., 2006).
Many studies have shown that sediments can provide evidence of human impact on the environment since they present a historical record of human activity and pollution history (Vesely et al., 1993). In this case, Cadmium, Mercury and Lead reference values in the Mediterranean Sea have been estimated from different studies having collected sediment cores throughout the whole Mediterranean area.

During 1994-1995 the RNO collected five cores within the French Mediterranean coasts. For <u>Mercury</u>, background levels were estimated to an average value of 100 ng/g dw taking into consideration chemical fractions (i.e. organic matter, carbonates) and sediment grain-size (RNO, 2001). Similarly, other studies have reported reference values up to 38 ng/g dw for the Strait of Sicily (Di Leonardo et al., 2006) and ranging 100-200 ng/g dw in the Gulf of Naples (Baldi et al., 1983). In the same way, 0.15 µg/g dw was established as the <u>Cadmium</u> limit concentration in non-polluted sediments of the French coasts (RNO, 2001). Data from a survey by IFREMER revealed lower Cd background values ranging 0.06-0.08 µg/g dw in coastal areas from Morocco (RNO, 2001). For Lead, sediments registering levels higher than 30 µg/g dw were considered as polluted in the French coastal area (RNO, 2001). Previously, concentrations of 25 µg/g dw had been established as reference values (Whitehead, 1984, in RNO, 2001). Again, data from the Moroccan coastal area reported lower background levels of 17-21 µg/g dw (RNO, 2001).

Taking into consideration current levels found in the Mediterranean Sea and published data concerning background concentrations, it may be suggested that Hg pollution occurs mostly in the coastal sediments, while Hg values in offshore areas are within the natural range values. For Cadmium, all the study sites described in the present report were far beyond the established background levels in the Mediterranean Sea. In the case of Lead, all coastal sediments reveal pollution levels except for the Southern Evoikos Gulf, whose Pb concentrations lay within background concentration ranges. Sediments distant from coasts also report natural Pb levels.

3.2.2 Heavy Metals (Cd, Pb, Hg) in biota

MED POL data (Phase III) provides a general overview of the content of trace elements in biota in the Mediterranean region. Although data do not cover the entire Mediterranean coastline and cannot be used at this stage to draw conclusions on regional pollution levels, the available data present an average total Hg concentration above 150 ng/g and an average Cadmium concentrations about 500 ng/g (see Figure 7)





Figure 7 MED POL Phase III – monitoring of Total Hg and Cd in the Mediterranean region. Source: MED POL.

<u>Mussels</u> are worldwide recognized as pollution bioindicators and they are used in mussel watch programs since they accumulate pollutants in their tissues at elevated levels in relation to pollutant biological availability in the marine environment. However, in the Mediterranean Sea, research studies concern mostly the North-western basin, and scarce data has been identified in the scientific literature concerning Hg levels in mussels. Some data on Total Hg, Cd and Pb concentrations in mussels is shown in Table 7.

Location	Sampling year	Concentration	Reference		
Mali Ston Bay (Eastern Adriatic)	1998-2005	Cd : 1.15 μg/g dw Hg : 0.15 μg/g dw Pb : 1.09 μg/g dw	Kljatovic-Gaspic et al. 2007		
Gulf of Taranto	1999-2000	Cd: 0.23 - 0.77 μg/g dw Pb: 1.19 - 4.29 μg/g dw	Cardellicchio et al. 2008		
Turkish-Aegean Sea coast	2002-2003	Cd: 0.04 - 0.52 μg/g ww Pb: 0.49 - 1.72 μg/g ww	Sunlu 2006		
Tyrrhenian Sea	2000	Cd: 0.23 - 0.77 μg/g dw Pb: 1.19 - 4.29 μg/g dw	Conti and Cecchetti 2003		
Venice Lagoon	1993	Cd : 0.05 - 4.64 μg/g dw Pb : 6.18 - 80.26 μg/g dw	Conti and Cecchetti 2003		

Table 7 Trace metal level contents in the Blue Mussel (*Mytilus galloprovincialis*) in some specific coastal areas in the Mediterranean Sea.

Kljakovic-Gaspic et al. (2007) monitored the Blue Mussel (Mytilus galloprovincialis) in the Mali Ston Bay, located on the eastern Adriatic coast, from 1998 to 2005. The content of trace metal concentrations in the edible tissue of mussels (averages Cd: 1.15 μ g/g dw.; Hg: 0.15 μ g/g dw.; Pb: 1.09 μ g/g dw.; see Table 7) fell in the range of values usually found in low to moderately contaminated marine coastal areas, although according to EU and WHO legislation and guidelines, consumption of the edible tissue

of the mussels was not harmful for humans. Analysis of temporal trends during the 7 years of monitoring showed that metal concentrations had not changed over time.

Similarly, a monitoring survey carried out during the 2001-2005 period in the Croatian coast using the blue mussel as an indicator species, determined that Pb and Hg were significantly elevated in the urban and industrial areas, while Cd was more uniformly distributed across the monitored sites, being also high in mussels from rural areas located far away from anthropogenic sources of pollution. The majority of values were yet below the maximum thresholds for fresh seafood. Again, metal concentrations had not changed during the five year-period (Kljakovic-Gaspic et al., 2007).

Blue Mussel individuals sampled in the Gulf of Taranto revealed Cd levels ranging from 0.23 up to 0.95 μ g/g dw between 1999 and 2000, slightly lower than those registered in the Adriatic Sea, while Pb concentrations were higher, ranging from 1.19 to 4.49 μ g/g dw (Cardellicchio et al. 2008).

In contrast, the Tyrrhenian Sea has recorded lower metal contents in the same species, analysed in 2000. Cadmium ranged between 0.32 and 0.49 μ g/g dw while Pb levels ranged from 1.67 up to 2.49 μ g/g dw. These values appear to be particularly low when comparing to highly polluted areas such as the Venice Lagoon, where Cd and Pb levels have been recorded to reach 4.64 and 8.26 μ g/g dw respectively (Conti and Cecchetti, 2003).

Mussels from the Turkish-Aegean Sea also appear to be more polluted, since trace metal values in M. galloprovincialis from 2002-2003 are more elevated. Cadmium ranged between 0.04 and 0.52 μ g/g ww (approximately 0.20 – 2.6 μ g/g in a dry weight basis using the "5" OSPAR Commission converting factor), while Pb ranged from 0.49 to 1.72 μ g/g ww (2.45 – 8.6 μ g/g dw) (Sunlu, 2006).

Concerning top predators, significant amounts of data are available concerning trace metal concentrations in different organs and tissues from predators at the top of the food chain in the Mediterranean Sea area. A review of data is shown in Table 8.

Storelli et al. (2005) analysed heavy metals in Bluefin Tuna (*Thunnus thynnus*) and Swordfish (*Xiphias gladius*) caught in the Ionian Sea in 1993. In both species, metal levels in livers were approximately twofold than those found in muscle tissues, except for cadmium which showed considerably higher concentrations in livers. Comparing the two species, a significant variation in certain metal concentrations was observed. Mean mercury, lead and cadmium concentrations in muscle tissues and in livers were about two to nine times higher in bluefin tuna than in swordfish. Bluefin tuna appeared hence more contaminated than swordfish. In contrast to swordfish, tuna appeared to be more able to concentrate large amounts of mercury, cadmium and lead, demonstrating a potential as a bioindicator of pollution of the open sea ecosystems. In comparison with data reported by other authors, mean levels of Cd and Pb in Bluefin tuna were similar to those reported in the same species from the Mediterranean Sea. In addition, Cd and Pb concentrations occurring in muscle tissues of swordfish were also comparable to levels already reported.

Similarly, comparable mercury concentrations have been reported in bluefin tuna of similar size from the Tyrrhenian Sea, while in specimens of a larger size noted much higher values, as Hg concentrations in fish increase with body size (Storelli et al. 2005).

Table 8 Trace metals content in Cetaceans in the Mediterranean Sea (ww: wet weight basis; dw: dry weight basis).

Species	Concentrations (µg/g) ^a			Weight	Location/	Reference
Fish	Total Hg	Pb	Cd	basis	year	

T. thynnus	M: 0.13 - 0.35 L: 0.27 - 0.60	M: 0.07 – 0.18 L: 0.11 - 0.39	M: 0.01 - 0.04 L: 0.06 - 2.72	ww	Ionian sea / 2003	Storelli et al. 2005
X. gladius	M: 0.02 - 0.15 L: 0.10 - 0.37	M : 0.04 - 0.08 L : 0.06 - 0.11	M: 0.002 - 0.01 L: 0.10 - 0.29	ww	Ionian sea / 2003	Storelli et al. 2005
Cetaceans						
B. physalus	M: 0.65 - 2.64 L:0.11	M : 0.051 - 0.137 L: 0.041	M: 0.04 L: 0.04 K: 1.56	dw	Ligurian Sea / 1990-2004	Capelli et al. 2007
P. macrocephalus	M: 1.13 L: 4.24	M: < l.o.d L: < l.o.d	M: < I.o.d L: < I.o.d K: 0.04	dw	Ligurian Sea / 1990-2004	Capelli et al. 2007
Z. cavirostris	M: 21.79 L: 258	M: < l.o.d L: 0.726	M: 0.06 L: 10.34 K: 60	dw	Ligurian Sea / 1990-2004	Capelli et al. 2007
G. griseus	M: 5.86 – 139 L: 19.25 - 2746	M: < I.o.d L: 0.390 – 2.687	M: < l.o.d - 0.52 L: 2.35 - 38 K: 20 - 71	dw	Ligurian Sea / 1990-2004	Capelli et al. 2007
T. truncatus	M: 2.57 – 162 L: 13.55 - 3737	M : < I.o.d - 0.263 L: 0.155 – 0.457	M: < l.o.d - 0.12 L: < l.o.d - 3.02 K: 0.03 - 9.83	dw	Ligurian Sea / 1990-2004	Capelli et al. 2007
S. coeruleoalba	M: 8.11 - 59.43 L: 137 - 452	M: < l.o.d - 0.223 L: 0.211 - 0.735	M: < l.o.d - 0.28 L: 1.60 - 5.39 K: 9.54 - 34	dw	Ligurian Sea / 1990-2004	Capelli et al. 2007
S. coeruleoalba	-	M: 0.12 - 0.48 L: 0.22 - 0.88	M: 0.04 - 0.16 L: 1.50 - 6.00	ww	South Italy / 1991	Cardellicchio et al. 2002
S. coeruleoalba	M: 52.83 L: 592.97	-	M: 0.10 L:4.43 K:27.51	dw	Ligurian – Tyrrhenian 1987-1994	Monaci et al. 1998
S. coeruleoalba	M: 27.77 L: 1043.14	-	M: 0.05 L: 3.95 K: 8.38	dw	Spanish Med. 1987-1994	Monaci et al. 1998

^a L: Liver; M: Muscle; K: Kidney

Regarding <u>cetacean species</u>, Monaci et al. (1998) studied trace metal concentrations in different tissues of striped dolphin (*Stenella Coeruleoalba*) from the Spanish coasts and the Ligurian and Tyrrhenian Seas between 1987 and 1994. Mean <u>concentrations of Hg</u> found in liver and other tissues were very high (mean for all liver samples of 976 μ g/g dw), but were in accordance with other reports from the same geographical area. As Hg accumulates with age in all tissues, it may reach concentrations of several hundreds of μ g/g (wet weight basis) in dolphins of 30-40 years. The highest concentration found was 5,441 μ g/g dw in liver.

On the other hand, Hg levels in dolphins from the Ligurian and Tyrrhenian area were significantly higher than those from the Spanish area (see Table 8). In this case, the pattern of bioaccumulation of Hg found in the tissues of striped dolphins stranded along the Spanish and Italian coasts suggested the existence of two populations, distinct in terms of spatial niche and position in the food chain, presumably exposed to different dietary levels of these elements as a result of different man-made and natural inputs in the two geographical areas.

In addition, striped dolphins of the Mediterranean seem to have substantially higher concentrations of Hg than those of the Pacific and Atlantic. Mercury mean values of 205 μ g/g ww have been reported in liver of dolphins captured near the Japanese coasts (Monaci et al., 1998). Moreover, liver concentrations of Hg in dolphins stranded on the Mediterranean coasts of France have been found to be 6-7 times higher than those in dolphin stranded on the Atlantic side of the same country. In line with these statements, other studies have found mean concentrations of 668 μ g/g ww in 13 dolphins stranded on the Mediterranean coasts of France (Monaci et al., 1998).

More recent studies concerning Hg in cetaceans' species have also shown elevated levels. Capelli et al. (2007) studied Hg, Cd and Pb content of six cetacean species in the Ligurian Sea, where these species find their breeding and feeding needs, in order to assess anthropogenic pressure on this rich faunal biodiversity (see Table 8).

Mercury concentrations were largely variable: low values were found in *B. physalus*, *P. macrocephalus*; higher concentrations were observed in *Z. cavirostris* and *S. coeruleoalba*, although it must be pointed out that Hg levels in *S. coeruleoalba* were lower than those observed by Monacci et al. more than one decade before; finally, extremely high levels in *G. griseus* and one *T. Truncatus* were stated.

In the same species, the low range concentrations corresponded to the younger individuals, indicating the strong effect of age on Hg accumulation. The highest concentrations found in *G. griseus* and *T. truncatus* reached more than 100 μ g/g dw Hg in muscle. Other values in literature are comparable and even higher to those results, with the maximum ranging from 156 to 334 μ g/g dw. in *T. truncatus* and from 123 to 1580 μ g/g dw in *G. griseus* and (Capelli et al., 2007). The liver was again the organ where the highest mercury concentrations were detected, exceeding 2,000 μ g/g dw.

When comparing to the Atlantic populations, Hg concentrations in muscle and liver of specimens from the Atlantic were lower. *S. coeruleoalba* and *T. truncatus* are the most frequently studied species. Higher Hg concentrations in Mediterranean individuals are frequently detected in *T. truncatus* when comparing to the Atlantic ones (Capelli et al., 2007).

Between 1987 and 1994, <u>Cd concentrations</u> found in tissues of dolphins from Ligurian and Spanish Mediterranean waters were slightly lower than those reported in previous studies (see Table 8). Tissue levels of Cd are influenced by dolphin diet, which varies with circumstances and availability. Cephalopods, an important dietary item for striped dolphins, are efficient accumulators of Cd and are therefore the dolphins' main source of exposure to this metal (Monaci et al., 1998).

Spatial trends observed in Cd concentrations in dolphins from the two analysed areas, the Ligurian Sea and the Spanish coasts, were similar to those of Hg. Dolphins from the Tyrrhenian and Ligurian Seas revealed higher Cd contents with respect to those from the Spanish coastal area, which may be due to greater Cd contamination from man-made sources in the former areas, or to the fact that the Italian dolphins come closer to the coast than Balearic dolphins, since the water is deep close to the Italian coasts (Monaci et al., 1998). Cardellicchio et al. (2002) studied *S. coeruleoalba* caught in 1991 from the South Italian waters, and found Cd levels up to 0.04 and 1.50 µg/g ww

in muscle and liver respectively (0.16 and 6 μ g/g in a dry weight basis using the Becquer et al. (1995) 0.25 converting factor). As it can be observed, Cd values from the Monaci et al. (1998) and Cardellicchio et al. (2002) studies are similar, as they concern the same species in the same geographical area and the same timeframe.

Regarding the study of Capelli et al. (2007), contemporary Cd levels in cetaceans from the Ligurian Sea have been reported to be in several cases below detection limit, and are usually low (between 0.01 and $0.82 \mu g/g dw$) except for the liver and kidney of *G. griseus* (38 and 71 $\mu g/g dw$, respectively) (see Table 8). Cadmium levels in *S. coeruleoalba* are still elevated and very similar to concentrations reported in the research studies previously described.

It has been reported that kidney is the critical organ for Cd accumulation. As suggested by other authors, Capelli et al. (2007) have also attributed the high Cd values measured in *G. griseus*, *Z. cavirostris*, and *S. coeruleoalba* to the big consumption of squids, generally rich in cadmium. *T. truncatus* shows renal Cd levels lower than *S. coeruleoalba*, as a result of the different amount of cephalopods in their diet.

Concerning <u>Pb levels</u>, Capelli et al. (2007) found that about 50% of the Pb values measured fell below the detection limit; values were low and ranged between 0.04 and 0.74 μ g/g dw, except for an anomalous high range value (2.7 μ g/g dw) in the liver of *G*. *griseus*. These values can be compared to data from more than one decade before. Cardellicchio et al. (2002) found slight higher Pb levels of 0.48 μ g/g dw in muscle and 0.88 μ g/g dw in liver in *S*. *Coeruleoalba* species from the South Italian coasts.

3.2.3 Organic tin

Organotins (OTs) have been widely used during the last decades as biocides, agricultural pesticides, polymer stabilisers, wood preservatives, and catalysts in a number of industrial processes. Nevertheless, their main source in the marine ecosystem is related to their use as antifouling paint biocides (Diez et al., 2002). OTs degrade slowly in the environment and in particular in sediment, and their high persistence and ecotoxicological risk has been widely documented since their discovery in Arcachon Bay (France) in the early 1980s. They are responsible for many deleterious effects to nontarget aquatic life (i.e. imposex, oyster malformation, mussel larvae mortality) at very low concentration levels (few ng/kg) (Diez et al., 2002).

Several countries have banned its use and restricted its application to large vessels. The French authorities banned the use of antifouling paints containing tributyltin (TBT) on boats less than 25 m long in 1982 and similar regulations on the usage of TBT in paints came into effect few years later in the European Union in 1989 (Diez et al., 2002). Following the retail ban on TBT-based antifouling paints in the late 1980s in most of the developed countries, monitoring programmes are currently carried out in order to assess the effectiveness of present regulations. Surveys are carried out in different coastal areas (France, United Kingdom, Atlantic and Pacific US coasts, The Netherlands and Japan) revealing a decline in the TBT concentration in seawater but still exceeding the non-effect level for the most sensitive species (Diez et al., 2002; Morcillo et al., 1996). Similar surveys have been conducted in limited areas of Southern European countries such as South Atlantic coast of Spain or Mediterranean coast of France.

Diez et al. (2002) performed a study concerning OT levels in <u>sediments</u> from the Northern and Southern areas of the Spanish Mediterranean Sea, between 1995 and 2000. OT concentrations in sediments from this area varied widely depending on the

location. Results for the 1995 sampling survey revealed that butyltin compounds were predominant in the whole area of study and the highest levels were found in the Barcelona commercial harbour with average levels of 4,487 ng/g for TBT, although maximum concentrations TBT peaked up to 18,700 ng/g (see Table 9). In contrast, in the Masnou marina where pleasure boats are predominant, OT concentrations were lower (920 ng/g for TBT, with a maximum of 1650 ng/g) comparing to the Barcelona commercial harbour. On the contrary, OTs concentrations in Sant Carles harbour reached moderately high levels, 1,600 ng/g TBT (with maximum levels up to 5226 ng/g), higher than expected according to the harbour characteristics.

Data from 2000 revealed that most of the locations in the Barcelona commercial harbour increased compared to the concentrations obtained 10 yr before. In Masnou marina, a decrease in OT concentrations could indicate an effective fulfilment of the TBT regulation, although sediments were exceeding 4 times the expected values. Also, the Sant Carles fishing harbour exhibited an increase in the OT levels. Therefore, TBT regulations were still not effective for commercial harbours of the Catalan Sea after 10 years of application (Díez et al., 2002).

A study carried out by Martinez-Lladó et al. (2007) concerning TBT levels in the Barcelona harbour showed that the most enriched sediments were found in Port Vell, with levels ranging 326–4,702 ng/g dw (see Table 9). The higher content of TBT in this area might be due to the continuous moorings of recreational boats, as well as to the proximity to the fuelling stations and to the painting dry-dock operations. In the outer harbour, a slight lowering of TBT contents towards the harbour mouth (where 98 ng/g were recorded) was also observed.

In the Alboran Sea, OT concentrations in sediments of nine harbours and twelve sites have also been determined. The Almería harbour was the only commercial harbour and showed the highest values for OTs among the ports located into the southern basin, with maximum levels reaching 2,135 ng/g for TBT (see Table 9). A remarkable difference in the concentration levels between this harbour and the Barcelona harbour is yet noticeable, attributable to the enormous contrast of traffic and passenger traffic (i.e. Barcelona doubles Almería). All of the rest of the marinas from the Southern Spanish coast analysed showed values averaging 975 ng/g of TBT, except Sotogrande reaching around 3,868 ng/g of TBT (Díez et al., 2002).

Ecoregio	n	Location	ng TBT/g dw	ng Sn/g dw	Reference
NW coast	Spanish	Barcelona harbour	4487	-	Diez et al. 2002
		Masnou marina	920	-	Diez et al. 2002
		St Carles harbour	1617	-	Diez et al. 2002
		Tarragona	76	-	Diez et al. 2002
		Barcelona harbour	326-4,702	-	Martínez-Lladó, et al. 2007
SW coast	Spanish	Total range	200-3868	-	Diez et al. 2002
		Sotogrande	3868	-	Diez et al. 2002
		Almeria port	2135	-	Diez et al. 2002
		Duquesa	1669	-	Diez et al. 2002
		Alquerimar	481	-	Diez et al. 2002
		Almeria marina	200	-	Diez et al. 2002
Egyptian Sea	Med.	Total range	-	35-975	Barakat, 2004
		Alexandria/ port	-	1-2,067	Barakat, 2004

Table 9 TBT sediment contents in several regions from the Mediterranean Sea.

	Malta		20 1 500	Axiak	et	al.
Central Sea	Maila	-	30-1,500	2000		

In general, butyltin levels found were higher than those reported previously in different areas of the world (i.e. USA: East Gulf and Pacific coasts; and Auckland in New Zealand). However, comparison with other areas like the Hong Kong marina and Portland and Boothbay Harbours in Maine, with similar tidal regimes and dilution effects, reflected that in the Mediterranean Spanish coast OTs occur in moderate to high levels (Díez et al., 2002).

Similarly, OTs were measured again in 38 sediments collected in harbours of the Western Mediterranean Sea and domestic and industrial sewage disposal sites (Diez et al., 2003). Butyltins were the predominant tin species identified and TBT widespread in the whole area, suggesting recent inputs of OTs. The highest levels of TBT were detected in commercial harbours associated with inputs from large vessels (mean value: 2000 ng/g as Sn). Moreover, relatively high TBT values were also detected in fishing and recreational boating areas (mean level. 400 ng/g as Sn). Phenyltin derivatives occurred at lower levels than butyltins.

Furthermore, a comparative study of the OT occurrence in the sewage sludge disposal sites offshore Barcelona and Almeria (domestic) and into the Tarragona harbour (industrial) showed that domestic primary sewage sludge effluents can also contribute to coastal OT pollution (100 ng/g of TBT as Sn), although sewage sludge is a secondary source of OT contamination in the coastal environment in comparison to commercial harbours (Diez et al., 2003).

Concerning the Levantin Basin, a recent review from the Egyptian Mediterranean Sea reported levels in sediments from the Alexandrian coast in the range of 35–975 ng Sn/g dw (see Table 9), with the highest levels reported in the harbour and levels from sediments collected in Alexandria port ranging 1–2,067 ng Sn/g dw (Barakat, 2004). These results may indicate that antifouling paints are still of concern in marinas, ports and, particularly, in sites adjacent to vessel repair facilities. The high relative concentrations of TBT found in the sediments indicated that degradation processes in the sediments are minor, due to the anoxic sedimentary conditions at the sampling sites or to relatively recent inputs of TBT to these sites (Barakat, 2004).

In Malta, butyltins in superficial sediments also determined that the two main local sources of marine contamination by TBT were ship-repairing dockyards and marinas. In sediments concentrations ranged 30-1,500 ng/g Sn dw (see Table 9). At TBT levels found in local harbours, several sublethal biological responses were observed (i.e. imposex, inhibition of enzymatic processes), evident at TBT concentrations below the environmental quality standard (20 ng TBT/L) (Axiak et al., 2000).

<u>Marine bivalves</u> are among the most studied organisms and have also been chosen as sentinel organisms in TBT pollution monitoring programmes. A few reports are available concerning the accumulation of organotin compounds in fishes. A review of several studies concerning organotin content in mussels is reported in Table 10.

Morcillo et al. (1996) performed a study concerning TBT content in mussels (*Mytilus galloprovincialis*) from the Barcelona, the Masnou and the Sant Carles harbours in 1995. The maximum concentration of organotin compounds was found in molluscs collected in Masnou marina, a recreational harbour, where the mean concentration of total organotin compounds was 5,444 ng/g dw as Sn, which was 4.5-fold higher than the concentration found in mussels from Barcelona (1,165 ng/g dw), a harbor with an important commercial traffic, and 44-fold higher than the residue detected in mussels from St. Carles (123 ng/g dw), a fishing harbor with approx. 200 moored boats (see Table 10). The concentration of TBT detected in mussels from Masnou marina was

3,500 ng/g dw Above 2,000 ng/g dw of TBT, significant adverse biological effects can be measured in adult mussels. The contamination by OTs was much lower in St. Carles harbor than in the other studied areas, but nevertheless detectable. However, mussel and clams taken from the marine farms (Alfacs bay) located approx. 3 kilometres away from the harbor showed very low or even undetectable levels of TBT. Thus, dissipation of TBT has been observed to occur over several kilometres from the major point source (Morcillo et al., 1996).

In general, TBT was present at substantially higher levels than DBT or MBT, particularly in Masnou area. This indicates that the fresh inputs of the antifouling agent dominate the degradation product. The sampling coincided with the greatest sailing activity in the area, thus probably new TBT is added to the environment (Morcillo et al., 1996).

In the Aegean Sea, TBT values averaging 17.1 ng/g ww were recorded in *M. galloprovincialis* collected between 2002-2003, similar or even lower than levels reported worldwide (Chandrinou et al., 2006). In contrast, in the Egyptian coast, marine organisms were found to accumulate TBTs to levels considerably greater than those present in the surrounding water (see Table 10). However, with a cessation of inputs, TBT concentrations have been calculated to be lost in a relatively short time of the order of 1 year. Mussels and clams collected in the Alexandria harbours were analyzed and exhibited concentrations of 97–420 and 93–320 ng/g ww of TBT, respectively (Barakat, 2004).

Concerning <u>OT</u> contents in <u>fish species</u> Morcillo et al. (1996) also studied organotin compounds in grey and red mullet (*Liza aurata* and *Mullus barbatus*) collected in 1995 in harbours (grey mullet) and offshore (red mullet). With regard to fish analysis, the concentration of total organotin compounds was considerably lower. Grey mullet, *Liza aurata*, was sampled in Barcelona harbor and no organotin compound was detected in the muscle. The highest concentration was detected in the liver (187 ng/g dw as Sn) which is six fold lower than the value reported in mussels from the same area (see Table 10). Samples of red mullet, *Mullus barbatus*, caught offshore along the coast, showed lower concentration of organotin compounds in the liver (88–133 ng/g dw as Sn) than grey mullets. The fact that no organotin compound was detected in the muscle of the studied fish points out the high metabolic potential for organotin compounds in these organisms, but also stresses the poor transference of these contaminants through the trophic chain.

	Region	Location	Levels	Unit Basis	Reference
Mussels					
М.	NW	Barcelona		ng Sn/g	Morcillo et al.
galloprovincialis	Mediterranean	port	5,444	WW	1996
М.		Masnou		ng Sn/g	Morcillo et al.
galloprovincialis		marina	1,165	WW	1996
М.		St Carles		ng Sn/g	Morcillo et al.
galloprovincialis		harbour	123	WW	1996
М.				ng TBT/g	Chandrinou et
galloprovincialis	Aegean Sea		17.1	WW	al. 2006
М.	Egyptian Med.	Alexandria		ng TBT/g	
galloprovincialis	Sea	port	97-420	WW	Barakat, 2004
Fish					
L. aurata	NW	NW Spanish	187	ng Sn/g dw	Morcillo et al.

 Table 10 Organotin content in biota

	Mediterranean	coast			1996
		NW Spanish			Morcillo et al.
M. barbatus		coast	88-133	ng Sn/g dw	1996
		Moroccan	10-	ng TBT/g	Hassani et al.
M.Cephalus	Alboran Sea	coast	18,000	WW	2006
	Egyptian Med.	Alexandria		ng TBT/g	
T. lastovizo	Sea	coast	161-250	WW	Said et al. 2006
		Alexandria		ng TBT/g	
D. sargaus		coast	155-212	WW	Said et al. 2006
	NW		174-	ng Sn/g	Borgui and
M. moro	Mediterranean		1,668	WW	Porte 2002
				ng Sn/g	Borgui and
L. lepidion			43-260	WW	Porte 2002
				ng Sn/g	Borgui and
A. rostratus			5	WW	Porte 2002
Top predators					
	Western		1,200-	ng OT/g	Kannan et al.
T. truncatus	Mediterranean	Italian coast	2,200	WW	(1995)
	Tyrrhenian			ng OT/g	Focardi et al.
T. truncatus	/Aegean Seas	-	27-43	WW	(2000)
	Tyrrhenian		15-	ng OT/g	Focardi et al.
S. ceruleoalba	/Aegean Seas	-	1,020	WW	(2000)

OTs levels were also determined in the sea mullet, *Mugil cephalus*, collected along the northern Mediterranean coast of Morocco as well as in the south Mediterranean coast of Spain (Hassani et al., 2006). TBT was the predominant compounds in the analyzed samples, reaching higher concentrations in liver than in muscle. In the Moroccan coast, the lowest concentration was 10 ng/g ww while the highest value reached 18,000 ng/g ww and was found in the inner harbour of Tangier (see Table 10). Generally, the total OTs concentration in most liver samples was higher than in muscle. The presence of OT compounds in fish samples collected from the harbours of Tangier and Tetouan suggested that these compounds are widely distributed in the studied area and bioaccumulated in fish. Concerning the Spanish coast, the study demonstrated the absence of pollution in fish in the Spanish coast, although the presence of TBT in some sediment samples reflected its elevated use in the past.

In this case, all harbour sites from Morocco showed high levels of contamination, correlating well with traffic and with high maritime activity. Thus, samples from areas near or in sites where ships are repaired and maintained were subject to high contamination levels. However, pollution decreased significantly from the inner part to the open area of the Harbour of Tangier, considered the most contaminated site as a result of the many ship repairing/modelling factories and more than a thousand ships passing daily through the Strait of Gibraltar. M'diq, a small fishing harbour situated in Tetouan, was also considered as a contaminated site to the use of nets, boats, and others utilities treated with antifouling biocides (Hassani et al., 2006).

In the Alexandria coast, specimens of *Triglaparus lastovizo* (a demersal fish) and *Diplodus sargaus* (a pelagic fish) were analysed. Result values, ranging from 161 to 250 ng/g ww for *T. lastovizo* and from 155 to 212 ng/g ww for *D. sargaus* appeared to be within the range of levels also found in other marine areas such as the Italian coast as well as the Baltic and North Seas (Said et al., 2006).

Borghi and Porte (2002) determined organotin contamination in deep-sea ecosystems, which have been rarely studied. Several <u>deep-sea fish</u> species (*Mora moro, Lepidion lepidion, Coryphaenoides guenteri, Alephocephalus rostratus* and *Bathypterois mediterraneus*) were collected between 1000 and 1800 m depth in the NW

Mediterranean and analysed to determine butyltin and phenyltin compounds. Organotin levels differed greatly among species. Total butyltin residues were up to 175 ng/g ww (see Table 10), and they were comparable to levels found in coastal fish collected along the Catalan coast. The highest butyltin and phenyltin residues were recorded in the liver of *M. moro* (174 and 1,668 ng/g ww as Sn, respectively) followed by *L. lepidion* (43 and 260 ng/g wet wt as Sn), both species from the *Moridae* family. The lowest residues were detected in *A. rostratus* (5 ng/g ww in the liver).

Interestingly, deep-sea fish contained much higher levels of phenyltins (up to 1,700 ng/g ww, and particularly TPT (up to 1,430 ng/g ww), than previously reported concentrations in shallow-water organisms. The obtained results confirmed the long-range transport of OTs to the deep-sea environments, and the subsequent exposure of fish inhabiting nonpoint source areas. The use of TPT in agriculture or as an antifouling agent, its transport to the deep-sea environment associated to particulate matter, and its nonbiodegradable nature in the food chain may account for the high residue levels detected in deep-sea organisms Borghi and Porte (2002).

Regarding <u>OTs</u> in <u>top predators</u>, Kannan et al. (1995) studied TBT and its breakdown products (MBT) and (DBT) in bottlenose dolphin (*Tursiops truncatus*), bluefin tuna (*Thunnus thynnus*) and blue shark (*Prionace glauca*). Samples were collected from the Italian coast of the Mediterranean Sea in 1992–1993.

Concentrations of total butyltin in the liver of dolphin ranged 1,200–2,200 ng/g ww and were an order of magnitude higher than in the blubber (48–320 ng/g wet wt) (see Table 10). TBT was the predominant butyltin species in the blubber while DBT accounted for a higher proportion in the liver of dolphins. Butyltin concentrations in bluefin tuna were lower than those in dolphins, again with TBT highest in the muscle and DBT in the liver. Finally, levels of BTs in blue sharks were lower than those in dolphin and tuna, with kidney having the highest concentrations. TBT was the predominant form of butyltin derivatives in all the tissues of shark (Kannan et al., 1995).

On the other hand, Focardi et al., 2000 determined concentrations of TBT and degradation products, (MBT) and (DBT), in the liver and kidney of striped dolphins (*Stenella coeruleoalba*) and bottlenose dolphins (*Tursiops truncatus*) found stranded along the western Italian (Tyrrhenian Sea) and Greek coasts in the period 1992-1994. Butyltin (BT) compounds were detected in almost all the samples analyzed and were higher in the kidney than in the liver. The highest BT concentrations were found in *S. coeruloealba* ranging 780-8,050 ng/g ww in kidney and 15-1,020 ng/g ww in liver (see Table 10). Bottlenose dolphins had lower BT concentrations than striped dolphins according to values found by Kannan et al. (1995) ranging 1,020 – 2,010 ng/g ww, although levels still remained elevated (liver: 27-43 ng/g ww; kidney 1,024-2,014 ng/g ww). Of the breakdown products, DBT was predominant in most liver samples and MBT was more abundant in kidney. The greater polarity of this BT compound with respect to DBT and TBT could explain the high concentrations in the kidney.

Although BT concentrations are known to be found in cetaceans inhabiting waters of developed countries, these results strongly suggested that concentrations found in *S. coeruleoalba* were either similar to or higher than those reported for other *Stenella* species collected from coastal areas close to harbours or marinas. Concentrations of BT compounds measured in the kidney of bottlenose dolphins collected on the Tyrrhenian coast of Italy were at least one order of magnitude higher than those found in bottlenose and Atlantic spotted dolphins. Mean BT concentrations in *S. coeruleoalba* fell within the same range as those reported for *S. frontalis* collected on the Atlantic and Gulf coasts of the USA. However, they were three to five times higher than those found in *S. longirostris* from the Bay of Bengal and the Sulu Sea, two coastal areas where organotins are used on a large scale. Current results show thus considerable

contamination of dolphins, particularly *Stenella*, by this type of organic pollutant (Focardi et al., 2000).

3.3 Polycyclic Aromatic Hydrocarbons

Investigations on PAH levels in the Mediterranean marine environment have been focused on sediments, especially in the North Western Mediterranean and the Adriatic Sea. In these areas, some temporal trends are also available, as a result of the French and Italian monitoring networks. In general, PAH pollution in the Mediterranean is widespread detected in coastal areas, clearly influenced by urban and industrial emissions to air and water. Atmospheric inputs are the main source of pollution in the open sea.

In <u>sediments</u>, research has been focused on ports, coastal lagoons, river mouths and coastal enclosures closed to urban centres. Accordingly, only few data is available in the open sea for deep sediments. A review of some investigations is shown in Table 11. Although the total number of measured individual PAHs is not always the same, in general higher levels are usually detected in harbours, especially in Alexandria, Trieste and Toulon. High levels of PAHs have also been measured in the Gulf of Taranto or the Izmit Bay, where a significant industrial and oil refining activity is located.

Location	∑PAH (ng/g dw)	PAHs	Reference
Western Harbour, Alexandria, Egypt	8 - 131150	20	Mostafa et al. (2003)
Trieste harbour, Italy	2340 - 64570	16	Adami et al. (2000)
Taranto Gulf, Italy	130 - 68508	16	Cardellicchio et al. (2006)
Lazaret Bay, Toulon Harbour, France	86.5 - 48090	14	Benlahcen et al. (1997)
Izmit Bay, Turkey	2500 - 25000	17	Tolun et al. (2001)
Marsala lagoon, Italy	65 - 17701	16	Culotta et al. (2006)
Rovijn coastal area, Croatia	32 - 13681	16	Bihari et al. (2006)
Gemlik Bay, Marmara Sea, Turkey	50.8 - 13482	14	Unlu i Alpar (2006)
Elefsis Bay, Greece	481 - 11182	24	Sklivagou et al. (2001)
Sfax-Kernennah coastal area, Tunisia	113 - 10720	17	Zaghdem et al. (2007)
Barcelona harbour, Spain	580 - 10320	16	Martinez-Lladó et al. (2007)
Rhone Delta, France	872 - 5007	11	Bouloubassi i Saliot (1993)
River mouths, Catalan coast, Spain	74 - 3650	16	Eljarrat et al. (2001a)
Abu-Qir Bay, Egypt	69 - 1464	11	El Deeb et al. (2007)
Gulf of Rijeka, Croatia	213 - 695	11	Bihari et al. (2007)
Gulf of Trieste, Italy	25 - 604	15	Notar et al. (2001)
Bizerte lagoon, Tunisia	83 - 444	16	Trabelsi i Driss (2005)

Table 11 Levels of PAHs in sediments in some Mediterranean coastal areas.

Measured levels in <u>biota</u> around the Mediterranean have also been reviewed in the scientific literature and are presented in Table 12, along with results from RNO and SIDIMAR campaigns. Maximum levels of PAHs in biota are usually lower than those reported in sediments (see above). As it can be observed, the highest levels (up to

46700 ng/g dw) have been detected for mussels and fish in the Egyptian coasts (El-Sikaily et al., 2002; El Deeb et al., 2007). Levels of up to 3000-4000 ng/g dw have been detected in French and Italian coasts, while in other regions they are generally below 1000 ng/g dw.

In general, levels are higher in mussels than in fishes, as mussels are filtering organisms that accumulate PAHs and present much lower elimination rates than those observed in vertebrates. However, significant accumulation of PAHs has been observed in cetaceans of cetaceans by Marsili et al. (2001). In this study, subcutaneous blubber samples of fin whales were collected in 1993 and 1996 in the Ligurian Sea, whereas 25 striped dolphins were sampled in 1993 in both the Ionian and the Ligurian Seas. In whales, the median value of total PAH14 was 1970 ng/g ww., while in dolphins the accumulation was higher, with a median value of 29500 ng/g ww. Comparing these levels to other regions, the authors indicate that PAHs are toxicologically stressful for cetaceans in the studied area.

Region	Matrix	Conc. (ng/g dw)	PAHs	n	Survey year(s)	References
Egyptian coasts	Mussels	1218 - 46741	16	20	2000	El-Sikaily et al. (2002)
Abu Qir Bay, Egypt	Mussels	mean: 5564 ^ª	14	NA	2004	El Deeb et al. (2007)
	Fish	7084 – 8787 ^a	14	NA	2004	
French Med coasts	Mussels	8.7 - 3919	16	224	1994- 2006	RNO
Italian coasts	Mussels	0.3 - 3313	16	447	2001- 2006	SIDIMAR
Mar Piccolo, Italy	Mussels	75 – 3225 ^a	8	10	1995	Storelli & Marcotrigiano (2001)
Thermaikos Gulf, Greece	Mussels	165 - 750 ^a	15	NA	1992	Kilikidis et al. (1994)
Sicilian coasts, Italy	Limpets	21.5 – 688 ^a	15	20	2003	Gianguzza & Orecchio (2006)
Gulf of Rijeka, Croatia	Mussels	251 – 671 ^a	11	6	2004	Bihari et al. (2007)
Venice lagoon, Italy	Mussels	56.5 - 527	16	8	2005	Nesto et al. (2007)
NW Mediterranean	Mussels	25 - 340	14	12	1996	Baumard et al. (1998)
Izmit Bay, Turkey	Mussels	7.6 – 256 ^a	16	8	1999	Telli-Karakoç et al. (2002)
Adriatic Sea	Mussels	110 - 245 ^a	8	40	2004	Nesto et al. (2007)
	Fish	3.1 – 61	16	8	2005	
Gulf of Naples, Italy	Fish	28 - 85 ^a	11	NA	2004	Perugini et al. (2007)

Table 12 Levels of PAHs in biota in some Mediterranean coastal areas.

^a Converted from ww to dw (x5) ; NA: Not Available

Some temporal <u>trends</u> can also be observed using data from RNO and SIDIMAR. According to the RNO set of data, in French Mediterranean coasts the overall median concentrations of PAH16 in mussels have decreased from 157 ng/g dw in 1994 to 73 ng/g dw in 2006 (see Figure 8). Measured levels after the year 2000 are in general lower than those detected in the 90s. In Italian coasts the range of measured levels is very wide, and no clear trend is observed from SIDIMAR data.



Figure 8 Levels of ∑PAH16 in mussels in French (RNO) and Italian coasts (SIDIMAR).

3.4 Organohalogen compounds

3.4.1 PCBs

Polychlorobyphenyls (PCBs) are ubiquitous global pollutants which can be often found in different environmental compartments, although their use and production in Europe has presently been severely restricted since 1987. They have been used in numerous industrial applications, such as dielectric fluids, insulators, additives and preservatives (Castells et al., 2008; Borrell and Aguilar, 2007).

Many data is available in the Mediterranean Sea region, and extensive reviews have been published by Tolosa et al. (1995) and recently by Gómez-Gutiérrez et al. (2007). This latter review considered concentrations in <u>sediments</u> from Mediterranean remote areas as a reliable approximation to background values, and adopted the 1 to 5 ng/g dw (Aroclor eq.) interval as a reference for non polluted PCB sediments in the Mediterranean Sea (see Table 13).

Highest concentrations in the Mediterranean Sea were reported closed to urban and industrial areas (e.g. from Marseille, Barcelona, Naples) as well as in river discharges (e.g. from the Rhône, Ebro and Nile). Castells et al. (2008) found average levels for 12 PCB congeners in sediments from the Barcelona coastal area varying between 2.33 and 23.51 ng/g dw, with the most elevated concentration reaching 44.00 ng/g dw, although other studies have reported much higher PCB concentrations up to 2,224 ng/g dw in the same area (Gómez-Gutiérrez et al., 2007). The Marseille's coastal sediments have also registered very high PCB levels, varying between 14 and 15,815 ng/g dw. In the South Western Basin, PCBs have been found up to 323 ppb in sediments from Oran, Algeria, while in the Eastern Basin, values from the Alexandria coastal area ranged from 0.1 up to 96 ng/g dw.

 Table 13 PCBs contents in sediments - Mediterranean Sea area.

		PCBs	
Area	Sub-basin	concentration	Reference
		(ng/g Aroclor eq.)	
Urban areas			
Marseille	NWE	14 - 15815	In: Gómez-Gutiérrez et al. 2007
Barcelona	NWE	6 - 2224	In: Gómez-Gutiérrez et al. 2007
Barcelona	NWE	2.33 - 23.51	Castells et al. 2008
Oran	SWE	323	In: Gómez-Gutiérrez et al. 2007
Alexandria	SLE	0.1 - 96	In: Gómez-Gutiérrez et al. 2007
Naples	TYR	2 - 3200	In: Gómez-Gutiérrez et al. 2007
Thessalonica	AEG	1 - 299	In: Gómez-Gutiérrez et al. 2007
Piraeus	AEG	1 - 775	In: Gómez-Gutiérrez et al. 2007
River mouth			
areas			
Rhone	NWE	1 - 472	In: Gómez-Gutiérrez et al. 2007
Ebro	NWE	6 - 200	In: Gómez-Gutiérrez et al. 2007
Po	NWE	13 - 129	In: Gómez-Gutiérrez et al. 2007
Nile	SLE	53 - 1500	In: Gómez-Gutiérrez et al. 2007
Lake Burullus	SLE	4.6 - 213.9	Said et al. 2008
Background values		1 - 5	In: Gómez-Gutiérrez et al. 2007
Worldwide levels		0.2 - 400	Zang et al., 2007

Bays and Gulfs have also been largely studied. PCBs in the Naples and Pozzuolo Bays (Tyrrhenian Sea) have registered elevated concentrations up to 3,200 ng/g dw. In the Aegean Sea high values are also found, as the Thessalonika and Thermaikos Gulf reported up to 299 ng/g dw and the Piraeus and Saronikos Gulf reached 775 ng/g dw.

Finally, important PCB levels are also found in areas of river discharge. In the Northern Basin, the Rhone and Ebro Prodeltas recorded 1 to 472 ng/g dw of PCBs and 6 to 200 ng/g dw respectively, while the Po River registered lower concentrations from 13 to 129 ng/g dw. Higher levels have been reported from the Nile River, in the South Eastern Basin, varying between 53 and 1500 ng/g dw (Gómez- Gutiérrez et al., 2007).

When comparing registered levels in the Mediterranean coastal areas to the estimated background values, it appears that very high values are found in the nearshore areas, and most of them are considered as hotspots for PCBs. The Mediterranean Sea region is hence considered as one of the major PCB polluted zones worldwide (Borrell and Aguilar, 2007).

However, decreasing concentration gradients have also been found in transects offshore from these sources, clearly observed in studies concerning PCB concentrations in the suspended particulate matter from coastal and open Western Mediterranean waters. In a recent study covering the whole Western basin, a spatial gradient was observed from the continental shelf (3.5 - 26.6 pg/kg) towards the open

sea (1.7-6.6 pg/kg) and a relatively important enrichment (8.4 pg/kg) in open sea stations located in higher productivity frontal zones (UNEP/GEF, 2002).

Due to their chemical stability and their lipophilic character, PCBs persist in the environment and accumulate in <u>organisms</u>, especially in top predators of the food chain. However, according to some studies on temporal PCB trends in different matrices (mussels, sediment, vertebrates) from the north-western Mediterranean, levels might be tending to decline (Borrell and Aguilar, 2007) (see also a review of data in Table 14).

In this sense, an attenuated decreasing trend was observed by the French <u>bivalve</u> monitoring IFREMER/RNO network for coastal pollution during the period 1979–1998 (Borrell and Aguilar, 2007). The French study showed that the decline in chlorinated pesticide concentrations followed the order: DDT > HCHs >> PCB. The PCB decrease was hence not as marked as for the other organochlorines. Likewise, Villeneuve et al. (1999) showed a decrease in PCB concentrations in the blue mussel (*Mytilus galloprovincialis*) from the period 1973-1974 to the 1988-1989. Range values dropped from 18-668 ng/g ww to 4-126 ng/g ww during the fifteen year-period. In the Balearic coasts, similar low range values of 1.6-6.6 ng/g ww were also found in mussels analysed between 1996 and 2000 (Deudero et al., 2007).

Similarly, PCB levels in *Merluccius merluccius* from the Adriatic Sea have been shown to slightly decrease between 1993 and 2003 from 1,380 ng/g to 943 ng/g lipid weight (Storelli et al., 2004), although the remaining levels are still high and the declining trend was not statistically significant. Such values are in accordance to the PCB concentrations in other fish species from the same marine region. Between the years 2000 and 2002, PCB in *Scyliorhinus canicula* from the South Adriatic reached high levels ranging from 500 up to 2,351 ng/g lipid weight (Storelli et al., 2006). In the same line, specimens of *Dicentrarchus labrax* from the Strait of Messina sampled in 2004 reported elevated PCB levels ranging from 63,200 to 109,400 ng/g lipid weight (Lo Turco et al., 2007).

		Concentr	ation of PCBs	Sampli		
Species	Location	cation (ng/g ww) (ng/g lipid w)		ng Year	Reference	
Mussels						
M.galloprovin cialis	North Western Med.	18-668	-	1973- '4	Villeneuve e 999	t al.
M. Ialloprovincialis	North Western Med.	4-126	-	1988- ¦9	Villeneuve e 999	t al.
M.galloprovin ialis	Tyrrhenian Sea	-	787 - 2,679	2003	Naso et al. 20	05
M. Ialloprovincialis	Balearic Med. Sea	2.9 (1.6- 6.6)	-	1996- 2000	Deudero et	al.
Fishes						
M. merluccius	Adriatic Sea	-	943 - 1380	1993- 2003	Storelli et al. 2	004
D. labrax	Strait of Messina	-	63,200 - 109,400	2004	Lo Turco e 2007	t al.
S. canicula	South Adriatic	-	500 - 2351	2000- 2002	Storelli et al., 2	2006
T. thynnus	Ionian Sea	5.3-35.0	526	2005	Storelli et al., 2	2008
T. thynnus	Mediterranea	196	_		Porte	and

Table 14 Comparison of PCBs concentrations (ng/g ww and ng/g lipid wt) in Mediterranean marine biota.

	n Sea			lbaiges, 1993*
T. thynnus	Tyrrhenian Sea	87	_	Corsolini et al., 996*
T. thynnus	Mediterranea n Sea	262.46	_	Stefanelli et al., :002*
T. thynnus	Ionian Sea	224– 660	_	Kannan et al., :002*
T. thynnus	Strait of Messina	1.00– 2.20	49 - 3,792	Di Bella et al., :006*
T. thynnus	Pacific Ocean	_	700 - 1,500	Ueno et al., 2002*
T. thynnus	Pacific Ocean	-	12.80	Hashimoto et al., :003*
Cetaceans				
T. truncatus	North Western Med.	-	116,000 - 1978- 708,000 <u></u> 2002	Borrell and Aguilar, 007

*Literature data cited in Storelli et al. (2008).

Concerning levels in <u>top predators</u>, information regarding organochlorine compounds in tunas is, in general, scarce and particularly limited in Mediterranean Sea. Storelli et al. (2008) carried out a comparison between PCB levels in juvenile bluefin tunas in the Ionian Sea. Even though their result values were rather low (average 15.92 ng/g ww), recent studies in the Mediterranean region show that adult tuna specimens may reach range values of 224 to 1,660 ng/g ww in the same region and up to 262 ng/g ww in specimens from the whole Mediterranean. Thus, the comparison with literature data (see Table 14) showed that concentrations found by Storelli et al. (2008) were markedly lower than those detected in specimens from the Tyrrhenian Sea, Ionian Sea and western Mediterranean Sea, which was attributed to biological parameters such as sex, age and size. Different studies performed in the Mediterranean are higher than those caught in other marine areas (e.g. Pacific Ocean), which lay in the low range of the Mediterranean Sea concentrations (Storelli et al., 2008).

On the other hand, concentrations of PCB in bottlenose dolphin blubber (*Tursiops truncatus*) from the North Western Mediterranean have also found to be very high, although they point to a decrease in levels. However, and as in other matrices, PCB decline in bottlenose dolphin between 1978 and 2002 has been found to be much less pronounced than that of other organochlorine pesticides (i.e. DDT). While DDT decreased by a factor of 23.7 during the 25-year period, PCB only decreased by a factor of 6.1, dropping from 708,000 ng/g lipid weight in 1978 to 116,000 ng/g lipid weight in 2002. Similar results from other studies suggest that there is a steady source of these chemicals in the Mediterranean ecosystem (Borrell and Aguilar, 2007).

3.4.2 Dioxins and Furans

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are a group of 210 chemical compounds that are highly persistent in the environment. Seventeen of their congeners (those with a 2,3,7,8 substitution) are among the most toxic anthropogenic contaminants formed as a by-product in combustion processes, and have been classified as Persistent Organic Pollutants (POPs) and regulated by the Stockholm Convention since 2001 (Munschy et al. 2008).

PCDDs and PCDFs enter the environment from a number of potential sources. In the marine environment PCDD/Fs are ubiquitous, since this compartment may represent

their ultimate receptor (Munschy et al. 2008). These hydrophobic chemicals are highly persistent in the environment and have a strong affinity with sediments and an elevated potential for accumulating in biological tissues (Eljarrat et al. 2001a). Hence, they tend to bioaccumulate further up the food chain and PCDD/F levels in fish are often 100,000 times greater than those found in the surrounding environment. Their toxic effects have even been described at extremely low concentrations (Rotllant et al., 2006).

Different restrictions for PCDD/Fs contents in the environment have been set up in recent years. The European Community established a limit of 20pg WHO-TEQ/g of PCDD/Fs for sediments (Eljarrat et al., 2001a, 2005) while 4 pg WHO-TEQ/g of PCDD/Fs is the concentration threshold for fish and fish products on a wet weight basis (Rotllant et al., 2006).

Little research has been carried out in the Mediterranean Sea concerning PCDD/Fs, although studies focusing on these compounds are gradually increasing. Some data is yet available regarding <u>PCDD/Fs</u> in <u>sediments</u> for Italy and Spain, especially concerning coastal lagoons, and also regarding biota. In general, the North-western basin appears to be the most PCDD/Fs contaminated part of the Mediterranean Sea.

Recent studies have focused on levels in sediments from the Catalan coast. Concentrations in the range of 0.06 to 8.14 ng/g dw (0.40-39.24 pg/g dw WHO-TEQ) have been measured in 45 bottom marine sediments collected from 10 rivers of Catalonia flowing into the Mediterranean Sea in 2000 (Eljarrat et al. 2001a). The total WHO-TEQ (TEQ-PCDD/F + TEQ-PCB) values ranged between 0.43 and 42.8 pg/g dw. Therefore, the safe sediment value of 20 pg TEQ/g dw was exceeded for some of the samples analysed, corresponding to the Besós, Francolí, and Llobregat areas.

A similar study was performed by the same authors concerning coastal sediments from different Spanish pollution hotspots, such as the Tarragona and Almeria harbours or the mouths of the Besós and Llobregat Rivers near Barcelona (Eljarrat et al., 2005). Sediments were collected in 2002 and treated in order to quantify PCDD/Fs contents. When comparing both studies (Eljarrat et al. 2001 and Eljarrat et al. 2005), result values appear to be similar and even slightly higher in 2002, as it can be observed in Figure 9; white columns correspond to levels detected in 2000 and grey columns to concentrations in 2002.

In 2002, levels ranged from 0.1 to 48 pg TEQ/g dw for PCDDs and PCDFs, the total (TEQ-PCDD/F+TEQPCB) ranging between 0.3 and 75 pg TEQ/g dw. The suggested sediment quality guideline was again exceeded for some samples in 2002. From the 15 sediments analysed, four samples of the Besós and Tarragona areas exceeded the safe value set at 20 pg TEQ/g dw (Eljarrat et al., 2005).

Figure 9 Time trend of PCDD, PCDF and PCB contamination in the Barcelona area. Source: (Eljarrat et al., 2001a; Eljarrat et al., 2005)



Hence, high contamination was again detected in samples collected at the Besós area (samples symbolized as B3, B4 in Figure 9) as well as in sediments near Tarragona.

The high contamination found in samples from Tarragona could be attributed to the high industrial impact of this area. In the case of samples collected in the mouth of the Besós River, the high levels could be attributed to the sewage sludge discharges into the sea. However, as regards the Llobregat area (samples B1, B2), a significant decrease of contamination was also observed between samples collected during 2000 and 2002 (see Figure 9) (Eljarrat et al., 2005).

Munschy et al. (2008) performed a study concerning <u>PCDD/Fs levels</u> in <u>mussels</u> (*Mytilus galloprovincialis* and *M. edulis*) in the French coastal areas between 1981 and 2005. The results provide evidence of a general decrease in PCDD/F concentrations in the French coastal marine environment over the 24-year period at almost all study sites, with elevated levels remaining in Toulon. This overall decrease probably reflects the general drop in PCDD/F emissions in Europe since 1980.

Recent PCDD/F concentrations ranged between 3.77 and 184 pg/g dw (data from 2004 and 2005). PCDF concentrations were higher than PCDD concentrations in the majority of samples (see Table 15) with the exception of the PCDD higher levels recorded at the Rhône delta sites in 2004 (Munschy et al., 2008).

As said, the highest PCDD/F levels were recorded in mussels from the Toulon site in 2004 (see Table 15), reaching up to 184.01 pg/g dw (2.76 pg TEQ/g ww). This fact coincides with data on regional atmospheric emissions, since most airborne contamination in temperate climatic zones is deposited adjacent to its sources (Munschy et al., 2008).

On the contrary, the lowest contamination level (3.77 pg/g dw) was determined in mussels from Corsica (0.052- 0.089 pg WHO-TEQ/g ww). This concentration could be considered as a contemporary background reference level for French coasts and is in the range of the reference level proposed by for mussels from the North Sea (0.1– 0.2 pg TEQ/g ww). Relatively low results have also been found in the Thau Lagoon, with 18.96 pg/g dw (WHO-TEQ levels ranging from 0.28-0.29 pg TEQ/g ww).

The contamination levels determined in this study were within the broad range reported in Europe (from 0.02 to 5.59 pg WHO-TEQ/g ww). However, levels are apparently lower in North America and Oceania (0.02–1.0 pg TEQ/g ww) and do not appear to reach the high values found in Europe. Moreover, levels reported for Asian mussels (0.01–1.58 pg TEQ/g ww) were unexpectedly low in relation to the high environmental contamination by PCDD/Fs estimated in Asian countries due to high industrialization, although an increase in the contamination of coastal areas by PCDD/Fs has been reported in some Asian countries in response to rapid urban and industrial development.

	Thau lagoon		Rhône delta		Marseille		Toulon		Sant'Amanza (Corsica)	
2004	pg/g dw	pg/g ww WHO- TEQ	pg/g dw	pg/g ww WHO- TEQ	pg/g dw	pg/g ww WHO- TEQ	pg/g dw	pg/g ww WHO- TEQ	pg/g dw	pg/g ww WHO- TEQ
PCDF s	10.09	0.23	10.75	0.19	20.29	0.47	124.8 7	2.56	1.9	0.05
PCDD s	8.87	0.05	36.55	0.12	11.31	0.1	59.14	0.2	1.86	0.002
PCDD/ Fs	18.96	0.28- 0.29	47.3	0.30- 0.31	31.6	0.57- 0.57	184.0 1	2.76- 2.76	3.77	0.052- 0.089

Table 15 PCDD/Fs levels in mussels (*Mytilus edulis* and *Mytilus galloprovincialis*) along French coastlines. Source: Munschy et al. (2008).

2005										
PCDF	19.18	0.4	_	-	_	-	67.22	1.57	-	-
S										
PCDD	6.67	0.05	_	_	_	_	19.77	0.16	_	-
s										
PCDD/	25.85	0.45-	_	-	_	-	86.99	1.73-	_	_
Fs		0.46						1.74		

Rotllant el al. (2006) performed a study on PCDD/Fs contents in rose shrimp (*Aristeus antennatus*), a deep-sea species living at depths between 600 and 2500m. Specimens from the Western basin (Catalan and Balearic coasts) and from the Eastern basin (Western and Eastern Ionian) were collected and analysed in 2001. The rose shrimp was chosen as a biological indicator to assess contamination in deep environments from the Mediterranean Sea on account on its broad longitudinal and bathymetric distribution throughout the whole Mediterranean basin.

The Sicily Straits was found to act as a barrier between the two major depressions of the Mediterranean. In Figure 10, several congeners are represented; as it can be observed, total PCDD/Fs and all individual PCDD/F congener concentrations were clearly higher in shrimps caught in the western Mediterranean (grey columns) than in those caught in the eastern Mediterranean (striped columns) both at depths of 600–650 m (153 vs. 61 pg/g lipid weight) and 1000 m (242 vs. 206 pg/g lipid weight). On the contrary, total PCDD/F values were similar in shrimps caught throughout the Ionian Sea at 800 m, ranging between 114 and 128 pg/g lipid weight. Regarding western samples, the data belonging to shrimps caught off Barcelona, a high industrialized area, presented higher values than those measured in samples from the Balearic Sea (less industrialized region compared with Barcelona), and specifically for the high chlorinated PCDDs.

Figure 10 Comparison between PCDD/Fs congeners between the Balearic (grey) and the Ionian (striped) coasts at 600m (upper figure) and 1000m (lower figure). Source: Rotllant et al. (2006).



Furthermore, a tendency of PCDD/F levels to increase with depth was also observed. PCDD/F levels in shrimps increased from 153 to 416 pg/g lipid weight in the Balearic

Sea (western Mediterranean) and from 61 up to 206 pg/g lipid weight in the western lonian Sea (eastern Mediterranean). Thus, these results allowed reporting the presence of PCDD/Fs in deep-sea organisms and showed that deep-sea environments are not as undisturbed as might be supposed (Rotllant et al., 2006).

Concerning <u>fish species</u>, Bayarri et al. (2001) carried out a study regarding PCDD/Fs content in anchovy (Fam. *Engraulidae*), mackerel (Fam. *Scombridae*) and red mullet (*M. Barbatus*) from the Adriatic Sea. In general, PCDD and PCDFs contamination levels were found to be low (see Table 16), ranging from 0.33 to 0.50 pg/g ww PCDD and 0.71-1.53 pg/g PCDFs for anchovy, 0.32-0.53 pg/g ww PCDD and 2.49-3.38 pg/g ww PCDFs for mackerel and finally 0.29-0.60 pg/g ww PCDD and 0.99-1.49 pg/g ww PCDFs. As it can be observed, PCDFs analytical contributions were higher than those of PCDD.

I-TEQ results were greater for those species at higher levels in the trophic web (mackerel > red mullet > anchovy), although the higher fat content of these species should also be taken in account for part of the greater fresh weight-based PCDD/Fs measured. Contamination levels fell within 0.23 and 1.07 pg TEQ/g ww in the aforesaid species. Moreover, PCDD/Fs in species from the northern area were in general greater than those from the central and southern areas. Thus, these species showed a trend towards higher contamination levels associated with areas showing increased anthropogenic impact (Bayarri et al., 2001).

Levels of PCDD/Fs residues found in the analyzed fish specimens were of the same order as those observed in most developed countries. These results were hence comparable with PCDD/Fs concentrations observed in fat sea fish from the Netherlands (between 6.65 and 11 pg TEQ/g fat). In Japan, coastal and marketing fatty sea fish has been reported to be contaminated with 0.33 and 0.87 pg TEQ/g ww, and levels of 0.6 pg TEQ/g ww have also been determined in mackerel from United Kingdom. However, higher dioxin levels have been found in sea fish from Germany (34–43 pg TEQ/g fat) or Sweden (1.8–9.0 pg TEQ/g ww) (Bayarri et al., 2001).

Species	Location	Sampling year	PCDD	PCDFs	WHO-TEQs PCDDs, PCDFs
			pg/g ww	pg/g ww	pg/g ww
Anchovy	Northern,		0.33-0.50	0.71-1.53	0.23-0.47
Mackerel	Central,	2 campaigns	0.32-0.53	2.49-3.38	0.59-1.07
Red mullet	Southern areas of Adriatic Sea	1998	0.29-0.60	0.99-1.49	0.37-0.56

Table 16 PCDD/Fs content in different fish species from the Adriatic Sea. Source: Bayarri et al. (2001)

Concerning top predators in the Mediterranean environment, in particular cetacean species tend to accumulate high concentrations of organochlorines (OCs) and toxic metals, incurring high toxicological risk (Fossi et al., 2004). Since marine mammals feed at the top of the marine food webs and have elevated lipid contents, they are the most exposed to bioaccumulate high levels of organochlorines. Cetaceans are hence useful for monitoring the trophic transfer of chemical contaminants (Jimenez et al., 1999).

Jimenez et al. (1999) studied liver samples from five cetacean species found along the Italian shore of the Tyrrhenian, Adriatic, and Ligurian Seas within the period 1987-1992. Striped dolphin (*Stenella coeruleoalba*), bottlenose dolphin (*Tursiops truncatus*), Risso's dolphin (*Grampus griseus*), pilot whale (*Balaenoptera physalus*), and long-finned pilot whale (*Globicephala melaena*) were the target species (see Table 17).

Total PCDD and PCDF levels ranged from 13 up to 112 pg/g ww. The highest levels were found both in striped dolphins with a maximum value of 112 pg/g ww and in Risso's dolphins with a maximum value of 91 pg/g ww. In contrast, the lowest levels were recorded in bottlenose dolphins. Regarding the contribution of PCDDs and PCDFs to total levels, in general a higher percentage contribution was found from PCDFs, which in some cases contributed up to 77%. Generally, the most abundant congener was OCDD, accounting for between 23 and 54% of the total PCDD and PCDF concentrations. The contribution of congener OCDF, (range of 6-44%) was also noteworthy.

Total calculated TEQs ranged from 1 to 6 pg/g ww. The species exhibiting the highest TEQs was the striped dolphin with a maximum level of 7 pg/g, followed by the Risso's dolphin with a maximum level of 6 pg/g. Total TEQ levels were lower in the rest of the species studied; the lowest value observed was found in bottlenose dolphins with a concentration of 1.14 pg/g. It must also be pointed out that the major contributors to WHO-TEQs values in all studied species were coplanar congeners of PCBs rather than PCDD/Fs compounds (see Table 17).

Sampling areas (Ligurian, Ionian, and Adriatic) were also compared, and individuals from the Adriatic Sea appeared to have the lowest PCDD and PCDF levels; PCDD/Fs concentrations were higher in individuals from the Ligurian Sea. The direct correlation stated between human exploitation of the coast and rivers and water pollution may explain high contents in specimens from the Ligurian area. In Italy, the Ligurian Sea is one of the most polluted seas since there is a considerable amount of industrial activity as well as intensive farming and horticulture. Moreover, the area is heavily contaminated with organochlorines from the nearby Rhone Estuary (Jimenez et al., 1999). The widespread occurrence of OCDD, OCDF, and TCDF found in these cetaceans suggests combustion processes as the local PCDD/Fs sources to these marine mammals. Moreover, High levels of OCDD and OCDF have already been reported in crabs and sediments from different areas in the Mediterranean Sea, and their prevalence has been attributed to combustion sources (Jimenez et al., 1999).

Species	Location	Sampling year	PCDD/F	WHO- TEQs PCDD/Fs	WHO-TEQs PCDDs, PCDFs, co-planar PCBs	Reference
			pg/g ww	pg/g ww	pg/g ww	
S. coeruleoalb a	South Tyrrhenia n- Aeolian Sea	2002	73.91	-	18	Fossi et al. (2004)
S. coeruleoalb a	Ligurian Sea Tyrrhenia	1987-1992	39.86 - 112.44	1.54 - 6.74	26.78 - 733.34	Jiménez et al. (2000)
T. truncatus	n Sea Adriatic		13.03 - 15.72	1.14 - 2.28	5.40 - 267.64	Jiménez et al. (2000)
G. griseus	Sea		19.46 - 91.33	1. <mark>84 -</mark> 6.36	26.09 - 43.27	Jiménez et al. (2000)
B. physalus			23.86	2.92	1457.64	Jiménez et al. (2000)

Table 17 PCDD/Fs levels and WHO-TEQs in cetaceans.

G. malaena			22.74	2.27	9.73	Jiménez et al. (2000)
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Fossi et al. (2004) investigated the presence of PCDD/Fs in blubber of nine striped dolphin *Stenella coeruleoalba* sampled in the Mediterranean Sea (southern Tyrrhenian Sea – Aeolian area) in 2002. Total PCDD/Fs levels reached 73.91 pg/g ww, in accordance with the concentration range of 13-112 pg/g ww found previously by Jimenez et al. (1999) (see Table 17). The equivalent WHO-TEQs values were 18 pg/g ww, much lower than those obtained in the previous study when co-planar PCB congeners were also taken into account. Regarding the contribution of PCDDs and PCDFs to total PCDD/F levels, it was found the same percentage contribution from both PCDDs and PCDFs. The lowest contribution to total TEQs came from PCDFs, while the contribution of PCDDs and co-planar PCBs was almost the same.

These results were also compared to populations from the Ligurian and Ionian Seas. In this case, the striped dolphins from the Aeolian area appeared to be less exposed to PCDD/Fs and other organochlorine compounds than specimens from the other Mediterranean areas (Fossi et al., 2004), what was also in accordance to previous studies (Jimenez et al., 1999).

3.4.3 Brominated flame retardants

Brominated flame retardants (BFRs), and in particular polybrominated diphenyl ethers (PBDEs) are high production volume chemicals, popularly used as additive flame retardants by the polymer industry. They are environmental contaminants ubiquitous in the environment and magnify in fish tissue. These compounds have been found to be widely distributed in the European environment, according to a recent review of levels and trends (Law et al., 2006).

Although these compounds are usually are considered as 'emergent pollutants', it has been observed that currently there is a very active research in this area. In the Mediterranean, all the studies identified have been published during the last 5 years (see Table 18).

In <u>sediments</u>, three different coastal areas of the Spanish Mediterranean coasts (n=15) where sampled in 2002 by Eljarrat et al. (2005). A total of 40 PBDEs where included in the analyses, and measured concentrations ranged between 2.7 and 134 ng/g dw, being the BDE-209 the main congener detected. This congener can debrominate in the environment to form less-brominated BDE congeners which are more bioavailable than BDE-209 itself (Law et al., 2006).

The <u>biota</u> has focused the effort of most of the identified studies. Taking into account the limited data available for the Mediterranean marine environment, levels of BFRs in freshwater fishes in rivers and lakes of the region have also been included in the review presented in Table 18. As it can be observed, the maximum concentrations of PBDEs have been detected in cetaceans (in particular dolphins) sampled around the Italian coasts (Pettersson et al., 2004). Freshwater fish and mussels show generally higher levels than swordfish and European eels (see Table 18). The BDE-47 is the most prevalent congener in all the studies.

Table 18 Levels of BFRs in biota (ng/g lipid weight) in the Mediterranean region.

Location	Species	Conc. (ng/g l.w.)	Nr BDEs (Main	of	Survey year(s)	References	
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			congener detected)		
Italian coasts	Cetaceans (4 sp.)	L: 66 - 8133	8 (BDE-47)	1990- 1992	Pettersson et al. (2004)
Llobregat river, Spain	Feral carp	M : 29 - 744	9 (BDE-47)	2000	Labandeira et al. (2007)
Sir Dam Lake, Turkey (<i>freshwater</i>)	Fish (4 sp.)	M: ND - 597 L: ND -163	8 (BDE-47)	2003	Erdogrul et al. (2005)
Lake Maggiore, Italy (freshwater)	Zebra mussel	40 – 447	14 (BDE- 47)	2005	Binelli et al. (2008)
South Tyrrhenian Sea	Swordfish	M: <0.02 - 20.9 L: 7.4 - 69.9	19 (BDE- 47)	2005	Corsolini et al. (2008)
Orbetello lagoon, Italy	European eels	M: 0.9 - 14.14	12 (BDE- 47)	2002	Mariottini et al. (2008)

M: muscle; L: liver;

Comparing to other regions, Bodiguel et al. (2008) found out that concentrations of PBDEs in European hakes (*Merluccius merluccius, L.*) from the Gulf of Lions were up to 13.6 higher than hakes of similar size from the Bay of Biscay (Atlantic). On the other side, Johansson et al. (2006) observed higher levels of PBDEs in mussels sampled in the English Channel (France), than in a Mediterranean coastal lagoon (although the concentrations were lower than those reported in North and South America), as shown in Figure 11.



Figure 11 Concentrations of the major PBDEs determined in mussels collected at the French coasts in 2001/2002. Source: Johansson et al. (2006).

In the above study for French coasts, the temporal <u>trend</u> observed in mussels from the Seine estuary, indicated an exponential increase in BDE concentrations during the period 1982–1993, which levelled off in 1999 and 2001 and then began to decline after 2002 (Johansson et al., 2006).

In fact, the rate and temporal trends at which PBDE and other organohalogen compound concentrations rise and fall in the environment and in humans is still a source of much research interest. Indeed, it is not yet clear how future trends for these compounds could be anticipated, given the different environmental behaviour of the PBDE congeners and current changes in their industrial applications and in their regulatory measures. Data on the temporal trends in biological samples of the PBDEs are still relatively sparse and these studies require good sample sets of archived samples (Johansson et al., 2006). However, it must be noted that inputs of 'emergent' pollutants can be much higher than 'classic' organohalogen. For example, the input of BDEs (especially BDE209) to the Baltic Sea by atmospheric deposition now exceeds that of PCBs by a factor of almost 40 times (ter Schure et al., 2004).

3.4.4 PFOS

Perfluorinated compounds (PFCs), and in particular perfluorooctane sulfonate (PFOS), have also been identified as priority pollutants in the marine environment. PFCs have been manufactured for over half a century, for numerous consumer and industrial applications that entail their use as surfactants and surface protectors. In 2001, perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) were reported to be globally distributed in humans and wildlife (Giesy and Kannan, 2001; Hansen et al., 2001). As a result, the major producer, the 3M Company, announced the phase-out of the production of perfluorooctanesulfonylfluoride (POSF)-based compounds such as PFOS in 2000. However, a variety of related PFCs are still being produced by several manufacturers worldwide (Hart et al., *in press*).

In the Mediterranean, very few data on the occurrence of these compounds in the marine environment has been identified. Kannan et al. (2002) reported concentrations of PFCs in cormorants, marine mammals and fishes from the Italian coasts, from specimens sampled between 1991 and 1998 (see Table 19). Higher levels of PFOS were detected in livers of dolphins (up to 940 ng/g ww.), followed by whales, tuna and swordfish. A recent study in the same area (Corsolini et al., 2008) found that the concentrations of PFOS in swordfish were below detection limits (1.5 ng/g ww.).

Location	Species / tissueª	Conc. (ng/g ww.)	n	Survey year(s)	Referenc	es	
Southern Tyrrhenian Sea	Swordfish / L	< 1.5	17	2005	Corsolini (2008)	et	al.
Italian coasts	Dolphins / L	< 1.4 - 940	12	1991-1998	Kannan	et	al.
	Whales / L,M	L: 279	1	1996-1998	(2002)		
		M: <19 - 52	2		_		
	Swordfish / L	<1 - 13	5	1999			
	Tuna / L	25 - 87	5	1999			

Table 19 Levels of PFOS in biota in the Mediterranean region.

^a M: muscle; L: liver;

In other regions, PFOS in liver samples of gray and ringed seals in the Baltic where observed in the range of 130-1100 ng/g ww (Kannan et al., 2002). These ranges are similar to those detected in the Gulf of Mexico: 6.6 - 1520 ng/g dw in dolphins and whales (Kannan et al, 2001).

Regarding temporal trends, it has been indicated that as a result of the progressive phase-out of production of perfluorooctanesulfonyl-based compounds, concentrations of perfluorooctanesulfonate (PFOS) in marine mammals from North American and European coastal waters have been declining since the early 2000s (Hart et al., *in press*). In Japanese coasts, median concentrations of PFOS in whales have been increasing during the last 25 years, with peak concentrations detected in 2001/2002 (18-117 ng/g dw, in liver) (Hart et al., *in press*).

3.4.5 Chlorinated paraffins

Polychlorinated n-alkanes or Chlorinated paraffins (PCAs) are a group of technical mixtures of polychlorinated alkanes classified as persistent organic pollutants according to their hazardous properties and their widespread and poorly restricted use. These compounds have been produced since the 1930s and are used for a variety of industrial applications such as lubricating additives and cutting fluids as well as flame retardants in plastics and sealants (Castells et al., 2008; Eljarrat and Barceló, 2006).

Since they are produced with free radical chlorination, a single PCA formulation comprises thousands of different compounds with a range of physical and chemical properties. The total number of possible congeners is unknown, but by far exceeds 10.000. PCA mixtures are the most complex of all halogenated mixtures of contaminants, and their complexity makes its analysis extremely difficult. This is certainly one of the reasons why they have so rarely been determined in the environment (Bayen et al., 2006; Eljarrat and Barceló, 2006). Thus, several research programmes such as MED POL, SIDIMAR or RNO do not include PCA within their monitored pollutants (EU, 2005). Moreover, very little is known of the regional levels of these contaminants, especially in regions outside North America, Europe and Japan (Bayen et al., 2006).

According to raising concerns over PCAs and the severe data gaps existing in our knowledge, environmental levels of PCAs, especially short chained chlorinated paraffins (SCCPs), should be monitored more extensively in the near future. There is therefore a growing need to establish quality assured analytical methods for the determination of CPs in environmental sample (Bayen et al. 2006; Eljarrat and Barceló, 2006). Although many procedures for separation and quantification of these contaminants have been described, much effort is nowadays performed in order determine adequate analysing methodologies allowing to assess their spatial and temporal distribution.

CPs environmental levels in marine sediments :

Even though information about their environmental levels is still very limited, CPs have been detected in a wide variety of environmental matrices, such as air, seawater, freshwater, freshwater sediments, aquatic biota, terrestrial biota, marine mammals and human tissues, as well as in both industrial and non-industrial areas (Castells et al., 2008; Parera et al., 2004). Concentrations of CPs are even recorded in remote areas such as the Arctic Lakes. The wide range of CP usage and the improper disposal of products containing CPs are likely to be the source of their ubiquity in the environment (Parera et al., 2004).

Very little research has been carried out in the Mediterranean region concerning these substances. Castells et al. (2008) found total CP concentrations varying from 210 to 2,090 ng/g dw. in marine sediments from the Barcelona (Spain) coastal environments. These results were relatively high, about one order of magnitude higher than concentrations generally found in marine sediments in different parts of the world, such as Canada (0.005–0.257 ng/g dw), and the Baltic Sea and the North Sea (8-63 ng/g dw) (Castells et al., 2008).

In addition, concentrations obtained were similar to the low range values reported from (non marine) soil and sediments collected in industrial or semi-industrial areas from Germany (2.14–189 μ g/g dw), England and Wales (0.2–65.1 μ g/g dw), and the USA (0.76–170 μ g/g dw) (Castells et al., 2008).

Further research in CPs levels in marine environment (sediments, biota) is particularly necessary in order to assess spatial distribution trends of these compounds in the Mediterranean Sea.

3.5 Organohalogenated pesticides/biocides

3.5.1 DDTs

Despite the ban on the production and use of DDTs, elevated levels of contamination are still present in the Mediterranean Sea, which has been considered one of the marine regions with the highest levels of PCB and tDDT worldwide (Borrell and Aguilar, 2007). At present time, inputs have been reported still reaching the Mediterranean coastal environment, mainly by atmospheric deposition of DDT and DDT leaching from agricultural soils, followed by discharges into estuarine areas that would help maintaining DDT presence in the coastal environment (Said et al., 2008).

Gómez-Gutiérrez et al. (2007) carried out a comprehensive review of reported DDT contents in <u>sediments</u> of the Mediterranean region, including main hotspots under the influence of densely occupied areas, and compared them to background values estimated from remote areas of the Mediterranean Sea (see Table 20).

As it can be seen, high concentrations in sediments near urban and mouth river areas were found in different Mediterranean sub-basins. In the Western Basin, the Rhone and Ebro prodelta registered DDTs levels from 1 to 472 ng/g and 6 to 200 ng/g respectively; concurrently, the coastal areas of Marseille and Barcelona recorded concentrations up to 225 ng/g and 195 ng/g. In the Ligurian Sea, sediments from the mouth of the Po River reached 129 ng/g, while in the Tyrrhenian Sea, the bay of Naples and Pozzuolo recorded up to 312 ng/g. Finally, in the South Western Basin, an average of 40 ng/g DDTs was found in Alger (Algeria).

However, the highest DDT values have been found in the Eastern Basin. Sediments in the delta of the Nile River registered very high concentrations (up to 1,500 ng/g) in the early 90s, although rather low values were recently recorded in sediments of Burullu Lake (Nile prodelta) with a maximum concentration of 17.39 ng/g (Said et al., 2008). In contrast, very high DDT levels were again found in the coastal sediments of Alexandria reaching 826 ng/g, which resulted from diffuse agricultural runoff and agricultural untreated wastes. In the Aegean Sea, the Piraeus Bay registered similar elevated concentrations up 1,406 ng/g for DDTs in the mid 70s, although recent studies have also pointed out high concentrations in this area.

Area	Sub-	DDTs (ng/g dw)
	basin	
Urban areas		
Marseille	NWE	2 - 225
Barcelona	NWE	1 - 195
Alger	SWE	40
Alexandria	SLE	29 - 826
Naples	TYR	1 - 312
Thessalonica	AEG	0.3 – 33
Piraeus	AEG	0.3 - 1406
River mouth areas		

Table 20 Review DDT levels in sediments in the Mediterranean Sea. Source: Gómez-Gutiérrez et al. (2007).

Rhone	NWE	1 - 472
Ebro	NWE	6 - 200
Po	NWE	13 - 129
Nile	SLE	53 - 1500
Background values		0.08 - 5

It must also be pointed out that despite the high and widespread occurrence of DDT in the Mediterranean Sea, a general decline in marine sediments and several segments of the marine biota along the north-western Mediterranean coasts has been generally observed between the 1960s and 2000s (Borrell and Aguilar, 2007). A decreasing temporal trend in sediment concentrations is also quite evident from the review carried out by Gomez-Gutierrez et al. (2007).

Many data is available concerning DDT concentrations in <u>biota</u>; however, it primarily concerns the western Mediterranean Sea. High levels are still found in mussels, fish and top predators, but a decreasing trend is also generally observed. This negative trend is consistent with the chemicals history of use. DDT was particularly used after the 1950s and its production increased exponentially until the 1970s. Manufacture ceased in the western world in the 70s, due to environmental concerns which led to restrictive legislation. Such regulations included most countries bordering the Mediterranean Sea. However, DDT and their derivatives are still being used as precursors of dicofol in some manufacturing plants (Spain) and, besides, the existing stockpiles of obsolete pesticides are poorly controlled or unregulated (Borrell and Aguilar, 2007).

The blue mussel *Mytilus galloprovincialis* has been frequently used as a bioindicator for pollution in the Mediterranean Sea. It was used between 1973 and 1974 in a contaminant survey carried out in the North Western Mediterranean basin; at that time, data reported on synthetic chlorinated hydrocarbons had showed very high concentrations of total DDT compounds in soft tissues of mussels, up to a maximum of 1,212.6 ng/g ww. Interestingly, DDT concentrations in the samples were generally higher than DDE and DDD metabolites (low p,p'-DDE/DDTs ratio), which was due to direct exposure to the pesticide (Villeneuve et al., 1999). While in 1973-1974 range values of total DDT were 18 – 668 ng/g ww with an average of 146 ng/g ww, in 1988–1989 the concentrations of DDTs had dropped to an average value of 26 ng/g ww and ranged between 4 and 126 ng/g ww (see Figure 12). These data indicate a decline of DDT concentrations in the coastal environment of NW Mediterranean since the early 1970s, which is in agreement with the ban on DDT. The decreasing average factor is 5.6 between 1973-1974 and 1988-1989 (Villeneuve et al., 1999).

Figure 12 Comparison of DDTs and PCBs in mussels in the NW Mediterranean from two surveys carried out with 15-year intervals (ng/g dw). Source: Villeneuve et al., 1999.



Contemporary studies show some differences concerning DDT range contents in mussels among sub-regions (see a review in Table 21). In the Balearic coasts, levels ranged between 1.6 to 6.6 ng/g ww (Deudero et al., 2007); higher contents have yet been detected in the Gulf of Naples reaching an average value of 177.2 ng/g lipid weight (range 32.1-308.8 ng/g lipid weight), also considerably higher than those reported for similar species from the coastal areas of Norway, Japan, China and the Philippines, subject to high anthropogenic impact (Naso et al., 2005).

		Concentratio	on of DDTs	
Species	Location	(ng/g ww)	(ng/g lipid w)	Reference
M.galloprovinci alis	North Western Med.	26 (4 - 126)		Villeneuve et al. 999
M.galloprovinci Ilis	Tyrrhenian Sea		32.1 - 308.8	Naso et al. 2005
M.galloprovinci	Balearic Med. Sea	2.9 (1.6 - 6.6)		Deudero et al. 2007
O. niloticus	Egyptian Med. Sea	2.76 – 24.23		Said et al. 2008
Clarries sp.	Egyptian Med. Sea	14.16 - 45.13		Said et al. 2008
D. labrax	Strait of Messina		5.1 – 9.0	Lo Turco et al. 2007
S. canicula	South Adriatic Sea		247.0- 1875.0	Storelli et al. 2006
M. merluccius	Adriatic Sea		618-1132	Storelli et al. 2004
X. Gladius	South Tyrrhenian Sea	155 (±125)		Corsolini et al. 2008
S.	Western		6500–	Borrell and Aguilar,
Coeruleoalba	Mediterranean		548800	2007
T. thynnus	Ionian Sea	13.06	435	Storelli et al. 2008
T. thynnus	Tyrrhenian Sea	61	_	Corsolini et al. 1996*
T. thynnus	Mediterranean Sea	178.11	-	Stefanelli et al. 2002*
T. thynnus	Ionian Sea	61–110	_	Kannan et al. 2002*
T. thynnus	Ionian Sea	74	_	Corsolini et al. 2005*
T. thynnus	Strait of Messina	2.70–3944	242–4558	Di Bella et al. 2006*
T. thynnus	Pacific Ocean	_	430–950	Ueno et al. 2002*
T. thynnus	Pacific Ocean	-	_	Hashimoto et al. !003*

Table 21 Comparison of DDT levels in biota (different species).

*Literature data cited in Storelli et al. (2008).

Wide differences in DDT range values characterize fish species in the Mediterranean Sea. Low DDT levels are found in the *Dicentrarchus labrax* species in the Strait of Messina (Lo Turco et al., 2007), while much higher levels have been reported in mussels or bluefin tuna in the same area. Slightly higher values were recorded in *Clarries* sp. and *Oresochromus niloticus* in the Egyptian Mediterranean Sea (Said et al., 2008). In contrast, *Scyliorhinus canicula* from the South Adriatic Sea reflected high values with a mean of 1,170.9 ng/g lipid weight and reaching up to 1,875.0 ng/g lipid weight (Storelli et al., 2006) (see Table 21).

However, decreasing trends have also been found within fish species. Storelli et al. (2004) showed a substantial reduction of DDT contents in codfish (*Merluccius merluccius*) from the Adriatic over a period of 10 years running from a maximum value of 1132 ng/g lipid weight basis in 1993 to a minimum of 618 ng/g lipid weight in 2003. The decline of concentrations of these contaminants in the marine environment can be ascribed to the restrictions introduced at the beginning of the 1970s in different countries of Europe. The p,p'-DDE compound had the highest influence on the total DDT. The p,p'-DDE/DDTs ratio was 0.9.

Concerning DDT contents in top predators, the comparison performed by Storelli et al. (2008) between DDT levels in juvenile bluefin tunas (*Thunnus Thynnus*) in the Ionian Sea and other available data (see Table 21) allowed concluding a similar pattern to the PCB concentrations (see PCB Section above). Their result values were low (13.06 ng/g ww) but were also in contrast with recent studies concerning the Mediterranean region. Adult tuna individuals may reach range values of 61 to 110 ng/g in the Ionian Sea and up to 178 ng/g in the Mediterranean area, clearly exceeding concentrations found in other regions such as the Pacific Ocean. The p,p'-DDE/DDTs ratio of juvenile tunas was rather high (0.9).

On the other hand, Corsolini et al. (2008) analysed organochlorine compounds in muscle samples of swordfish (*Xiphias gladius*) in the South Tyrrhenian Sea. DDT values in muscle and liver tissues where high, of 155 ng/g ww (\pm 125) and 309 ng/g ww (\pm 273) respectively. Among the DDTs, p,p'-DDE was largely the most abundant isomer. Consequently, the *p*,*p*'-DDE/ Σ DDTs ratio was 0.75, which is in accordance with other contemporary results (Storelli et al., 2008).



Figure 13 Decreasing trend in tDDT concentration in bottlenose dolphin blubber from 1978 to 2002, in the Western Mediterranean. Source: Borrell and Aguilar, 2007.

A rigorous analysis of DDT in bottlenose dolphins blubber between 1978 and 2002 in different areas from the Western Mediterranean coasts allowed to observe high concentrations overall (6,500–548,800 ng/g lipid weight basis). However, a declining temporal trend was observed between 1978 and 2002 for total DDT concentrations, which decreased by a factor of 23.7 (see Figure 13). As in other study cases, an increment of the DDE/tDDT ratio was also observed (Borrell and Aguilar, 2007).

High p,p'-DDE/DDTs ratios have been generally found in contemporary study cases (Corsolini et al., 2008; Storelli et al., 2008; Borrell and Aguilar, 2007). This ratio acts as an indicator of temporal trends for the DDTs, and high values (over the critical threshold of 0.6) may indicate that DDT contamination in specimens may not be due to present use but to remote use of DDT in agricultural activity. Thus, the ratios obtained (0.9 for Storelli et al. (2008) and 0.75 for Corsolini et al. (2008)) should indicate that the Mediterranean Sea does not receive new inputs of DDTs (Corsolini at al., 2008; Storelli et al., 2008).

It must be taken into consideration when interpreting the former indicator that p,p'-DDE is very stable in the environment and is the major metabolic product of DDT accumulating in the lipid fraction of fish carcasses, what would unavoidably contribute to the augmentation (and skew) of the ratio. Moreover, it is well-known that several countries are still using DDT-based pesticides even within the European Community, where DDT is permitted for uses other than plant protection, and that due to its high

persistence and long-range transport potency, DDT can also reach the Mediterranean area from other parts of the world where it is still used intensively (Corsolini et al., 2008). However, despite the former considerations, the high p,p'-DDE/DDTs ratios may indicate that no significant new inputs of DDT have occurred in the north-western Mediterranean in recent decades, or are negligible in comparison to pre-1970s inputs (Borrell and Aguilar, 2007).

3.5.2 Hexachlorobenzene

Hexachlorobenzene (HCB) was first introduced in 1945 as fungicide for seed treatments of grain crops, and used to make fireworks, ammunition, and synthetic rubber. Today it is mainly a by-product in the production of a large number of chlorinated compounds, particularly lower chlorinated benzenes, solvents and several pesticides. HCB is emitted to the atmosphere in flue gases generated by waste incineration facilities and metallurgical industries (UNEP/GEF, 2002). HCB has a relatively high bioaccumulation potential and long half-life in biota.

In a recent review of POPs levels in Mediterranean sediments, Gomez-Gutierrez et al. (2007) collected available data on HCB concentrations from 361 samples since the 70s, especially from NW Mediterranean, the Tyrrhenian and Adriatic Seas. Higher concentrations are reported in harbours and coastal lagoons (0.1-2800 and 0.3-2400 ng/g dw, respectively), comparing to background levels in deep sea sediments (0.04-0.8 ng/g dw). HCB concentrations in areas influenced by river discharges ranged between 0.05-39.4 ng/g dw (with highest levels in the Ebro and Rhone river mouths), while levels in urban areas were 0.01-60 ng/g dw, with peak concentrations in Venice (up to 2400 ng/g dw), as shown in Table 22.

According to the review of Gomez-Gutiérrez (2007), HCB concentrations in Mediterranean sediments did not show a clear temporal trend, although data available for the last period (2000 to present) was in the low range of concentrations. The lack of data in the period of 1970-1980, when its agrochemical application was more important greatly limits the analysis. Furthermore, the fact that HCB is also generated inadvertently as a by-product and/or impurity in several chemical processes or incomplete combustion could also modify any possible temporal trend (Gomez-Gutiérrez, 2007).

Area		Sub- basin	HCB (ng/g dw)
Urban areas			
Venice		ADR	2 - 2400
Marseille		NWE	0.2
Barcelona		NWE	3 - 40
Alexandria		SLE	5 - 60
Naples		TYR	0.2 - 1.3
Thessalonica		AEG	0.1 - 1.3
Piraeus		AEG	0.1 - 5.2
Background	(deep		0.04 - 0.8
sea sed)			

Table 22 Review HCB levels in sediments in the Mediterranean Sea. Source: Gómez-Gutiérrez et al. (2007).

HCB is also widely distributed in Mediterranean marine <u>biota</u>. As shown in Table 23, higher levels have been reported in marine mammals, followed by fish and mussels.

Villeneuve et al. (1999) reported concentrations of HCB in mussels from NW Mediterranean coasts one or two orders of magnitude higher in 1973-1974 than in 1988-1989 (0.08-1.9 ng/g dw). In the NW Mediterranean HCB levels were also measured by Sole et al. (1994) during the 80s in the Ebro Delta (up to 1.8 ng/g ww) and from 1996 to 2000 in the Balearic coasts (0.1-1.1 ng/g ww) (Deudero et al., 2007). HCB have also been recently surveyed in the Gulf of Naples (Naso et al., 2005).

Species /	Location /	Concentration	on (ng/g)	Poforonco						
Tissue ^a	Sampling year	НСВ	ү-НСН	Reference						
Mussels										
M.galloprovin	NW Med coasts /	0.08 - 1.9	0.8 -3.1	Villeneuve et al.						
cialis	1988-89	dw	dw	1999						
M.galloprovin	Gulf of Naples / 2003	ND - 25.7		Naso et al. 2005						
cialis		l.w.								
M.galloprovin	Balearic coasts /	0.1 - 1.1	0.2 - 2.7	Deudero et al.						
cialis	1996-2000	WW.	WW.	2007						
M.galloprovin	Ebro Delta / 1980-	ND – 1.8	ND – 0.6	Sole et al. 1994						
cialis	1992	WW.	WW.							
Fish										
M. barbatus /		35 – 215		Pastor et al. 1996						
<u>M</u>	- Ebro Delta / 1992 -	I.W.								
D. labrax / M		97 – 127								
	A 1 : /: 0 / 4000	I.W.								
M.	Adriatic Sea / 1993-	8.6 - 14.7	3.3 - 7.6	Storelli et al. 2004						
meriuccius /	2003	l.w.	l.w.							
<u> </u>	Snanish coasts /	16 5-173	10.8 - 37	Serrano et al. 2008						
0. aurata / m	2001-2002	40.0 170 Iw	10.0 07							
O niloticus /	2001 2002		0.03 - 2.1	2000						
M	Burullus Lake (Nile		WW.	Said et al. 2008						
Clarries sp. /	Delta) / 2006		1.6 - 8.6							
M	,		WW.							
Marine mammals										
T. truncatus /	NW Med / 1978-	100 – 5200		Borrell and						
В	2002	l.w.		Aguilar, 2007						
S.	SW/ Tyrrhenian /	6.9 – 306 dw		Fossi et al. 2004						
Coeruleoalba	2002									
/ B		GVV.								
М.	Greek coast / 1995-	43 - 732		Borrell and						
monachus /	1999	l.w.		Aguilar, 2007						
В										

Table 23 Levels in biota of HCB and HCH in the Mediterranean region.

^a M: Muscle; L: Liver; B: blubber

In fishes, significant levels of HCB (35-215 ng/g l.w.) have been reported in the Ebro Delta (Pastor et al. 1996) and along Spanish coasts (46.5 – 173 ng/g l.w.) (Serrano et al., 2008). Concentrations measured in codfish (*M. merluccius*) from the Adriatic dropped from 14.7 to 8.6 ng/g l.w. between 1993 and 2003 (Storelli et al., 2004). Lower concentrations (0.12-0.67 ng/g ww) were reported for deep sea fishes (Porte et al., 2000).

Decreasing temporal trends have also been observed in bottlenose dolphins (*T. truncatus*) from the Spanish coasts, where HCB mean concentrations in blubber

decreased from 2260 to 0.46 ng/g l.w. between 1987 and 2002 (Borrell and Aguilar, 2007).

HCB was also found in monk seals (*M. monachus*) from Western Sahara and Greece (Borrell and Aguilar, 2007). Mediterranean individuals presented significantly higher levels of HCB concentrations (as well as tPCB, and DDTs) than their counterparts from the Atlantic.

3.5.3 Lindane (γ-HCH)

"Lindane", which is essentially pure γ -HCH, has been of the most widely used insecticides in the world. Its insecticidal properties were discovered in the early 1940s. It controls a wide range of sucking and chewing insects and has been used for seed treatment and soil application, in household biocidal products, and as textile and wood preservatives (UNEP/GEF, 2002). Lindane and other HCH isomers are relatively persistent in soils and water, are much less bioaccumulative than other organochlorines because of their relatively low liphophilicity.

According to the UNEP/GEF (2002) review, HCHs in <u>sediments</u> were detected during the 80's in coastal sediments from the Western, Central and Eastern part of the Mediterranean, with mean values of 0.5-2.5 ng/g. In the 90s, levels of 0.02-0.94 ng/g dw (Σ HCHs) were reported in the Ebro prodelta, 10-51 ng/g dw (γ -HCH) in Abu Quir and El-Mex Bays, and 7-140 ng/g dw (α + γ -HCH) in Thermaikos Gulf (UNEP/GEF, 2002). Said et al. (2008) recently reported levels of nd-22.8 ng/g dw (γ -HCH) in sediments of Lake Burullus (Nile Delta).

In <u>biota</u>, a large survey of mussels performed during 1995-99 in the French Atlantic and Mediterranean coasts (over 700 samples) have shown mean values of 0.8/3.6 ng/g dw and 0.5/2.0 ng/g dw for α/γ -HCHs, respectively (UNEP/GEF, 2002). According Villeneuve et al. (1999), average concentrations of lindane in mussels from NW Mediterranean coasts decreased from 49 to 2 ng/g dw (0.8-3.1) between 1973-1974 and 1988-1989 (see Table 23). Some negative trends were also observed in mussels from the Balearic coasts between 1996 and 2000 (Deudero et al. 2007).

An extensive survey of *Mullus barbatus* carried out between 1986 and 1991 in 8 coastal stations of the Aegean Sea revealed concentrations of α and γ -HCH of 0.1-0.5 ng/g ww and 0.6-3.5 ng/g ww, respectively (UNEP/GEF, 2002). Higher concentrations (0.03 – 8.6 ng/g ww) have recently been reported in fishes from Lake Burullus, Nile Delta (Said et al., 2008). In the Adriatic Sea, γ -HCH concentrations in codfish decreased from 7.6 to 3.7 ng/g l.w. between 1993 and 2003 (Storelli et al., 2004), while in Spanish coasts levels of 19.8 - 37 ng/g l.w. have recently been reported in *S. aurata* (Serrano et al., 2008).

3.6 Other

3.6.1 Nonyl- and Octyl-phenols

Nonyl- and Octyl-phenols (NP and OP) are the starting material in the synthesis of alkylphenol ethoxylates (APEs), first used in the 60s. These compounds are highly effective cleaning agents or surfactants that have been widely used in a number of industrial sectors including textiles, pulp and paper, paints, adhesives, resins and protective coatings. Alkylphenols can also be used as plasticizers, stabilisers for

rubbers, lube oil additives, and the alkylphenol phosphite derivatives can be used as UV stabilisers in plastics (UNEP/GEF, 2002).

Limited information on the occurrence of NP and OP in the Mediterranean region is available. Some studies have been reported in freshwater, sewage sludge and coastal waters (UNEP/GEF, 2002).

<u>Sediment</u> samples were analysed in the Venice Lagoon, being the sum of NP, NP1EO and NP2EO in the range 150-13700 ng/g dw (Marcomini et al., 1990). In the Barcelona harbour, Diez et al. (2006) measured levels of 3.8-77 ng/g dw of NP.

In <u>biota</u>, NP, OP and their ethoxylates were detected in edible molluscs, cuttlefishes and squids, caught from 15 harbours along the Italian coast in 1997. NP reached the maximum concentration of 696 ng/g ww in the squids from the central Adriatic Sea. Levels were lower in mussels and clams (246-270 ng/g fresh tissue). OP generally occurred at levels 30 times lower than NP (Ferrara et al., 2001). A similar study on 8 edible marine species from the Adriatic Sea (Ferrara et al. 2005), determined levels of NP in the range 118-399 ng/g ww and 9.5-1431 ng/g ww in crustaceans and fish, respectively. OP was found at respective levels of 2-7-4.7 and 0.3-3.8 ng/g ww in crustaceans and fish.

Alkylphenols were also measured in red mullet (*M. barbatus*) collected from different sampling sites in the NW Mediterranean (Martin-Skilton et al., 2006). Levels of NP were 280-83100 ng/g bile, and OP levels 10-340 ng/g bile. Evidences of significant alterations in the endocrine system of red mullets were detected.

Corsi and Focardi (2002) determined levels of *p*-NP in fishes (*Zosterisessor ophiocephalus*) in 3 sites of the Orbetello lagoon (Italy) during 1998 and 1999. Mean levels were between 0.12 and 1.41 ng/g ww.

3.6.2 Phthalates

They encompass a wide family of compounds. Dimethylphthalate (DMP), diethylphthalate (DEP), dibutylphthalate (DBP), benzylbutylphthalate (BBP), di(2-ethylhexyl)phthalate (DEHP)(C24H38O4) and dioctylphthalate (DOP) are some of the most common. DBP and in particular **DEHP** have been identified as common priority substances for the marine environment. They are widely used as plasticizers, insect repellents, solvents for cellulose acetate in the manufacture of varnishes and dopes. Vinyl plastic may contain up to 40% DEHP (UNEP/GEF, 2002).

No studies have been identified addressing phthalates occurrence in the Mediterranean marine environment (sediments or biota). Only some unpublished data on DEHP levels (6-9 μ g/g dw) in sediments located off-shore Barcelona (Spain) are reported in the UNEP/GEF review (2002).

3.7 Overview

In Table 24 an attempt is made to summarize the main general findings and trends regarding the occurrence of pollutants in the Mediterranean marine environment, according to the information and data reviewed within this report. It must be noted that a deeper analysis of the identified information, and additional data (e.g. from national monitoring programs) may modify this preliminary overview.

 The lack of comprehensive data to properly assess the state of pollution in the Mediterranean region is a well known limitation, which has been emphasized in previous assessments of the Mediterranean environment (Civili and Jeftic, 1987; UNEP/MAP, 1996; Carvalho and Civili, 2001; EEA, 2006). Data is not homogeneously available in time and space. Most of the information has been published after the 90s, very few temporal trends are available, and data is mainly concentrated in the north western basin (although some significant amount of information is also available for the Aegean and Egyptian coasts).

Table 24 Overview of the occurrence of pollutants in the Mediterranean marine environment according to the reviewed information.

	Availability of data		Indications from available temporal trends ^b		Maximum reported levels in:		
	Sed.	Biota	Mainly in ^a :	Sed.	Biota	Matrix	Where
Metals and related	compoun	ds					
Cadmium	Regular	Good	NW/ADR/AEG	NA	Upw.	Cetaceans	NW
Lead	Regular	Good	NW/ADR/AEG	NA	NA	Mussels	ADR
Mercury	Regular	Good	North & SLE	NA	Upw.	Cetaceans	NW
Organic tin	Poor	Regular	NW/ADR/SLE	Upw. / Downw.	NA	Sed / biota	NW / ALB
РАН	Good	Regular	North & SLE	NC	NC/Downw.	Sediments	NW / SLE
Organohalogen							
PCBs	Good	Good	North & SLE	NC	Downward	Cetaceans	NW
Dioxins & Furans	Poor	Regular	NW/ADR	NA	NC/Downw.	Cetaceans	
BFRs	Very poor	Poor	NW	NA	NA	Cetaceans	NW
PFOS	No data	Very poor	NW/ADR	NA	NA	Cetaceans	NW
Chlorinated paraffins	Very poor	No data	NW	NA	NA	NA	NA
DDTs	Good	Good	North & SLE	Downward	Downward	Cetaceans	NW
HCB	Regular	Poor	NW/ADR	NC	Downward	Cetaceans	NW
Lindane	Very poor	Poor	NW/ADR/AEG	NA	Downward	Sediments	SLE
Other organic							
Nonyl/Octyl- phenols	Very poor	Very poor	NA	NA	NA	NA	NA
Phthalates	No data	No data	NA	NA	NA	NA	NA

NA: Not Available information to be defined.

^a NW: North western basin (including NWE, TYR, ION); ADR: Adriatic; AEG: Aegean; North (NW&ADR&AEG); SLE: South Levantin East; ALB: Alboran.

^b Upw.: Upward; Downw.: Downward; NC: not clear

<u>Heavy metals (Cd, Pb, Hg), PAHs, PCBs and DDTs concentrates the majority of available data</u>, especially in biota (mussels). Information is also available to partially assess the occurrence of organotins, dioxins and furans, and hexachlorobenzene, while for other 'emergent' priority pollutants, like BFRs, PFOS, chlorinated paraffins, alkylphenols or phthalates, very few data or no data has been identified in the Mediterranean.
- All the considered pollutants for which a certain amount and diversity of data is available, are found to be <u>widely distributed</u> in the Mediterranean environment.
- Regarding temporal trends, the 'old' organohalogen (DDT, PCB, HCB, lindane,...) generally show downward trends in measured concentrations, especially in biota. This is consistent with the phase out and restriction of use of these substances. Non intentional emissions like PAHs or dioxins and furans show also some indications of downward trends in biota, but this is not so evident everywhere. Upward trends in concentrations have only been reported in some cases for heavy metals (Cd, Hg; according to MED POL preliminary data), and TBTs (which would be expected to progressively decrease in the forthcoming years due to restrictions on its use as antifouling paints). Other emergent pollutants might have experienced upward trends during the last years, but not enough data is available to this respect.
- Generally, the <u>higher levels</u> of pollutants are detected in sediments and biota of coastal areas, mainly close to urban centres, harbours and river mouths. However, due to the persistence and liability to bioaccumulate of most of the considered substances, the maximum concentrations are usually reported in <u>cetaceans and top predators</u> (e.g. whales, dolphins, sharks, or tuna). These levels have been mainly reported in the NW basin; unfortunately very few data is available for these species in the eastern basin. Higher levels of PAHs are reported in sediments, which is consistent with the ability that fishes have to metabolize these compounds. The higher levels of lindane in sediments might be related with its relatively low liphophilicity.
- Another consideration to be highlighted is that when the concentrations of pollutants are compared with other regions, several authors conclude that <u>the</u> <u>Mediterranean environment is more affected by the input of pollutants</u>, which is usually attributed to its enclosure conditions. This has been mainly observed for PCBs, DDTs, and dioxins and furans. On the other hand, other pollutants like BFRs or PFOS appear to occur at similar or lower concentrations than in other areas.

Finally, it must be noted, that the potential risk that the actual occurrence of the considered pollutants may pose on the environment or the human health has not been addressed within this report. However, the main evidences in the Mediterranean have been observed for the imposex effect as a consequence of TBT pollution. In the Adriatic, no risk to human health was observed from the exposure to Cd, Pb and PCB through consumption of different seafood. In contrast, the mercury exposure due to consumption of certain fish species indicated that human health risk might be of concern (Storelli, 2008).

4. Emission of substances of concern in Mediterranean countries

4.1 Sources of data

The key source of emission data at regional level is the National Baseline Budget (UNEP/MAP, 2002), which includes emission data to air and water for SAP priority pollutants in all MAP countries. The baseline year is 2003, and the database compiled by MED POL can be organized by substance, sector, subsector, country and administrative region. So, this database has a major potentiality to be used as a baseline on current national and regional loads of pollutants, and to analyse the specific sources of pollutants by sector and administrative regions. However, to be used as a baseline, it should be ensured that all countries have followed the NBB

guidelines (UNEP/MAP, 2002) to elaborate their inventories, the same substances are considered, and the same approach to delimit the geographic scope has been used.

Countries may have also their own national inventories, or participate in other regional initiatives, like the European Pollutant Emission Register (EPER)⁹, which is similar to the NBB, but do not include all the same substances.

For complementary purposes, for some substances or specific sectors, information can also be obtained from the MAP Technical Reports Series, or from the European Environmental Agency (EEA). Comprehensive regional assessment (both from sources, pathways and levels in the environment) are also available for Persistent and Toxic Substances (PTS) (UNEP/GEF, 2002).

In the following sections, an analysis of available data in the NBB is provided, with an emphasis on the sources (activity sectors) of priority pollutants identified above.

4.2 The National Baseline Budget: available data

The NBB database compiled by MED POL contains about 7600 records, each record indicating the emission of a substance for a given activity sector and subsector, in an administrative region and country. The analysis of the number of records by region, sector, and substance, can provide an idea of the availability of data in the NBB database.

The majority of data have been reported by northern Mediterranean countries (77% of records), while eastern and southern countries accounts for 12% and 11% of records, respectively (see Figure 14). Differences in the number of records can be related with the size and level of industrial development in each country, the regional and sectoral scope of the inventory, the availability of data, and the level of detail that each country operates its inventories.



⁹ http://eper.eea.europa.eu/eper/

Figure 14 Number of records (n) in the NBB database, per country and subregion.

The NBB 'universe' covers about 80 different substances or groups of substances and parameters. The total number of records for each substance is shown in Figure 15, where a distinction is made for those substances that have been identified as '<u>substances of concern</u>' for the marine environment in different international lists, as presented above (see also Annex 1), and '<u>other substances</u>' or groups of substances or <u>general parameters</u> that are usually considered to monitor pollution to air and water, as for example BOD, VOC, TSS, etc. Indicators for nutrients (e.g. Total Nitrogen or Total Phosphorus) can also be considered under this latter category.

As it can be observed, generic parameters or non hazardous substances accounts for the majority of records in the NBB database (68%), while substances of concern, which represent 68% of the number of different considered substances, accounts for 32% of total records. This is not surprising, as general parameters like BOD or nutrients are commonly emitted and reported by many different sectors and countries, while substances of concern are more sector specific, and difficult to measure and report. Within this group, it can be generally observed that there is more information (i.e., number of records) for metals, dioxins and phenols, than for PAHs and benzenes, and much more than for organohalogens, for which very few records have been reported.



Figure 15 Number of records (n) in the NBB database, per substance.

Regarding activity sectors, the NBB database contains more information for the food packing industry (15% of records), production of energy (12%), manufacture of metals (10%), manufacture of cement (7%), inorganic chemicals, oil refining and organic chemicals (5%). The total number of records is shown in Figure 16. It can be considered that the sectors with more reported records are those that a) are usually present in all economies (e.g. food industry, energy production, metal industry); b) many industrial facilities exist, with typical emissions commonly measured (e.g. BOD in food industry); c) although fewer but big facilities exist, production data and emission factors are well established/available (e.g. energy production, cement, oil refining); or d) many different substances can be released (e.g. chemical industry).



Figure 16 Number of records (n) in the NBB database, per sector.

Taking into account the proportion of substances of concern that have been reported for each sector (as a way to observe the 'hazardous profile' of each sector emissions), the ranking presented above is submitted to some significant variations. For example, as represented in Figure 17, according to the available data, several sectors related with waste and wastewater management activities appears to have high proportions of records of substances of concern. On the opposite, the 'hazardous profile' of the food industry is one of the lowest.

A new ranking combining both criteria, i.e., the total availability of data (e.g. nTotal of sector S > mean) and the 'hazardous profile' (e.g. >20% of records including substances of concern), would result in the following list of sectors (sorted by nSubstances of Concern):

1. Production of energy

UNEP(DEPI)/MED WG. 328/Inf. 1 page 74

- 2. Manufacture of metals
- 3. Manufacture of cement
- 4. Oil refining
- 5. Treatment of urban wastewater
- 6. Organic chemicals
- 7. Waste management
- 8. Inorganic chemicals
- 9. Tanning and dressing of leather
- 10. Transport

11. Manufacture of paper



Figure 17 Number of records (n) in the NBB database, per sector and type of substance ('hazardous profile').

It must be noted that the above analysis is influenced by the availability of data, which indicates that most of the reported substances of concern are metals, which are mostly emitted in the energy and metal industry. This is an analysis of available data in the NBB database; it does not necessarily mean that these sectors are causing the major harmful emissions for the Mediterranean marine environment.

4.3 Emissions by activity sectors

In this section some information on total emissions and its sources, according to the NBB database, is presented. As the available data is not comprehensive, and in order to focus on those substances that can be widespread emitted, the analysis is focused on some selected chemicals according to the following criteria: a) compounds are common priority substances of concern, as presented above; b) a minimum number of records (i.e. >25) have been reported in the database (see Figure 15); and c) the substance's emissions have been reported by a minimum number of sectors (i.e. >5 out of 30).

Data for some selected substances according to these criteria is shown in Table 25. According to this results, the metal industry accounts for major emissions of several metals, such as air emissions of cadmium, lead, or chromium, and emissions to water of cadmium, nickel and zinc. The manufacture of fertilizers accounts for the majority of emissions to water of lead and mercury, while mercury air emissions are produced by the cement, energy, and metal industry. Chromium to water is mainly emitted by oil refining, followed by the fertilizers and tanning industry. Finally, the energy sector accounts for the majority of reported air emissions of nickel. According to these data, the metal industry, manufacture of fertilizers, production of energy, oil refining, and cement industry are significant sources of metals. Results for some priority pollutants (Cd, Pb, Hg) are shown also in Figure 18.

Regarding organic pollutants, the manufacture of metals is also relevant for PAHs and benzene releases. Oil refining accounts for the majority of phenols emissions, and is also relevant for benzene and PAH emissions (to water). Transport accounts for significant air emissions of PAH and dioxins.

The NBB database includes also a good set of data for nutrients. The main sectors contributing to Total Nitrogen and Total Phosphorus emissions are shown in Figure 19. As it can be observed, according to the NBB database, Total N is mainly emitted by the treatment of urban waste water (31%), farming of animals (19%) and metal industry (11%), while the manufacture of fertilizers accounts for the majority of Total P emissions (63%), followed by the farming of animals (20%) and treatment of urban waste water (8%). It can be observed how a few group of activity sectors account for the majority of releases of nutrients in the Mediterranean region. This is also the case for other generic parameters of pollution, like BOD or suspended solids, where the food packing industry is an important sector in both cases (see Table 26).

						Metals									Organic po	ollutants	
Sector	Cd (gas)	Cd (liq)	Pb (gas)	Pb (liq)	Hg (gas)	Hg (liq)	Cr (gas)	Cr (liq)	Ni(gas) N	li (liq)	Zn (gas)	Zn (liq)	Benzene	PAH (gas)	PAH (liq)	PCDD/PCDF (gas) ¹	Phenols
Agriculture										115.60		42.00					
Aquaculture				1.60				4,000.20		216.00		22.50					348.50
Building and repairing of ships and boats		4.00		242.83		0.77		8,525.70		7.90		2,748.30			35.00		
Food packing	33.10	80.00	1,153.51	690.00	364.11		2,124.46	4,710.00				2,226.00				0.00	12.10
Installations for melting mineral substances	82.60																
Management of urban solid waste		0.00		0.02		0.00				0.32		0.22				0.02	
Manufacture of cement	193.43		5,420.90	147.45	2,086.14		2,271.47	112.77			1,988.00		7,560.00			403,750.20	260.00
Manufacture of electronics products		0.08		35.40				66.88		246.74		1,177.90					26.10
Manufacture of fertilizers	1,980.00			1,041,800.00		1,020,800.00		1,610,800.00				26,000.00					
Manufacture of metals	6,911.30	4,208.60	468,824.02	15,052.12	1,060.00	240.90	2,845,475.13	146,979.39	461.00	17,352.16	41,586.00	7,360,714.83	195,720.00	73,151.94	5,547.01	463,520.08	64,089.00
Inorganic chemicals	189.00	170.60	2,388.99	816.80	446.60	109.40	1,357.00	594,965.20	1,383.50	2,391.50	4,760.00	37,654.20	87,220.00	269.70)	13,608.12	44,080.90
Organic chemicals	29.00	208.00	3,047.00	22,401.19	143.00	1,017.90	135.00	722.80	1,803.00	881.90		11,673.33	29,910.00	330.00	49.30	19.00	260.10
Manufacture of paper		164.80		555.20		30.05		494.00		559.70		1,739.00				46,335.74	2,158.00
Manufacture of pharmaceuticals		17.70		418.80		3.50		876.20		968.00		2,100.00					2,177.80
Oil refining	151.20	82.92	27,667.55	11,419.43	137.10	9.61	1,356,992.63	5,418,767.64	22,977.00	2,195.50	9,356.00	5,366.72	127,390.00	459.80	1,288.60)	187,133,387.76
Manufacture of textiles		515.50		10,405.22				101,856.87	·	139.90		36,979.40					1,774.39
Mining and quarrying							150.00		117.00								
Production of energy	1,155.99	488.70	3,979.00	3,329.80	1,152.52	102.00	10,604.13	46,575.39	217,469.95	5,772.87	10,851.00	22,966.00	1,912.00	6,487.96	480.00	1,344,000.09	9,055.00
Recycling activities			1,140.70					0.65									5.02
Tanning and dressing of leather				14,440.00				1,646,709.62									38,246.51
Tourism		0.02		0.31										0.02			
Transport			79,153.00	30.00				30.00		10.00		436.00		409,036.85	7.40	2,356,644.88	85.80
Treatment/storage of hazardous wastes	10.90																97.00
Treatment of sewage sludge		62.30		282.30		96.40		8,145.90		4,067.00		6,467.00					357.00
Treatment of urban wastewater		2,173.72	30.74	4,550.92		318.36		1,504.87		1,418.60		18,977.10		143.17	0.00	44.52	2,373.95
Waste incineration	10.90					2.80											97.00
Waste management activities	12.60	229.00	833.00	2,939.50	75.10	54.60	1,391.00	6,913.00	1,168.00	2,906.90	2,818.00	15,163.00				0.00	3,072.40
Not defined	1,401.51	489.95	35,249.38	1,616.31	789.24	90.47	14,548.95	5,218.60			101,222.02	26,700.72	105,531.33	14,119.80	924.29	0.02	6,463.07
Total	12,161.53	8,895.90	628,887.79	1,131,180.00	6,253.81	1,022,876.75	4,235,049.77	9,607,986.57	245,379.45	40,011.39	172,581.02	7,581,213.82	555,243.33	503,999.24	8,331.60	4,627,922.64	187,308,427.40

Table 25 Total loads of some selected pollutants (kg/yr), reported by Mediterranean countries in the NBB, by sector.

¹ mg/yr



Figure 18 Total loads (main sectors, in %) of some selected metals, reported by Mediterranean countries in the NBB.



Figure 19 Total loads (main sectors, in %) of nutrients, reported by Mediterranean countries in the NBB.

Table 26 Main activity sectors discharging BOD, nutrients and suspended solids in the

 Mediterranean region, according to NBB data.

Parameter	Sectors	% of total emission in the Med region
	Oil refining	
BOD	Food packing	87%
	Farming of animals	
	Food packing	
TSS	Manufacture of textiles	72%
	Treatment of urban wastewater	
	Manufacture of fertilizers	
Total P	Farming of animals	91%
	Treatment of urban wastewater	
	Treatment of urban wastewater	
Total N	Farming of animals	61%
	Manufacture of metals	

It must be noted that the sources of several of the common priority substances for the marine environment can hardly be assessed through the National Baseline Budget. This is because of the nature and scope of the NBB, which is more oriented to address actual and point source releases. In contrast, some of the substances of concern have already been phase-out or its use has been restricted, and therefore its actual sources into the marine environment are usually non-point sources or from environmental reservoirs. This can be observed in the review of main sources of Persistent and Toxic Substances in the Mediterranean region (UNEP/GEF, 2002) shown in Table 27. In several cases (e.g. pesticides, PCBs, BFRs, phthalates), main releases (marked in bold) are from product or equipment stocks. Some of the main sources of PAHs are combustion from traffic and oil spills, which are not covered by the NBB, while main sources of alkylphenolethoxylates is runoff from industrial and domestic detergent use. TBTs have a very specific key source to the marine environment, the use of antifouling paints in shipping, which is neither easy to be address trough the NBB.

Table 27 Main sources, environmental vectors and reservoirs for PTS in the Mediterranean region. Source: UNEP/GEF (2002).

Compound type	Air sources	Soil sources	Freshwater	Seawater sources
			sources	
Pesticides	Agriculture use,	Stockpiles,	Runoff from	Major rivers and
	spraying/land	production waste	agriculture use.	coastal runoff
	application	DDT, dicofol	DDT, dicofol	
		production	production.	
PCBs	Emissions from	Equipment	Leakage from	Major rivers and
	equipment and	stocks and	equipment	coastal runoff
	stocks	landfills		Sewage sludge dumping
	Sewage sludge	Sewage sludge		
	incineration			
PCCDs	Emissions from	By-products of		Major rivers and coastal
	combustion	PCBs		runoff
PAHs	Emissions from	Sewage sludge	Oil spills,	Oil spills in shipping
	combustion, oil,	Timber	sewage runoff	and refineries
	traffic	preservation		Sewage sludge dumping
	Sewage sludge	-		
	incineration			
BFRs	Emissions from	Landfilling of		
	the use of	obsolete		
	electrical and	equipment		
	electronic			
	equipment			
Alkylphenoletho		Sludges from	Runoff from	Major rivers and
xvlates		wastewater	industrial and	coastal runoff
5		treatment plants	domestic	
		1	detergent usage	
Phthalates	Emissions from	Landfilling of	·	
	treated PVC	materials		
TBT				Release of antifouling
				paint from shipping

5. Review of Emission Limit Values

5.1 ELVs adopted in international and regional frameworks

In this section a review of ELVs adopted in the following relevant international and regional frameworks has been carried out:

- European Union (Directives, Regulations, Decisions)
- OSPAR (Decisions and Recommendations)
- HELCOM (Recommendations)

The EU legal framework has been reviewed as several Mediterranean countries are Member States, accessing or candidate countries. The OSPAR and HELCOM Conventions have also been taken into account due to its similarities in goals and scope with the Barcelona Convention. The provisions and substances included in the Stockholm convention are already covered by the EU legislation.

The review has been focused on those pollutants identified in this report as common priority substances. The different relevant Directives, Regulations, Recommendations, etc., that contains information on adopted ELVs are included in **Annex B**. Those legal texts adopting the restriction on use or phase-out of any of the considered priority substances have also been included.

All this information has been summarized in Table 28, which indicates whether an ELV or phase-out measure has been adopted in any of the reviewed frameworks, for any of

the considered substances. The general activity sectors where these measures are enforceable have also been indicated.

This summary provides an overview of which substances and sectors have been more commonly addressed through ELV and elimination measures adopted at international level. However, it must be noted that ELV are further developed and adopted at national and local level, for a wider range of substances and specific sectors, but this is beyond the scope of this report. In any case, at international level the following trends are observed:

- The emissions of <u>metals</u> (especially cadmium and mercury) are the most common regulated substances in the different frameworks reviewed. ELVs for metals have been adopted for different sectors, mainly the metal industry, textiles, inorganic chemical industry and waste incineration.
- Within <u>organohalogens</u>, a certain frequency of adopted ELVs is observed for dioxins & furans and some halogenated aliphatic hydrocarbons (e.g. 1.2, dichloroethane, trichloroethylene, tetrachloroethylene, PVC), while the restriction on use or directly its elimination has been a common followed approach for short chained chlorinated paraffins, Brominated Flame Retardants or PCBs (in any sector).
- Many of the considered organochlorinated <u>pesticides</u> have been addressed through its ban of production and use in the agriculture. This includes the old pesticides, like those included in the Stockholm Convention (e.g. Aldrin, DDT, Dieldrin, or Heptachlor).
- Other ELVs have been identified for <u>PAHs</u> and <u>phenols</u> in the metal industry. <u>Nonylphenol ethoxylates</u> are also commonly addressed, in this case through its restriction or elimination of production and use.
- In general, ELV have been commonly applied in the metal sector, textiles, chemical industry and waste incineration, while the phase-out of substances has been applied in the agriculture sector.
- Finally, it must be noted that for the adoption of ELVs, a <u>previous review and</u> <u>adoption of Best Available Techniques (BATs) and Best Environmental Practices</u> (<u>BEPs</u>) in the applicable sectors is addressed. This is a common approach followed in OSPAR and HELCOM Conventions.

Table 28 Review of Emission Limit Values (ELVs) established in international regulatory frameworks for priority substances.

ACTIVITY SECTORS
stupp ust dust
that out is a weather that the search of the
modul istri peret ustri renit perit e inerti e
with the trainer with the start and the second second
ror hor ror ror hor hor hor hor hor hor

Substances of Groups of Subst.								
Metals and related compounds							 	
Metals								
Cadmium	ELV ^H	ELV ^{H,O}		ELV ⁰		ELV ^H	 ELV ^H	ELV ⁰
Lead		ELV ^{H,O}		ELV		ELV ^H	ELV ^H	
Mercury	ELV ^H	ELV ^{H,O}		Phs-out ^H		ELV ^{H,O,EU}	ELV ^H	ELV ^{O,EU}
Selenium							 	
Copper		ELV ^{n,C}		ELV ^{n,C}	ELV	ELV	 ELV	
Chromium		ELV ^{n, v}		ELV ^{n, v}	<u> </u>	ELV ^r	 ELV ⁿ	
Nickel	ļ	ELV ^{11,C}		ELV~	───	ELV''	 ELV''	
Zinc Matallia Compounds		ELV ^{.,,-}		ELV ^{,-}		ELV	 ELV	
organic tin compounds			Pestr ⁰					
Cadmium compounds			Neou.					
Nickel compounds					<u> </u>			
Organic Mercury compounds								
Organic Lead compounds								
Hydrocarbons								
Aliphatic HC								
cyclododecane								
1,5,9-cyclododecatriene								
Renzene								
Polycyclic Aromatic Hydrocarbons		FLV ⁰						FL V ^{EU}
Anthracene								
Napthalene								
Fluoranthene		ELV ⁰						
Benzo(a)pyrene								
Benzo(b)fluoranthene								
Benzo(g,h,i)perylene	ļ				 		 	
Benzo(k)iluorantnene							 	
Synthetic musk								
musk xylene								
Organohalogen compounds								
Halogenated Aliphatic HC					ELV ⁰			
Chlorinated paraffins, short chained (SCCP)		Bha-out ^{H*}						Poetr /Phe-out ^{0,EU}
Chiomateu parannis, short chanteu (CCC)		Pris-out						Restl./Plis-out
Chloroform (Trichloromethane)					<u> </u>			ELV ^{EU}
Dichloromethane		ELV ^O						
1,2-Dichloroethane					ELV ^{H,O}			ELV ^{EU}
Hexachlorobutadiene								ELV ^{EU}
Chloroethene	ļ	0			 		 	
		ELV [©]					 	
letrachioroethylene		ELV-		-	FLVH,0			ELV ²⁰
PVC Polyvillyl Chlorue					ELV			
Hexabromocyclododecane (HBCDD)		<u> </u>			<u> </u>			
Halogenated Aromatic HC								
Chlorobenzenes								
Trichlorobenzenes				Phs-out ^H				ELV ^{EU}
1,2,3-trichlorobenzene				Phs-out ^H				ELVEU
1,2,4-trichlorobenzene				Phs-out ^H				ELVEU
1,3,5-trichlorobenzene				Phs-out ^H				ELV ^{EU}
Pentachlorobenzene								
Prominated Hame Ketardands				L	<u> </u>		 	
Pentabrominated diphenyl ether								Phs-out ^{EU}
Polybrominated biphenyles (PBBs)								F 115-001
Hexabromobiphenyl								Phs-out ^{EU}
Octabromobiphenyl								
PCBs				Phs-out ^H				Phs-out ^{H,O,EU} /ELV ^{EU}
PCDDs/PCDFs					ELV ⁰		ELV ^H	ELV ^{EU}
2,4,6-bromophenyl 1-2(2,3-dibromo-2-								
methylpropyl)							 	
pentabromoethylbenzene					<u> </u>		 	
pentachloroanisole								
polychlorinated naphthalenes								
trichloronaphthalene								
tetrachloronaphthalene								
pentachloronaphthalene								
hexachloronaphthalene								
heptachloronaphthalene								
paphthalene, chloro derivs								
Chlorinated Phenolic Compounds								
phenol, 4.4'-(1-methylethylidene)bis[2.6-dibro	mo- / tetral	promobispho	enol A (TBP	P-A)				



Organohalogenated							
pesticides/biocides				ELV ^O			
Alachlor							
Atrazine							
1,2-Dibromoethane						Phs-out ^H	
Chlorophenoxyacids							
2,4-D						H	
2,4,5-T						 Phs-out'	
Acrylonitrile						 Phs-out'	
Aldrin						Phs-out ⁿ	Phs-out ^{E0}
Aramite						Phs-out ⁿ	
Chlordane						Phs-out"	Phs-out ^{EU}
Chlordecone (Kepone)						Phs-out"	Phs-out ²⁰
Chlordimetorm						 Phs-out'	
Chlorevrifes							
Dicofol							
DDTs					FI V ^{EU}	Phs-out ^H	Phs-out ^{EU}
Diuron							1 110 041
Dieldrin						Phs-out ^H	Phs-out ^{EU}
Endosulphan (alpha-endosulfan)							
Endrin						Phs-out ^H	Phs-out ^{EU}
Ethyl O-(p-nitrophenyl) phenyl							
phosphonothionate (EPN)							
Fluoroacetic acid and derivates						Phs-out ^H	
Flucythrinate							5.1
Hexachlorocyclohexane (HCH isomers)						Phs-out ^H	Phs-out ^{EU}
HCH (gamma-isomer, Lindane)						Phs-out ^H	Phs-out ^{EU}
alpha-HCH							Phs-out ^{EU}
beta-HCH						Phs-out ^H	Phs-out ^{EU}
Heptachlor						Phs-out ^H	Phs-out ^{EU}
Hexachlorobenzene						Phs-out ^H	Phs-out ^{EU}
Isobenzane						Phs-out ^H	5.1
Isodrin						 Phs-out [⊓]	 ELVEO
Isoproturon						B1 (H	
Kelevan						Phs-out'	
Misov						Dha out ^H	Dha aut ^{EU}
Marfamquat						Phs-out ^H	Plis-Oul
Nitrophon						Phs-out ^H	
Rentachlorophonol				Pho out ^H		Phs.out ^H	EI VEU
				F IIS-OUL		Phs.out ^H	
Simazine						FIIS-OUL	
Tetrasul							
Trifluralin							
Toxaphene						Phs-out ^H	Phs-out ^{EU}
Other organic compounds							
Phenols		ELV ^O					
2,4,6-tri-tert-butylphenol							
Nonylphenol/ethoxylates (NP/NPEs)		Phs-out ^H		Phs-out ^H			Restr./Phs-out ⁰
Nonylphenols							
Nonylphenol, 4-							
Octylphenols							
(para-tert-octylphenol)							
4-(dimethylbutylamino)dinbenylamin (6PPD)							
3,3'-(ureylenedimethylene)bis(3.5.5-trimethyl	cyclohexvl)	diisocvana	te			 	
Organic Oxigen Compounds	, , i,						
neodecanoic acid, ethenyl ester							
2-propenoic acid, (pentabromo)methyl ester							
dibutylphthalate (DBP)						 	
diethylhexylphthalate (DEHP)							
Pharmaceuticals							
diosgenin						 	
aloogonin					1		

EU: European Union; H: Helcom Convention; O: Ospar Convention

5.2 ELVs under the MAP system

a) The LBS Protocol

The development of <u>common ELVs</u> within the scope of action of the Barcelona Convention and the Mediterranean Action Plan, is considered under the **LBS Protocol**. In particular, in its Article 7 on *Common Guidelines, Standards and Criteria*, it is stated that:

"The Parties shall progressively formulate and adopt, in cooperation with the competent international organizations, common guidelines and, as appropriate, standards or criteria..."

These standards will deal in particular with coastal outfalls, effluents treatment, quality of the sea-water, control and progressive replacement of products and processes, and also (7.1(e)):

"Specific requirements concerning the quantities of the substances discharged (listed in annex 1), their <u>concentration in effluents</u> and methods of discharging them."

It is also worthy to mention that the notion of <u>differentiated approach</u> is also introduced in Article 7.2 when it states that

"[...], such common guidelines, standards or criteria shall take into account local ecological, geographical and physical characteristics, the economic capacity of the Parties and their need for development, the level of existing pollution and the real absorptive capacity of the marine environment."

Furthermore,

"The action plans, programmes and measures [...] shall be adopted by taking into account, for their progressive implementation, the capacity to adapt and reconvert existing installations, the economic capacity of the Parties and their need for development"

In practice, the ELVs are implemented at local level (i.e. facility level) when the competent authority in each country approve the discharge permit or authorization. In the LBS Protocol this is regulated by Article 6, where it is stated that provisions of the Protocol and its Annex II will be taken into account to set the authorizations. These elements refer to:

- a) Characteristics and composition of discharges
- b) Characteristics of discharge constituents with respect to their harmfulness
- c) Characteristics of discharge site and receiving environment
- d) Availability of waste technologies
- e) Potential impairment of marine ecosystems and sea-water uses
- b) Adopted measures for the Control of Pollution by 1995 (MTS 95)

To progressively implement provisions of the LBS Protocol, it was envisaged that by 1995 common measures would be adopted for all substances listed in Annexes I and II to the Protocol. Up to October 1995, the Contracting Parties to the Barcelona Convention and Protocols had adopted the following common measures for the control of pollution for:

- **Bathing Waters** (as required by the Article 7.1(c) of the LBS Protocol) (1985);
- **Mercury** (Article 7.1(c)) (1985);
- Mercury Pollution (Item 4 of Annex I) (1987);
- Shellfish Waters (Article 7.1(c)) (1987);
- Used Lubricating Oils (Item 6 of Annex I) (1989);
- Cadmium and Cadmium Compounds (Item 5 of Annex I) (1989);
- Organotin Compounds (Item 3 of Annex I) (1989);
- Organohalogen Compounds (Item 1 of Annex I) (1989);
- Organophosphorus Compounds (Item 2 of Annex I) (1991);
- Persistent Synthetic Materials (Item 7 of Annex I) (1991);
- Radioactive Pollution (Item 9 of Annex I) (1991);
- Pathogenic Micro-Organisms (Item 7 of Annex II) (1991); and
- Carcinogenic, Teratogenic and Mutagenic Substances (Item 8 of Annex I) (1993).

The full texts of all common measures were reproduced in the MAP Technical Reports Series No. 95 (UNEP, Athens, 1995). Regarding adoption of specific ELVs, the following measures can be highlighted:

- Measures to Prevent **Mercury** Pollution
- Measures for Control of Pollution by **Cadmium** and Cadmium compounds
- Measures for Control of Pollution by **Organotin** Compounds

The first one states that Contracting Parties shall ensure a maximum concentration (to be calculated as a monthly average) of **50 µg mercury per litre** (expressed as total mercury) for all effluent discharges before dilution into the Mediterranean Sea.

To control pollution by cadmium and its compounds, the CPs shall adopt a limit value of **0.2 mg cadmium per litre discharged** (monthly flow-weighted average concentration of total cadmium) for effluent discharges from industrial plants into the Mediterranean Sea before dilution.

Finally, to control pollution by **organotin** compounds, the CPs agreed (as from 1 July 1991) **not to allow the use** in the marine environment of preparations containing organotin compounds on hulls of boats having an overall length of less than 25 m, and on all structures, equipment or apparatus used in mariculture.

The other measures did not included specific ELVs or restrictions of use.

c) The Strategic Action Programme (SAP)

The Strategic Action Programme to address pollution from land-based activities (SAP) (MAP TRS No. 119, 1998) adopted in 1997 by the Tenth Ordinary Meeting of the Contracting Parties. The SAP includes targets and measures to prevent pollution from the urban environment, agricultural and industrial sectors, for a range of pollutants and wastes.

Regarding the substances of concern identified in this report, the SAP proposes specific targets for reduction of heavy metals, organochlorines, organotin, pesticides and other persistent and toxic substances (e.g. dioxins and furans, HCB). Specific measures on the restriction of use and <u>phase out</u> are included for organotin (as adopted in 1995) and persistent organic pollutants such as chlorinated pesticides and PCBs (as adopted by the Stockholm Convention). The specific **ELV**s for <u>mercury</u> and <u>cadmium</u> adopted by CPs in 1995 are also included in the SAP. Additionally, the following ELVs are further develop:

- To adopt and apply for the industries of the <u>alkaline chloride electrolysis sector</u>, as well as the previous standard (50 µg mercury per litre), the maximum value of 0.5 grams of **mercury** in the water per tonne of chlorine production capacity installed (brine recirculation), 5 grams of mercury in the water per tonne (lost brine technology) and, if possible, 2 g of mercury from total releases into water, air and products).
- To regulate releases of organochlorines by the <u>paper and paper pulp industries</u> by limiting discharges measured as **AOX** (adsorbable organic halogen) to 1 kg per tonne of pulp produced and by reducing it further through the promotion of alternative bleaching to molecular chlorine and the use of BAT and BEP.

For other substances (e.g. PAHs), it is stated that ELVs will need to be formulated by 2010. The SAP also includes targets and measures to reduce the inputs of BOD, nutrients and suspended solids.

The preparation of guidelines for **BATs and BEPs** in industrial installations is a common measure proposed throughout the SAP. To this respect, the sectoral studies prepared by the MAP Regional Activity Centre on Cleaner Production can be very relevant to identify specific measures in priority sectors.

Finally, it must be noted that when adopting the SAP in 1997 the CPs agreed that, once the 1996 LBS Protocol come into force, the Strategic Action Programme would be resubmitted for adoption, and that a review of the SAP would be made to proceed to a possible revision of target dates and activities, if necessary.

6. Conclusions

- A review of potential compounds to be considered as priority pollutants in the Mediterranean region has been carried out. To this end, the lists of substances of concern for the marine environment identified in other regional marine conventions (OSPAR, HELCOM) have been provided (Annex A). Also, common priority substances resulting from an international comparison (Stockholm Convention, OSPAR, HELCOM, EU) have also been identified (Table 5).
- The priority criteria commonly used are in agreement with the LBS provisions (persistence, liability to bioaccumulate, toxicological risk,...) therefore these lists can be used as a basic reference to identify priority substances in the Mediterranean, to be refined with regionally specific circumstances such as occurrence of pollutants in the Mediterranean Sea, or use and emissions of substances.
- The broader scope of LBS and SAP to address land-based pollutants and activities should also be taken into account (i.e. consideration of other target categories such as nutrients and suspended solids).
- Occurrence of common priority substances in the Mediterranean region has also been reviewed. However, significant gaps of information have been identified, which difficult the elaboration of conclusive assessments for most of the substances. An integration of data and information from scientific literature, national monitoring programs, and regional programs (i.e. MED POL) is strongly recommended to properly assess the state of the Mediterranean marine environment. This assessment might be designed according to the eco-regions being proposed to address the ecosystem approach.
- A lack of comprehensive data has also been observed for emissions of pollutants from Mediterranean countries. However, the National Baseline Budget provides a key basis to identify priority activity sectors, if data is properly updated and complemented.
- Taking into account the reviewed information on common priority substances, its occurrence and releases in the Mediterranean region, as well as the review of common ELVs adopted in other international or regional frameworks, the following different approaches might be proposed:
 - <u>Substances which are currently being released</u> (e.g. heavy metals, PAHs, dioxins and furans): to use available and complementary information to identify priority sources and activity sectors in the different Mediterranean basins. The development and adoption of ELVs might be focused on these substances and sectors. To follow-up/monitor the effect of this measures in the marine environment.
 - 2. <u>Substances with already adopted international or regional measures</u> to restrict or phase out its use (e.g. DDTs, PCBs, TBTs, Brominated Flame Retardands): to ensure that these measures are implemented in all Mediterranean countries. To follow-up/monitor the effect of this measures in the marine environment.
 - 3. <u>Substances of concern with not enough information on releases and levels in</u> <u>the marine environment</u> (e.g. chlorinated paraffins, PFOS, phthalates, nonyl/octyl phenols, pharmaceuticals, 'modern' pesticides,...): to assess its occurrence in the Mediterranean marine environment, and its main sources.

7. References

Adami, G., Barbieri, P., Piselli, S., Predonzani, S., and Reisenhofer, E. (2000) Detecting and characterising sources of persistent organic pollutants (PAHs and PCBs) in surface sediments of an industrialized area (Harbour of Trieste, northern Adriatic Sea). J.Environ.Monit., 2, 261-265.

Angelidis, M. O., Aloupi, M. (2000) Geochemical Study of Coastal Sediments Influenced by River-Transported Pollution: Southern Evoikos Gulf, Greece. Environment International, 29, 935-948.

Axiak, V., Vella, A.J., Agius, D., Bonnici, P., Cassar, G., Cassone, R., Chircop, P., Micallef, D., Mintoff, B., Sammut, M. (2000) Evaluation of environmental levels and biological impact of TBT in Malta (central Mediterranean). Science of the Total Environment, 258, 89-97

Baldi, F., Bargagli, R., Focardi, S., Fossi, C. (1983) Mercury and chlorinated hydrocarbons in sediments from the bay of Naples and adjacent marine areas. Marine Pollution Bulletin, 14, 108-111.

Barakat A.O. (2004) Assessment of persistent toxic substances in the environment of Egypt. Environment International, 30, 309-322.

Bayarri, S., Baldassarri, L.T., Lacovella, N., Ferrara, F., di Domenico, A. (2001) PCDDs, PCDFs, PCBs and DDE in edible marine species from the Adriatic Sea. Chemosphere, 43, 601-610.

Bayen, S., Obbard, J.P., Thomas, G.O. (2006) Chlorinated paraffins: A review of analysis and environmental occurrence. Environment International, 32, 915-929.

Benlahcen, K. T., Chaoui, A., Budzinski, H., Bellocq, J., and Garrigues, Ph. (1997) Distribution and sources of polycyclic aromatic hydrocarbons in some Mediterranean coastal sediments. Mar.Pollut.Bull.,34, 298-305.

Bihari, N., Fafandel, M., Hamer, B., Kralj-Bilen, B. (2006) PAH content, toxicity and genotoxicity of coastal marine sediments from the Rovinj area, Northern Adriatic, Croatia. Sci.Total Environ., 366, 602-611.

Bihari, N., Fafandel, M., Piskur, V.(2007) Polycyclic Aromatic Hydrocarbons and Ecotoxicological Characterization of Seawater, Sediment, and Mussel *Mytilus galloprovincialis* from the Gulf of Rijeka, the Adriatic Sea, Croatia. Arch.Environ.Contam.Toxicol., 52, 379-387.

Binelli, A., Guzzella, L., Roscioli, C. (2008) Levels and congener profiles of polybrominated diphenyl ethers (PBDEs) in Zebra mussels (*D. polymorpha*) from Lake Maggiore (Italy). Environmental Pollution, 153, 610-617.

Bodiguel, X; Tronczynski, J; Loizeau, V; Munschy, C; Guiot, N; Le Guellec, AM; Olivier, N; Roupsard, F; Mellon, C (2008) Classical and novel organohalogen compounds (PCBs and PBDEs) in hake (*M. merluccius*, L.) from the Mediterranean and Atlantic coasts (France). Environmental Toxicology II, 110, 157-166.

Borghi, V., Porte, C. (2002) Organotin pollution in deep-sea fish from the north-western Mediterranean. Environmental Science & Technology, 36, 4224-4228.

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Borrell, A., Aguilar, A. (2007) Organochlorine concentrations declined during 1987-2002 in western Mediterranean bottlenose dolphins, a coastal top predator. Chemosphere, 66, 347-352.

Böttcher, M. E., Rinna, J., Warning, B., Wehausen, R., Howell, M. W., Schnetger B., Stein, R., Brumsack, H. -J., Rullkötter, J. (2003) Geochemistry of sediments from the connection between the western and the eastern Mediterranean Sea (Strait of Sicily, ODP Site 963). Palaeogeogr., Palaeoclimatol., Palaeoecol., 190:165–194.

Boughriet, A., Proix, N., Billon, G., Recourt, P., Ouddane, B. (2007) Environmental impacts of heavy metal discharges from a smelter in Deule-canal sediments (Northern France): Concentration levels and chemical fractionation. Water Air and Soil Pollution, 180, 83-95.

Bouloubassi, I., Saliot, A. (1993) Investigation of anthropogenic and natural organic inputs in estuarine sediments using hydrocarbon markers (NAH, LAB, PAH). Oceanologica Acta, 16, pp 145-161.

Buccolieri, A., Buccolieri, G., Cardellicchio, N., Dell'Atti, A., Di Leo, A., Maci, A. (2006) Heavy metals in marine sediments of Taranto Gulf (Ionian Sea, Southern Italy). Marine chemistry, 99, 227-235.

Capelli, R., Das, K., De Pellegrini, R., Drava, G., Lepoint, G., Miglio, C., Minganti, V., Pogg, R. (2007) Distribution of trace elements in organs of six species of cetaceans from the Ligurian Sea (Mediterranean), and the relationship with stable carbon and nitrogen ratios. Sci.Total Environ., 390: 569-578.

Cardellicchio, N., Decataldo, A., Di Leo, A., Giandomenico, S. (2002) Trace elements in organs and tissues of striped dolphins (*Stenella coeruleoalba*) from the Mediterranean Sea (Southern Italy). Chemosphere, 49, 85-90.

Cardellicchio, N., Buccolieri, A., Di Leo, A., Giandomenico, S., Spada, L. (2008) Levels of metals in reared mussels from Taranto Gulf (Ionian Sea, Southern Italy). Food Chemistry, 107, 890-896.

Cardellicchio, N., Buccolieri, A., Giandomenico, S., Lerario, V.L., Lopez, L., Pizzulli, F. (2006) Distribution and occurrence of polycyclic aromatic hydrocarbons (PAHs) in sediments from the Mar Grande and Gulf of Taranto (Ionian Sea, Southern Italy). Annali di Chimica, 96, pp 51-64.

Carvalho, F., Civili, F. (2001) Monitoring of the Mediterranean Sea pollution (MED POL) and data quality assurance. The International Journal of Environmental Studies, 58, pp 139-158.

Castells, P., Parera, J., Santos, F. J., Galceran, M. T. (2008) Occurrence of polychlorinated naphthalenes, polychlorinated biphenyls and short-chain chlorinated paraffins in marine sediments from Barcelona (Spain). Chemosphere, 70, 1552-1562.

Chandrinou, S., Stasinakis, A.S., Thomaidis, N.S., Nikolaou, A., Wegener, J.W. (2006) Distribution of organotin compounds in the bivalves of the Aegean Sea, Greece. Environment International, 33, 226-232.

Choi, S.C., Wai, O.W.H., Choi, T.W.H., Li, X.D., Tsang, C.W. (2006) Distribution of cadmium, chromium, copper, lead and zinc in marine sediments in Hong Kong waters. Environmental Geology, 51, 455-461

Civili, F.S., Jeftic, L. (1987) The co-ordinated programme for research and monitoring of pollution in the Mediterranean. Chemosphere, 16, 633-649.

Conti, M.E., Cecchetti, G. (2003) A biomonitoring study: trace metals in algae and molluscs from Tyrrhenian coastal areas. Environmental Research, 93, 99-112.

Corsi I, Focardi S (2002) Nonylphenols in a lagoon environment: p-nonylphenol and nonylphenol ethoxylates in fish tissue. Bulletin of Environmental Contamination and Toxicology, 68, 908-914.

Corsolini, S., Guerranti, C., Perra, G., Focardi, S. (2008) Polybrominated Diphenyl Ethers, Perfluorinated Compounds and Chlorinated Pesticides in Swordfish (*Xiphias gladius*) from the Mediterranean Sea. Environ. Sci. Technol., 42, 4344-4349.

Culotta, L., De Stefano, C., Gianguzza, A., Mannino, MR., Orecchio, S. (2006) The PAH composition of surface sediments from Stagnone coastal lagoon, Marsala (Italy) Marine Chemistry, 99, pp 117-127.

Deudero, S., Box, A., March, D., Valencia, J.M., Grau, A.M., Tintore, J., Calvo, M., Caixach J. (2007) Organic compounds temporal trends at some invertebrate species from the Balearics, Western Mediterranean. Chemosphere, 68, 1650-1659.

Di Leonardo, R., Tranchida, G., Bellanca, A., Neri, R., Angelone, M., Mazzola, S. (2006). Mercury levels in sediments of central Mediterranean Sea: A 150+ year record from box-cores recovered in the Strait of Sicily. Chemosphere, 65, 2366-2376.

Diez, S., Ábalos, M., Bayona, J. M. (2001) Organotin contamination in sediments from the Western Mediterranean enclosures following 10 years of TBT regulation. Water Research, 36, 905-918.

Diez, S., Jimenez, J., Bayona, J.M. (2003) Recent status and historical trends of the organotin contamination in sediments from the Western Mediterranean Sea, Ciencias Marinas, 29, 547-560.

Diez, S., Jover, E., Albaiges, J., Bayona, J.M. (2006) Occurrence and degradation of butyltins and wastewater marker compounds in sediments from Barcelona harbor, Spain. Environment International, 32, 858-865.

EEA (2006) Priority issues in the Mediterranean environment. European Environment Agency (EEA). EEA Report No 4/2006, Copenhagen 2006.

El Deeb, K., Said, T.O., El Naggar, M.H., Shreadah, M.A. (2007) Distribution and Sources of Aliphatic and Polycyclic Aromatic Hydrocarbons in Surface Sediments, Fish and Bivalves of Abu Qir Bay (Egyptian Mediterranean Sea). Bull.Environ.Contam.Toxicol., 78, pp 373-379.

Eljarrat, E., Barcelo, D. (2006) Quantitative analysis of polychlorinated n-alkanes in environmental samples. Trac-Trends in Analytical Chemistry, 25, 421-434

Eljarrat, E., Caixach, J., Rivera, J. (2001a) Toxic Potency Assessment of Nonand Mono-ortho PCBs, PCDDs, PCDFs, and PAHs in Northwest Mediterranean Sediments (Catalonia, Spain). Environ.Sci.Technol., 35, pp 3589-3594.

Eljarrat, E., De La Cal, A., Larrazabal, D., Fabrellas, B., Fernandez-Alba, A.R., Borrull, F., Marce, R.M., Barcelo, D. (2005) Occurrence of polybrominated diphenylethers, polychlorinated dibenzo-p-dioxins, dibenzofurans and biphenyls in coastal sediments from Spain. Environmental Pollution, 136, 493-501.

Erdogrul, O., Covaci, A., Schepens, P. (2005) Levels of organochlorine pesticides, polychlorinated biphenyls and polybrominated diphenyl ethers in fish species from Kahramanmaras, Turkey. Environment International, 31, 703-711.

European Commission (2001) Identification of Priority Hazardous Substances, Modified procedure in accordance with Article 16(3) of the Water Framework Directive. Working Document ENV/191000/01 of the Commission Services. European Commission. Brussels, 16 January 2001.

Ferrara F., Funari E., De Felip E., Donati G., Traina M. Elsa, Mantovani A. (2001). Alkylphenolic compounds in edible molluscs of the Adriatic Sea (Italy)" Environ. Sci. Technol., 35, 3109-3112.

Ferrara, F., Fabietti, F., Delise, M., Funari, E. (2005) Alkylphenols and alkylphenol ethoxylates contamination of crustaceans and fishes from the Adriatic Sea (Italy). Chemosphere, 59, 1145-1150.

Focardi, S., Corsolini, S., Aurigi, S., Pecetti, G., Sanchez-Hernandez, J.C. (2000) Accumulation of butyltin compounds in dolphins stranded along the Mediterranean coasts. Applied Organometallic Chemistry, 14, 48-56.

Fossi, M.C., Marsilia, L., Lauriano, G., Fortuna, C., Canese, S., Ancora, S., Leonzio, C., Romeo, T., Merino, R., Abad, E., Jiménez B. (2004) Assessment of toxicological status of a SW Mediterranean segment population of striped dolphin (*Stenella coeruleoalba*) using skin biopsy. Marine Environmental Research, 58, 269-274.

GESAMP (1990) Review of potentially harmful substances. Choosing priority organochlorines for marine hazard assessment, Food and Agricultural organisation. Joint Group of Experts on the Scientific Aspects of Mainre Environmental Protection, Rome, Italy.

Giesy, J.P., Kannan, K. (2001) Global distribution of perfluorooctane sulfonate in wildlife. Environ. Sci. Technol., 35, 1339–1342.

Gomez-Gutierrez, A., Garnacho, E., Bayona, J.M., Albaiges, J. (2007) Assessment of the Mediterranean sediments contamination by persistent organic pollutants. Environmental Pollution, 148, 396-408

Hansen, K.J., Clemen, L.A., Ellefson, M.E., Johnson, H.O. (2001) Compound-specific, quantitative characterization of organic fluorochemicals in biological matrices. Environ. Sci. Technol., 35, 766–770.

Hart, K., Kannan, K., Isobe, T., Takahashi, S., Yamada, T.K., Miyazaki, N., Tanabe, S. (in press) Time Trends and Transplacental Transfer of Perfluorinated Compounds in Melon-Headed Whales Stranded along the Japanese Coast in 1982, 2001/2002, and 2006. Environ. Sci. Technol., DOI: 10.1021/es801224v.

Hassani, L.H., Garrido Frenich, A., Benajiba, M.H., González Rodríguez, M.J., Martínez Vidal, J.L., Debdoubi, A. (2006) Assessment of Assessment of Butyltin and Phenyltin Pollution in the Sea Mullet, *Mugil cephalus*, Along the Moroccan and Spanish Coasts (Mediterranean Sea) Archives of Environmental Contamination and Toxicology, 51, 608-614.

Jimenez, B., Gonzalez, M.J., Jimenez, O., Reich, S., Eljarrat, E., Rivera J. (1999) Evaluation of 2,3,7,8 Specific Congener and Toxic Potency of Persistent Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans in Cetaceans from the Mediterranean Sea, Italy. Environmental Science & Technology, 34, 756-763.

Johansson, I., Heas-Moisan, K., Guiot, N., Munschy, C., Tronczynski, J. (2006) Polybrominated diphenyl ethers (PBDEs) in mussels from selected French coastal sites: 1981-2003. Chemosphere, 64, 296-305.

Kannan, K., Koistinen, J., Beckmen, K., Evans, T., Gorzelany, J., Hansen, K.J., Jones, P.D., Giesy, J.P. (2001) Accumulation of perfluorooctane sulfonate in marine mammals. Environ. Sci. Technol., 35, 1593–1598.

Kannan, K., Corsolini, S., Focardi, S., Tanabe, S., Tatsukawa, R. (1995) Accumulation pattern of butyltin compounds in dolphin, tuna, and shark collected from Italian coastal Waters. Archives of Environmental Contamination and Toxicology, 31, 19-23.

Kannan, K., Corsolini, S., Falandysz, J., Oehme, G., Focardi, S., Giesy, J. P. (2002) Perfluorooctanesulfonate and related fluorinated hydrocarbons in marine mammals, fishes, and birds from coasts of the Baltic and Mediterranean Seas. Environ. Sci. Technol., 36, 3210–3216.

Klein, W., Denzer, S., Herrchen, M., Lepper, P., Müller, M., Sehrt, R., Storm, A., Volmer, J. (1999) Revised Proposal for a List of Priority Substances in the Context of the Water Framework Directive (COMMPS Procedure). Declaration Ref. 98/788/3040/DEB/E1. Fraunhofer-Institute, Schmallenberg, Germany, June 1999.

Kljaković-Gašpić, Z., Ujević, I., Zvonarić T., Barić, A. (2007) Biomonitoring of trace metals (Cu, Cd, Cr, Hg, Pb, Zn) in Mali Ston Bay (eastern Adriatic) using the Mediterranean blue mussel (1998-2005). Acta Adriat., 48, 73 – 88.

Labandeira, A., Eljarrat, E., Barcelo, D. (2007) Congener distribution of polybrominated diphenyl ethers in feral carp (*Cyprinus carpio*) from the Llobregat River, Spain. Environmental Pollution, 146, 188-195.

Lafabrie, C., Pergent, G., Kantin, R., Pergent-Martini, C., Gonzalez, J. L. (2007) Trace metals assessment in water, sediment, mussel and seagrass species – Validation of the use of *Posidonia oceanica* as a metal biomonitor. Chemosphere, 68, 2033-2039.

Law, R.J., Allchin, C.R., de Boer, J., Covaci, A., Herzke, D., Lepom, P., Morris, S., Tronczynski, J., de Wit, C.A. (2006) Levels and trends of brominated flame retardants in the European environment. Chemosphere, 64, 187-208.

Lo Turco, V., Di Bella, G., La Pera, L., Conte, F., Macri, B., mo Dugo, G. (2007) Organochlorine pesticides and polychlorinated biphenyl residues in reared and wild *Dicentrarchus labrax* from the Mediterranean Sea (Sicily, Italy). Environmental Monitoring and Assessment, 132, 411-417.

Marcomini, A., Pavoni, B., Sfriso, A., Orio, A. (1990). Persistent metabolites of alkylphenol polyethoxylates in the marine environment. Mar. Chem., 29, 307-323.

Mariottini, M., Corsi, I., Della Torre, C., Caruso, T., Bianchini, A., Nesi, I., Focardi, S. (2008) Biomonitoring of polybrominated diphenyl ether (PBDE) pollution: A field study. Comparative Biochemistry and Physiology C-Toxicology & Pharmacology, 148, 80-86.

Martinez-Llado, X., Gibert, O., Marti V., Diez, S., Romo, J., Bayona, J.M., de Pablo, J. (2007) Distribution of polycyclic aromatic hydrocarbons (PAHs) and tributyltin (TBT) in Barcelona harbour sediments and their impact on benthic communities. Environmental Pollution, 149, 104-113.

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Martin-Skilton, R., Lavado, R., Thibaut. R., Minier, C., Porte, C. (2006) Evidence of endocrine alteration in the red mullet, *Mullus barbatus* from the NW Mediterranean. Environmental Pollution, 141, 60-68.

Monaci, F., Borrell, A., Leonzio, C., Marsili, L., Calzada, N. (1998) Trace elements in striped dolphins (*Stenella coeruleoalba*) from the western Mediterranean. Environmental Pollution, 99, 61-68.

Morcillo, Y., Borghi, V., Porte, C. (1996) Survey of Organotin Compounds in the Western Mediterranean using Molluscs and Fish as Sentinel Organisms. Earth and Environmental Science, 32, 198-203.

Mostafa, A.R., Barakat, A.O., Qian, Y., Wade, T.L. (2003) Composition, distribution and sources of polycyclic aromatic hydrocarbons in sediments of the western harbour of Alexandria, Egypt. J.Soils Sediments, 3, pp 173-179.

Munschy, C., Guiot, N., Héas-Moisan, K., Tixier, C., Tronczyński, J. (2008) Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) in marine mussels from French coasts: Levels, patterns and temporal trends from 1981 to 2005. Marine Pollution Bulletin, 54, 657-668.

Naso, B., Perrone, D., Ferrante, M.C., Bilancione, M., Lucisano, A. (2005) Persistent organic pollutants in edible marine species from the Gulf of Naples, Southern Italy Science of the Total Environment, 343, 83-95.

Notar, M., Leskovsek, H., Faganeli, J. (2001) Composition, distribution and sources of polycyclic aromatic hydrocarbons in sediments of the Gulf of Trieste, Northern Adriatic Sea. Mar.Pollut.Bull., 42, pp 36-44.

Ogrinc, N., Monperrus, M., Kotnik, J., Fajon, V., Vidimova, K., Amouroux, D., Kocman, D., Tessier, E., Žižek, S., Horvat, M. (2007) Distribution of mercury and methylmercury in deep-sea surficial sediments of the Mediterranean Sea. Marine Chemistry, 107, 31-48.

OSPAR (2002) Guidance on How to Apply the Safety Net Procedure for the Inclusion of Substances in the List of Substances of Possible Concern. OSPAR Commission, Ref. 2002-10.

OSPAR (2005) Cut-Off Values for the Selection Criteria of the OSPAR Dynamic Selection and Prioritisation Mechanism for Hazardous Substances. OSPAR Commission Ref. 2005-9.

OSPAR (2006) Dynamic Selection and Prioritisation Mechanism for Hazardous Substances (New DYNAMEC Manual). OSPAR Commission Ref. 256/2006.

OSPAR (2007) OSPAR List of Chemicals for Priority Action (Update 2007). OSPAR Commission Ref. 2004-12.

Parera, J., Santos, F.J., Galceran, M.T. (2004) Microwave-assisted extraction versus Soxhlet extraction for the analysis of short-chain chlorinated alkanes in sediments. Journal of Chromatography A, 1046, 19-26.

Pastor, D., Boix J., Fernández, V., Albaigés, J. (1996). Bioaccumulation of organochlorinated contaminants in three estuarine fish species (*Mullus barbatus*, *Mugil cephalus* and *Dicentrarchus labrax*). Mar. Pollut. Bull., 32, 257-262.

Pettersson, A., van Bavel, B., Engwall, M., Jimenez, B. (2004) Polybrominated diphenylethers and methoxylated tetrabromodiphenylethers in cetaceans from the Mediterranean Sea. Archives of Environmental Contamination and Toxicology, 47, 542-550.

Porte, C., Escartin, E., Garcia, L.M., Solé, M., Albaigés, J. (2000). Xenobiotic metabolizing enzymes and antioxidant defences in deep-sea fish: relationship with contaminant body burden. Mar. Ecol. Progr. Series, 192, 259-266.

Roose, P., Brinkman, U. (2005) Monitoring organic microcontaminants in the marine environment: principles, programmes and progress. Trends in Analytical Chemistry, 24, pp 897-920.

Rotllant, G., Abad, E., Sardà, F., Ábalos, M., Company, J.B., Rivera, J. (2006) Dioxin compounds in the deep-sea rose shrimp *Aristeus antennatus* (Risso, 1816) throughout the Mediterranean Sea. Deep Sea Research Part I: Oceanographic Research Papers, 53, 1895-1906.

Roussiez, V., Ludwig, W., Monaco, A., Probst, J.L, Bouloubassi, I., Buscail, R., Saragoni, G. (2006) Sources and sinks of sediment-bound contaminants in the Gulf of Lions (NW-Mediterranean Sea): A multi-tracer approach. Continental Shelf Research, 26, 1843-1857.

Said, T.O., El Moselhy, K.M., Rashad, A.A.M., Shreadah, M.A. (2008) Organochlorine contaminants in water, sediment and fish of Lake Burullus, Egyptian Mediterranean Sea. Bulletin of Environmental Contamination and Toxicology, 81, 136-146.

Said, T.O., Farag, R.S., Younis, A.M., Shreadah, M.A. (2006) Organotin species in fish and bivalves samples collected from the Egyptian Mediterranean coast of Alexandria, Egypt. Bulletin of Environmental Contamination and Toxicology, 77, 451-458.

Schure, A.F.H., Larsson, P., Agrell, C., Boon, J.P., (2004) Atmospheric transport of polybrominated diphenyl ethers and polychlorinated biphenyls to the Baltic Sea. Environ. Sci. Technol., 38, 1282–1287.

Sklivagou, E., Varnavas, S.P., Hatzianestis, J. (2001) Aliphatic and Polycyclic Aromatic Hydrocarbons in surface sediments from Elefsis Bay, Greece (Eastern Mediterranean). Toxicological and Environmental Chemistry, 79, pp 195-210.

Storelli, M. M., Casalino, E., Barone, G., Marcotrigiano, G.O. (2008) Persistent organic pollutants (PCBs and DDTs) in small size specimens of bluefin tuna (*Thunnus thynnus*) from the Mediterranean Sea (Ionian Sea). Environment International, 34, 509-513.

Storelli, M.M., Barone, G., Santarnaria, N., Marcotrigiano, G.O. (2006) Residue levels of DDTs and toxic evaluation of polychlorinated biphenyls (PCBs) in *Scyliorhinus canicula* liver from the Mediterranean Sea (Italy). Marine Pollution Bulletin, 52, 696-700.

Storelli, M.M., D'Addabbo, R., Marcotrigiano, G.O. (2004) Temporal trend of persistent organic pollutants in codfish-liver from the Adriatic Sea, Mediterranean Sea, 1993-2003. Bulletin of Environmental Contamination and Toxicology, 73, 331-338.

Storelli, M.M., Giacominelli-Stuffler, R., Storelli, A., Marcotrigiano G.O. (2005) Accumulation of mercury, cadmium, lead and arsenic in swordfish and bluefin tuna from the Mediterranean Sea: A comparative study. Marine Pollution Bulletin, 50, 1004-1007.

Sunlu, U. (2006) Trace metal levels in mussels (*Mytilus galloprovincialis* L. 1758) from Turkish Aegean Sea coast. Environmental Monitoring and Assessment, 114, 273-286.

Tolun, L., Okay, O.S., Gainesb, A.F., Tolayc, M., Tüfekçi, H., Kiratli, N. (2001) The pollution status and the toxicity of surface sediments in Izmit Bay (Marmara Sea), Turkey. Environment International, 26, pp 163-168.

Trabelsi, S., Driss, M.R. (2005) Polycyclic aromatic hydrocarbons in superficial coastal sediments from Bizerte Lagoon, Tunisia. Mar.Pollut.Bull. 50, pp 344-359.

UNEP/GEF (2002) Regionally Based Assessment of Persistent Toxic Substances. Mediterranean Region. UNEP Chemicals, Geneva, 158 pp.

UNEP/MAP (1996) The State of the Marine and Coastal Environment in the Mediterranean Region. MPA Technical Reports Series, Nr 100. UNEP, Athens.

UNEP/MAP (1999) Strategic Action Programme to Address Pollution from Land based Activities (SAP MED). Athens, 1999.

UNEP/MAP (2002). Guidelines for the Preparation of the Baseline Budget of Pollutants Releases. Athens.

Unlu, S., Alpar, B. (2006) Distribution and sources of hydrocarbons in surface sediments of Gemlik Bay (Marmara Sea, Turkey). Chemosphere, 64, pp 764-777.

Vesely, J., Almquist-Jacobson, H., Miller, L. M., Norton, S. A., Appleby, P., Dixit, A. S., Smol, J. P. (1993) The history and impact of air pollution at Čertovo Lake, south-western Czech Republic. Journal of Paleolimnology, 8, 211-231.

Villeneuve, J.P., Carvalho, F.P., Fowler, S.W., Cattini, C. (1999) Levels and trends of PCBs, chlorinated pesticides and petroleum hydrocarbons in mussels from the NW Mediterranean coast: comparison of concentrations in 1973/1974 and 1988/1989. Science of the Total Environment, 238, 57-65.

Zaghden, H., Kallel, M., Elleuch, B., Oudot, J., Saliot, A. (2007) Sources and distribution of aliphatic and polyaromatic hydrocarbons in sediments of Sfax, Tunisia, Mediterranean Sea. Marine Chemistry, 105, 70-89.

Categories / Subcategories / Substances	CAS No	OSPAR	HELCOM
Metals and related compounds			
Metals			
Arsenic	7440382		Х
Cadmium	7440439		Х
Chromium	7440473		Х
Copper	7440508		Х
Lead	7439921		Х
Mercury	7439976		Х
Nickel	7440020		Х
Selenium	7782492		Х
Zinc	7440666		X
Metal compounds			
Cadmium Chloride	10108-64-2	Х	
Organometallic Compounds			
Nickel compounds			
Tetracarbonyl nickel	13463393		Х
Diphenylchloro arsine	712481		Х
Ethyldichloro arsine	598141		Х
Stannane, fluorotris-p-chlorophenyl-	427-45-2	X	
Organolead compounds			
Tetramethyllead (TML)	75-74-1	X	
Tetraethyllead (TEL)	78-00-2	X	X
Organotin compounds (Trialkyltin			
compounds)			
Tributyltin compounds		Х	Х
Dibutylbis (oxylauroyl) tin	77587		Х
Dibutyltinoxide	818086		Х
Tetrabutyltin	1461252		Х
Triphenyltin compounds	n.a.		X
Hydrocarbons (HC)	·		
Aliphatic HC			
Alkanes and Cycloalkanes			
Carbontetrachloride	56235		X
Pentane	109660		Х
Octane	111659		Х
Cyclohexane	110827		Х
Methylcyclohexane	108872		X
cyclododecane	294-62-2	X	
Alkenes and Cycloalkenes			
1-propene, tetramer	6842-15-5	X	
1,5,9-cyclododecatriene	4904-61-4	X	
cyclohexene, 1-methyl-4-(1-methylethenyl)-,	5080 27 5	v	
(R)-	0909-21-0	^	
bicyclo[3.1.1]hept-2-ene, 2,6,6-trimethyl-	80-56-8	Х	
bicyclo[2.2.1]heptane, 2,2-dimethyl-3-	79-92-5	х	
Ineuryiene-			
Aromatic HC			

Annex A. Lists of Substances of Possible Concern for the marine environment

Benzenes			
Benzene	71432		Х
Ethylbenzene	100414		Х
Isopropylbenzene	98828		Х
benzene, 1,1'-methylenebis-	101-81-5	Х	Х
benzene, 1,3,5-tris(1,1-dimethylethyl)-	1460-02-2	Х	
benzene, bis(1-methylethyl)-	25321-09-9	Х	
Biphenyl	92-52-4		Х
Terphenyl	26140-60-3	Х	
Toluenes and Xylenes			
1,2-xylene (o-xylene)	95476		Х
1,3-xylene (m-xylene)	108383		Х
1,4-xylene (p-xylene)	106423		Х
4-tert-Butyltoluene	98511		Х
Ethyltoluene (mixed isomers)	25550145		Х
Toluene	108883		Х
Polycyclic Aromatic Hydrocarbons			
PAHs	50328		х
Pvrene	129-00-0	Х	
benzo(a)pyrene	50-32-8	X	
benzolelpyrene	192-97-2	Х	
pyrene. 1-nitro-	5522-43-0	X	
pyrene, 1.3.6.8-tetrabromo-	128-63-2	X	
Fluoranthene	206-44-0		Х
benzo(k)fluoranthene	207-08-9	Х	
Anthracene	120-12-7	X	x
dibenz[a h]anthracene	53-70-3	X	
benz[a]anthracene	56-55-3	X	
benz[a]anthracene 7 12-dimethyl-	57-97-6	X	
7H-benz[de]anthracene-7-one	82-05-3	X	
7H-benz[de]anthracen-7-one 3.9-dibromo-	81-98-1	X	
dibenz[a i]anthracene	224-41-9	X	
Phenantrene	85018		х
benzolciphenanthrene	195-19-7	x	
pervlene	198-55-0	X	
benzo(a h i)pervlene	191-24-2	X	
naphthacene	92-24-0	X	
coronene	191-07-1	X	
Acenaphthene	83329		х
acenaphthylene 12-dihydro-	83-32-9	Х	
Naphthalene	91203		x
Chloronaphthalene (all isomers)	25586430	Х	X
pentachloronaphthalene	1321-64-8	X	X
trichloronaphthalene	1321-65-9	X	X
hexachloronanhthalene	1335871	X	X
tetrachloronaphthalene	1335-88-2	X	X
octachloronaphthalene	2231-13-1	X	x
heptachloronaphthalene	32241-08-0	X	x
naphthalene, chloro derivs	70776-03-3	X	
naphthalene, bis(1-methylethyl)-	38640-62-9	X	
perylo[3,4-cd:9,10-c'd']dipyran-1,3,8,10-	128 60 9	v	
tetrone	120-09-0	^	
benzo[rst]pentaphene	189-55-9	Х	

dibenzothiophene	132-65-0	X	
benz[j]aceanthrylene, 1,2-dihvdro-3-methvl-	56-49-5	Х	
triphenylene	217-59-4	X	
benzo[b]triphenvlene	215-58-7	X	
chrysene	218-01-9	X	
chrysene 6-methyl-	1705-85-7	X	
chrysene 1-methyl-	3351-28-8	X	
[1 1'-bianthracenel-9 9' 10 10'-tetrone 1 4'-	0001200		
diamino-	4051-63-2	Х	
dibenzo[b,def]chrysene	189-64-0	Х	
dibenzo[def,mno]chrysene	191-26-4	X	
dibenzo[def,p]chrysene	191-30-0	X	
naphtho[1,2,3,4-def]chrysene	192-65-4	X	
1,2,3,4,7,7-Hexachloronorbornadiene	3389717		Х
2-Chloroantraguinone	131099		Х
Products			
Mineral oil	8012951		х
anthracene oil	90640-80-5	x	
anthracene oil anthracene paste	90640-81-6	X	
anthracene oil, anthracene low	00640 82 7		
distillatos, coal tar, boavy oile	90040-02-7		
uistiliates, coal tai, fiedvy olis	90040-00-1	^	
anthracene oil, anthracene paste, anthracene fraction	91995-15-2	Х	
anthracene oil, anthracene paste, distn.	91995-17-4	х	
distillates (coal tar), heavy oils, pyrene	91995-42-5	x	
traction			
distillates (coal tar), pitch, pyrene fraction	91995-52-7	X	
residues (coal tar), pitch distn.	92061-94-4	X	
distillates (petroleum), alkene-alkyne manuf.	101316-50-1	x	
pyrolysis oil, condensed arom. ring-contg.			
Synthetic Musk			
1H-indene, 2,3-dihydro-1,1,3,3,5-	116-66-5	x	
pentamethyl-4,6-dinitro-			
2,4,6-trinitro-	81-15-2	X	X
benzene, 1-(1,1-dimethylethyl)-2-methoxy-4- methyl-3,5-dinitro-	83-66-9	х	
Phonols	·	•	
Butylphenol	98544	Y	X
Nonvinhenol	25151 52 2		^
	1044-52-5		v
Nonyipiterioi, 4-	104405	<u>^</u>	X
Nonyiphenoietnoxylate	9016459	X	X
Nonylphenolethoxylate carboxylic acid			X
Octylphenol	140669	X	X
Octylphenolethoxylate	9036195		Х
Butylhydroxyanisol	25013165	X	Х
phenol, 2,4-bis(1,1-dimethylpropyl)-	120-95-6	X	
phenol, 2-(2H-benzotriazol-2-yl)-4-(1,1,3,3-	3147 75 0		
tetramethylbutyl)-	5147-75-9	^	
phenol, 2-(2H-benzotriazol-2-yl)-4,6-bis(1,1-	38/6-71 7	x	
dimethylethyl)-			
4,4'-methylethylidenebisphenol	80-05-7	Х	
Isooctvl-phenol	11081-15-5	X	

phenol, 4-(1,1-dimethylethyl)-, hydrogen	21150-89-0	х	
phenol, 2-(2H-benzotriazol-2-yl)-4,6-bis(1,1-	25973-55-1	x	
dimethylpropyl)-	20070-00-1	^	
benzaldehyde, 2-hydroxy-5-nonyl-, oxime	50849-47-3	Х	
4-nonyl-phenol, branched	84852-15-3	X	
Nonyl-phenol, manuf. of, by-products from, high-boiling	90481-05-3	х	
1 1 3 3-Tetramethyl-4-butylphenol	140669		Х
2-Methoxy-4-propenyiphenol	97541		X
2-Methylphenol	95487		X
4 4'-Methylethylidenebisphenol	80057		X
Dinitro-2-methylohenol	1335850		X
phenol 2.6-bis(1-methylpropyl)-	5510-00-6	x	Χ
Dedeevlebanel (mixed isomers)	27102969	^	V
	27 193000		^
Organohalogen Compounds			
Halogenated Aliphatic HC			
chlorinated paraffins CP (C10-C30)			
Short-chained Chlorinated paraffins C10-C13	85535-84-8	Х	
Medium chained Chlorinated paraffins C14-	95525 95 0	v	
C17	00000-00-9	^	
Paraffin waxes and hydrocarbon waxes,	62440 20 9		
chlorinated	03449-39-0	X	
Dichloromethane	75092		Х
Trichloromethane	67663		Х
1,1-Dichloroethane	75343		Х
1,2-Dichloroethane	107062		Х
1.1.1-Trichloroethane	71556		Х
1.1.2-Trichloroethane	79005		Х
1,1,2,2-Tetrachloroethane	79345		X
Pentachloroethane	76017		X
Hexachloroethane	67721	x	X
1 2-Dichloropropane	78875		X
1-Chlorohexane	544105		X
1 6-Dichlorohexane	2163000		X
1 1 2-Trichlorotrifluoroethane	76131		X
hexane tetradecafluoro-	355_12_0	x	Χ
hexane 1112233445566	000-42-0	~	
tridecafluoro_6_iodo_	355-43-1	X	
	335-57-0	x	
1 butanesulfonvil fluoride 112233444	333-37-9	^	
	375-72-4	X	
1 boxanosulfonyl fluorido			
1.1.2.2.3.3.4.4.5.5.6.6.6-tridecafluoro-	423-50-7	X	
Tetabromomethane	558134		x
hovabromododocano	26447 40 4	v	^
	20441-49-4	^	
Chloroothono	75014		V
	107054		X
	107051		X
	75054		
1,1-Dichloroethene	/5354		X
1,2-Dichloroethene	540590	ļ	X
Trichloroethylene	79016		X

Tetrachloroethvlene	127184		Х
1.3-Dichloropropene	542756		X
2 3-Dichloropropene	78886		X
2-Chloro-1 3-butadiene	126998		X
hentachloronorbornene	28680-45-7	x	
hicyclo(2,2,1)bentan_2_one1,7,7_trimethyl_3_	20000 40 7	<u> </u>	
[(4-methylphenyl)methylene]	36861-47-9	X	
$\frac{123477}{12}$			
$beychloro_{-}$	3389-71-7	X	
Halogenated solvents			X
Halogenated Aromatic HC			<u></u>
Chlorobonzonos			
Monochlorobenzene	108007		V
Dichlorobonzono	100907		^
	106467		×
1,4-Dichlorobenzene	05501		
	90001		X
	541731		X
	12002481	X	X
1,2,3-trichlorobenzene	87-61-6	X	X
1,2,4-trichlorobenzene	120-82-1	X	X
1,3,5-trichlorobenzene	108-70-3	X	X
<u>Tetrachorobenzenes</u>			
1,2,4,5- Tetrachlorobenzene	95943	X	Х
benzene, 1,2,3,4-tetrachloro-	634-66-2	Х	
benzene, 1,2,3,5-tetrachloro-	634-90-2	Х	
benzene, pentachloro-	608935	X	Х
benzene, 1,1'-methylenebis[4-chloro-	101-76-8	X	
benzene, 1,4-dichloro-2,5-	11000-81-2	x	
bis(dichloromethyl)-	41999-04-2	^	
benzene, 1-chloro-2-(chlorodiphenylmethyl)-	42074-68-0	X	
hexabromo-benzene	87-82-1	Х	
pentabromoethylbenzene	85-22-3	Х	
benzene, 1,2,4,5-tetrachloro-3-methoxy-	6936-40-9	Х	
benzene, 1,3,5-tribromo-2-(2-propenyloxy)-	327889-5	X	
dibenzo[def,mno]chrysene-6,12-dione, 4,10-	4070 64 4	V	
dibromo-	4378-01-4	^	
benzene, 1,1'-(1-methylethylidene)bis[3,5-	21050 44 2	V	
dibromo-4-(2,3-dibromopropoxy)-	21000-44-2	^	
Toluenes and Xylenes			
2-Chlorotoluene	95498		Х
3-Chlorotoluene	108418		Х
4-Chlorotoluene	106434		Х
alpha,alpha-Dichlorotoluene	00070		V
(benzylidenechloride)	98873		X
alpha-Chlorotoluene (benzylchloride)	100447		Х
pentabromomethyl-benzene	87-83-2	X	
benzene, pentabromo(bromomethyl)-	38521-51-6	X	
pentachloroanisole	1825-21-4	Х	1
dicroden	1949071	X	1
Polybrominated diphenyl ethers (PBDEs)			1
Pentabrominated dinhenvl ether	32534-81-9	X	1
benzene $1 1'_{ovvhis[2 3 4 5 6_{-}]}$			
nentabromo-	32534-81-9	X	
benzene, 1.1'-oxybis octabromo deriv	32536-52-0	X	

Polybrominated biphenyls (PBBs)			Х
1,1'-biphenyl, hexabromo-	36355-01-8	Х	Х
octabromobiphenyl	27858-07-7	Х	X
nonabromobiphenyl	27753-52-2	Х	X
1,1'-biphenyl, 2,2',3,3',4,4',5,5',6,6'-	13654-09-6	v	v
decabromo-		^	*
1,1'-biphenyl, 4-bromo-2-fluoro-	41604-19-7	Х	Х
Polycholorobiphenyles (PCBs)		Х	Х
1,1'-biphenyl chlorinated	1336-36-3	Х	X
1,1'-biphenyl, 2,4,4'-trichloro-	7012-37-5	Х	X
1,1'-biphenyl, 2,2',4,4'-tetrachloro-	2437-79-8	Х	X
1,1'-biphenyl, 2,2',4,4',6,6'-hexachloro-	33979-03-2	Х	Х
1,1'-biphenyl, nonachloro-	53742-07-7	Х	X
1,1'-biphenyl, 2,2',3,3',4,4',5,5',6,6'-	0054.04.0	×	
decachloro-	2051-24-3	X	X
PCB Hydroxymetabolites			Х
Polychlorinated Terphenyles	61788-33-8	Х	Х
Polychlorinated dibenzo-p-dioxins (PCDD)			Х
2, 3, 7, 8- tetrachlorodibenzo-p-dioxin			
(2,3,7,8 TCDD)			X
17 isomers with chlorine substituted in the			
2,3,7,8 positions			X
dibenzo(b,e)(1,4)dioxin, 2,3,7,8-	4740.04.0	V	
tetrachloro-	1746-01-6	×	X
Polychlorinated dibenzofurans (PCDF)			Х
4,7-methanoisobenzofuran-1,3-dione,		V	
4,5,6,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-	115-27-5	^	X
1,3-isobenzofurandione, 4,5,6,7-	622 70 1	v	
1,3-isobenzofurandione, 4,5,6,7- tetrabromo-	632-79-1	Х	x
1,3-isobenzofurandione, 4,5,6,7- tetrabromo- benziodarone	632-79-1 68-90-6	X X	x
1,3-isobenzofurandione,4,5,6,7-tetrabromo-benziodaroneChlorinated Phenolic Compounds	632-79-1 68-90-6	X X	x
1,3-isobenzofurandione, tetrabromo-4,5,6,7-benziodaroneChlorinated Phenolic CompoundsChlorophenols	632-79-1 68-90-6	X X	x
1,3-isobenzofurandione, tetrabromo-4,5,6,7- tetrabromo-benziodaroneChlorinated Phenolic CompoundsChlorophenols2,3-Dichlorophenol	632-79-1 68-90-6 576249	X X	x
1,3-isobenzofurandione, tetrabromo-4,5,6,7- tetrabromo-benziodaroneChlorinated Phenolic CompoundsChlorophenols2,3-Dichlorophenol2,4-Dichlorophenol	632-79-1 68-90-6 576249 120832	X X	X X X X
1,3-isobenzofurandione, tetrabromo- benziodarone4,5,6,7- tetrabromo- benziodaroneChlorinated Phenolic CompoundsChlorophenols2,3-Dichlorophenol2,4-Dichlorophenol2,4-Dichlorophenol2-Amino-4-chlorophenol2-Amino-4-chlorophenol	632-79-1 68-90-6 576249 120832 95852	X X	X X X X X
1,3-isobenzofurandione, tetrabromo-4,5,6,7- tetrabromo-benziodaroneChlorinated Phenolic CompoundsChlorophenols2,3-Dichlorophenol2,3-Dichlorophenol2,4-Dichlorophenol2-Amino-4-chlorophenol2-Benzyl-4-chlorophenol	632-79-1 68-90-6 576249 120832 95852 120321	X X	X X X X X X X
1,3-isobenzofurandione, tetrabromo- benziodarone4,5,6,7- tetrabromo- benziodaroneChlorinated Phenolic CompoundsChlorophenols2,3-Dichlorophenol2,3-Dichlorophenol2,4-Dichlorophenol2,4-Dichlorophenol2-Amino-4-chlorophenol2-Benzyl-4-chlorophenol2-Chlorophenol2-Chlorophenol2-Chlorophenol	632-79-1 68-90-6 576249 120832 95852 120321 95578	X X	X X X X X X X X
1,3-isobenzofurandione, tetrabromo-4,5,6,7- tetrabromo-benziodaroneChlorinated Phenolic CompoundsChlorophenols2,3-Dichlorophenol2,4-Dichlorophenol2-Amino-4-chlorophenol2-Benzyl-4-chlorophenol2-Chlorophenol3-Chlorophenol	632-79-1 68-90-6 576249 120832 95852 120321 95578 108430	X X	X X X X X X X X X X
1,3-isobenzofurandione, tetrabromo- benziodarone4,5,6,7- tetrabromo- benziodaroneChlorinated Phenolic CompoundsChlorophenols2,3-Dichlorophenol2,3-Dichlorophenol2,4-Dichlorophenol2,4-Dichlorophenol2-Amino-4-chlorophenol2-Benzyl-4-chlorophenol2-Chlorophenol2-Chlorophenol3-Chlorophenol4-Chloro-3-methylphenol4-Chloro-3-methylphenol	632-79-1 68-90-6 576249 120832 95852 120321 95578 108430 59507	X X	X X X X X X X X X X X X
1,3-isobenzofurandione, tetrabromo- benziodarone4,5,6,7- tetrabromo- benziodaroneChlorinated Phenolic CompoundsChlorophenols2,3-Dichlorophenol2,3-Dichlorophenol2,4-Dichlorophenol2,4-Dichlorophenol2-Amino-4-chlorophenol2-Benzyl-4-chlorophenol2-Chlorophenol2-Chlorophenol3-Chlorophenol4-Chloro-3-methylphenol4-Chlorophenol	632-79-1 68-90-6 576249 120832 95852 120321 95578 108430 59507 106489	X X	X X X X X X X X X X X X X X X
1,3-isobenzofurandione,4,5,6,7-tetrabromo-benziodaroneChlorinated Phenolic CompoundsChlorophenols22,3-Dichlorophenol22,4-Dichlorophenol22-Amino-4-chlorophenol22-Benzyl-4-chlorophenol22-Chlorophenol33-Chlorophenol44-Chloro-3-methylphenol44-Chlorophenol7Trichlorophenol (all isomers)	632-79-1 68-90-6 576249 120832 95852 120321 95578 108430 59507 106489 95954	X X	X X X X X X X X X X X X X X
1,3-isobenzofurandione,4,5,6,7-tetrabromo-benziodaroneChlorinated Phenolic CompoundsChlorophenols22,3-Dichlorophenol22,4-Dichlorophenol22-Amino-4-chlorophenol22-Benzyl-4-chlorophenol22-Chlorophenol33-Chlorophenol44-Chloro-3-methylphenol44-Chlorophenol17richlorophenol2,4,5-trichlorophenol	632-79-1 68-90-6 576249 120832 95852 120321 95578 108430 59507 106489 95954 95-95-4	X X X	X X X X X X X X X X X X X X
1,3-isobenzofurandione, tetrabromo-4,5,6,7-benziodaroneChlorinated Phenolic CompoundsChlorophenols2,3-Dichlorophenol2,4-Dichlorophenol2-Amino-4-chlorophenol2-Benzyl-4-chlorophenol2-Chlorophenol3-Chlorophenol4-Chloro-3-methylphenol4-Chlorophenol1Trichlorophenol (all isomers)2,4,5-trichlorophenolpentachloro-benzenethiol	632-79-1 68-90-6 576249 120832 95852 120321 95578 108430 59507 106489 95954 95954 95-95-4 133-49-3	X X 	X X X X X X X X X X X X X X
1,3-isobenzofurandione,4,5,6,7-tetrabromo-benziodaroneChlorinated Phenolic CompoundsChlorophenols2,3-Dichlorophenol2,3-Dichlorophenol2,4-Dichlorophenol2,4-Dichlorophenol2-Amino-4-chlorophenol2-Benzyl-4-chlorophenol2-Chlorophenol2-Chlorophenol3-Chlorophenol3-Chlorophenol4-Chloro-3-methylphenol4-Chlorophenol11 isomers)2,4,5-trichlorophenol2,4,5-trichlorophenolethanol.1.1-bis(4-chlorophenyl) mixed	632-79-1 68-90-6 576249 120832 95852 120321 95578 108430 59507 106489 95954 95954 95-95-4 133-49-3 8072-20-6	X X X X X X X X X X X	X X X X X X X X X X X X X X
1,3-isobenzofurandione,4,5,6,7-tetrabromo-benziodaroneChlorinated Phenolic CompoundsChlorophenols22,3-Dichlorophenol22,4-Dichlorophenol22-Amino-4-chlorophenol22-Chlorophenol22-Chlorophenol33-Chlorophenol44-Chloro-3-methylphenol44-Chlorophenol17richlorophenol2,4,5-trichlorophenol2,4,5-trichlorophenolpentachloro-benzenethiolethanol, 1,1-bis(4-chlorophenyl)-, mixedphenol, 2,2'-methylenebis[3,4,6-trichloro-	632-79-1 68-90-6 576249 120832 95852 120321 95578 108430 59507 106489 95954 95-95-4 133-49-3 8072-20-6 70-30-4	X X X X X X X X X X X X X X	X X X X X X X X X X X X X X
1,3-isobenzofurandione,4,5,6,7-tetrabromo-benziodaroneChlorinated Phenolic CompoundsChlorophenols2,3-Dichlorophenol2,3-Dichlorophenol2,4-Dichlorophenol2,4-Dichlorophenol2-Amino-4-chlorophenol2-Amino-4-chlorophenol2-Chlorophenol2-Chlorophenol3-Chlorophenol3-Chlorophenol4-Chloro-3-methylphenol4-Chlorophenol1Trichlorophenol2,4,5-trichlorophenolpentachloro-benzenethiolethanol, 1,1-bis(4-chlorophenyl)-, mixedphenol, 2,2'-methylenebis[3,4,6-trichloro-phenol, 2,2'-methylenebis[4,6-dichloro-	632-79-1 68-90-6 576249 120832 95852 120321 95578 108430 59507 106489 95954 95954 95-95-4 133-49-3 8072-20-6 70-30-4 1940-43-8	X X X X X X X X X X X X X X	X X X X X X X X X X X X X X
1,3-isobenzofurandione,4,5,6,7-tetrabromo-benziodaroneChlorinated Phenolic CompoundsChlorophenols2,3-Dichlorophenol2,3-Dichlorophenol2,4-Dichlorophenol2,4-Dichlorophenol2-Amino-4-chlorophenol2-Benzyl-4-chlorophenol2-Chlorophenol2-Chlorophenol3-Chlorophenol3-Chlorophenol4-Chloro-3-methylphenol4-Chloro-3-methylphenol2,4,5-trichlorophenol2,4,5-trichlorophenolpentachloro-benzenethiolethanol, 1,1-bis(4-chlorophenyl)-, mixedphenol, 2,2'-methylenebis[3,4,6-trichloro-phenol, 2,4-dichloro-5-nitro-, carbonate (2:1)	632-79-1 68-90-6 576249 120832 95852 120321 95578 108430 59507 106489 95954 95954 95954 95954 133-49-3 8072-20-6 70-30-4 1940-43-8	X X X X X X X X X X X X X X	X X X X X X X X X X X X X X
1,3-isobenzofurandione, tetrabromo- benziodarone4,5,6,7- tetrabromo- benziodaroneChlorinated Phenolic CompoundsChlorophenols2,3-Dichlorophenol2,4-Dichlorophenol2-Amino-4-chlorophenol2-Benzyl-4-chlorophenol2-Chlorophenol3-Chlorophenol4-Chloro-3-methylphenol4-Chlorophenol17richlorophenol2,4,5-trichlorophenol2,4,5-trichlorophenolethanol, 1,1-bis(4-chlorophenyl)-, mixedphenol, 2,2'-methylenebis[3,4,6-trichloro- phenol, 2,4-dichloro-5-nitro-, carbonate (2:1) (ester)	632-79-1 68-90-6 576249 120832 95852 120321 95578 108430 59507 106489 95954 95-95-4 133-49-3 8072-20-6 70-30-4 1940-43-8 39489-75-3	X X X X X X X X X X X X X X	X X X X X X X X X X X X X X
1,3-isobenzofurandione,4,5,6,7-tetrabromo-benziodaroneChlorinated Phenolic CompoundsChlorophenols2,3-Dichlorophenol2,3-Dichlorophenol2,4-Dichlorophenol2,4-Dichlorophenol2-Amino-4-chlorophenol2-Benzyl-4-chlorophenol2-Chlorophenol3-Chlorophenol3-Chlorophenol4-Chloro-3-methylphenol4-ChlorophenolTrichlorophenol12,4,5-trichlorophenol2,4,5-trichlorophenolpentachloro-benzenethiolethanol, 1,1-bis(4-chlorophenyl)-, mixedphenol, 2,2'-methylenebis[3,4,6-trichloro-phenol, 2,4-dichloro-5-nitro-, carbonate (2:1)(ester)phenol, 4,4'-(1-methylethylidene)bis[2.6-	632-79-1 68-90-6 576249 120832 95852 120321 95578 108430 59507 106489 95954 95-95-4 133-49-3 8072-20-6 70-30-4 1940-43-8 39489-75-3 70-05-2	X X X X X X X X X X X X X X	X X X X X X X X X X X X X X
1,3-isobenzofurandione,4,5,6,7-tetrabromo-benziodaroneChlorinated Phenolic CompoundsChlorophenols2,3-Dichlorophenol2,4-Dichlorophenol2-Amino-4-chlorophenol2-Benzyl-4-chlorophenol2-Chlorophenol3-Chlorophenol3-Chlorophenol4-Chloro-3-methylphenol4-Chlorophenol17richlorophenol2,4,5-trichlorophenol2,4,5-trichlorophenolpentachloro-benzenethiolethanol, 1,1-bis(4-chlorophenyl)-, mixedphenol, 2,2'-methylenebis[3,4,6-trichloro-phenol, 2,2'-methylenebis[4,6-dichloro-phenol, 2,4-dichloro-5-nitro-, carbonate (2:1)(ester)phenol, 4,4'-(1-methylethylidene)bis[2,6-dichloro-	632-79-1 68-90-6 576249 120832 95852 120321 95578 108430 59507 106489 95954 95954 95-95-4 133-49-3 8072-20-6 70-30-4 1940-43-8 39489-75-3 79-95-8	X X X X X X X X X X X X X X	X X X X X X X X X X X X X X
1,3-isobenzofurandione,4,5,6,7-tetrabromo-benziodaroneChlorinated Phenolic CompoundsChlorophenols2,3-Dichlorophenol2,3-Dichlorophenol2,4-Dichlorophenol2,4-Dichlorophenol2-Amino-4-chlorophenol2-Benzyl-4-chlorophenol2-Chlorophenol2-Chlorophenol3-Chlorophenol3-Chlorophenol4-Chloro-3-methylphenol4-Chloro-3-methylphenol2,4,5-trichlorophenol2,4,5-trichlorophenol2,4,5-trichlorophenolpentachloro-benzenethiolethanol, 1,1-bis(4-chlorophenyl)-, mixedphenol, 2,2'-methylenebis[3,4,6-trichloro-phenol, 2,4-dichloro-5-nitro-, carbonate (2:1)(ester)phenol, 4,4'-(1-methylethylidene)bis[2,6-dichloro-Bromophenols1	632-79-1 68-90-6 576249 120832 95852 120321 95578 108430 59507 106489 95954 95954 95-95-4 133-49-3 8072-20-6 70-30-4 1940-43-8 39489-75-3 79-95-8	X X X X X X X X X X X X X X	X X X X X X X X X X X X X X X X X X X
1,3-isobenzofurandione, 4,5,6,7-tetrabromo- benziodarone Chlorinated Phenolic Compounds Chlorophenols 2,3-Dichlorophenol 2,4-Dichlorophenol 2-Amino-4-chlorophenol 2-Amino-4-chlorophenol 2-Benzyl-4-chlorophenol 2-Chlorophenol 3-Chlorophenol 2-Chlorophenol 3-Chlorophenol 2-Chlorophenol 3-Chlorophenol 2-Chlorophenol 3-Chlorophenol 4-Chloro-3-methylphenol 4-Chlorophenol 4-Chlorophenol 1 7richlorophenol (all isomers) 2,4,5-trichlorophenol 9entachloro-benzenethiol ethanol, 1,1-bis(4-chlorophenyl)-, mixed 9henol, 2,2'-methylenebis[3,4,6-trichloro- phenol, 2,2'-methylenebis[4,6-dichloro- 9henol, 2,2'-methylenebis[4,6-dichloro- phenol, 2,2'-methylenebis[4,6-dichloro- 9henol, 4,4'-(1-methylethylidene)bis[2,6-dichloro- phenol, 4,4'-(1-methylethylidene)bis[2,6-dichloro- 9henol, 4,4'-(1-methylethylidene)bis[2,6-dichloro- phenol, 4,4'-(1-methylethylidene)bis[2,6-dichloro-	632-79-1 68-90-6 576249 120832 95852 120321 95578 108430 59507 106489 95954 95-95-4 133-49-3 8072-20-6 70-30-4 1940-43-8 39489-75-3 79-95-8 79-95-8	X X X X X X X X X X X X X X	X X X X X X X X X X X X X X X X X X X
1,3-isobenzofurandione, 4,5,6,7-tetrabromo- benziodarone Chlorinated Phenolic Compounds Chlorophenols 2,3-Dichlorophenol 2,3-Dichlorophenol 2,4-Dichlorophenol 2,4-Dichlorophenol 2 2-Amino-4-chlorophenol 2 2-Benzyl-4-chlorophenol 2 2-Chlorophenol 3-Chlorophenol 3-Chlorophenol 4-Chloro-3-methylphenol 4-Chloro-3-methylphenol 4-Chlorophenol Trichlorophenol 2,4,5-trichlorophenol pentachloro-benzenethiol ethanol, 1,1-bis(4-chlorophenyl)-, mixed phenol, 2,2'-methylenebis[3,4,6-trichloro-phenol, 2,2'-methylenebis[4,6-dichloro-phenol, 2,2'-methylenebis[4,6-dichloro-phenol, 2,4-dichloro-5-nitro-, carbonate (2:1) (ester) phenol, 4,4'-(1-methylethylidene)bis[2,6-dichloro- phenol, 4,4'-(1-methylethylidene)bis[2,6-dichloro- phenol, 4,4'-(1-methylethylidene)bis[2,6-dichloro- phenol, 4,4'-(1-methylethylidene)bis[2,6-dichloro-	632-79-1 68-90-6 576249 120832 95852 120321 95578 108430 59507 106489 95954 95-95-4 133-49-3 8072-20-6 70-30-4 1940-43-8 39489-75-3 79-95-8 79-95-8 79-94-7	X X X X X X X X X X X X X X	X X X X X X X X X X X X X X X X X X X

Organohalogenated Pesticides/ Biocides				
benzene, 1,1'-(2,2,2-trichloroethylidene)bis[4-	50203	Y		
chloro-	30293	^	Х	
1,4:5,8-dimethanonaphthalene,				
1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-				
hexahydro-,	309002	X	Х	
(1.alpha.,4.alpha.,4a.beta.,5.alpha.,8.alpha.,				
8a.beta.)-				
2,7:3,6-dimethanonaphth[2,3-b]oxirene,				
3,4,5,6,9,9-hexachloro-1a,2,2a,3,6,6a,7,7a-	00574		×	
octanydro-,	60571	X	X	
(1a.alpna.,2.beta.,2a.alpna.,3.beta.,6.beta.,6				
a.alpna., 7.beta., 7a.alpna.)-				
2,7:3,6-dimethanonaphth[2,3-b]oxirene,				
3,4,5,6,9,9-nexachioro-1a,2,2a,3,6,6a,7,7a-	70000	v	V	
octanyoro-,	72208	X	X	
(1a.aipna.,2.beta.,2a.beta.,3.aipna.,6.aipna.,				
4,7-methano-1H-indene, 1,2,4,5,6,7,8,8-	57749	x	Х	
octacnioro-2,3,3a,4,7,7a-nexanydro-	440744			
Hexachlorobenzene (HCB)	118/41	X	X	
Isodrin	465736	X	X	
Chlordecone = Kepone	143500	X	Х	
Hexachlorocyclohexane (HCH)	608731	Х	Х	
Pentachlorophenol (PCP)	87865	Х	Х	
cyclohexane, 1,2,3,4,5,6-hexachloro-,				
(1.alpha.,2.alpha.,3.beta.,4.alpha.,5.alpha.,6.	58899	X		
beta.)-			Х	
beta-HCH	319857	X	X	
Chlorophenoxyacids (2,4 D / 2,4,5 T)	93765	X	X	
	1582098	X	X	
Iriazines (e.g. atrazine)	n.a.		X	
	1912249	X	Х	
1,3,5-triazine-2,4,6(1H,3H,5H)-trione, 1,3,5-	52434-90-9	X		
tris(2,3-dibromopropyi)-	70.405			
Methoxychior	72435	X		
4,7-methano-1H-indene, 1,4,5,6,7,8,8-	76448	X	V	
heptachioro-3a,4,7,7a-tetranyoro-	00000	V	X	
benzene, pentachioronitro-	02000	X	X	
	115297	X	X	
	115322	X	X	
Ioxaphene	8001352	X	Х	
4,7-methanoisobenzoturan, 1,3,4,5,6,7,8,8-	297789	X	×	
octacnioro-1,3,3a,4,7,7a-nexanydro-			Х	
1,3,4-metheno-1H-cyclobuta[cd]pentalene,				
1,1a,2,2,3,3a,4,5,5,5a,5b,6-	2385855	X		
dodecachiorooctanydro-	50474 44 0			
2,4-oxazoliaineaione, 3-(3,5-dichlorophenyl)-	504/1-44-8	X		
b-etnenyi-5-metnyi-	40007755			
benzene, 2,4-dichloro-1-(4-nitrophenoxy)-	1836755	X	X	
bromocylene	1/15408	X		
Hexachlorobutadiene	87683	X	X	
stannane, tributyl-, mono(naphthenoyloxy)	85409-17-2	x		
derivs.				

benzene, 1-chloro-2-[2,2-dichloro-1-(4-	53-19-0	x	
distannovano, hovohutul	56 25 0	v	
uisidiiiioxarie, riexabulyi-	50-55-9	^	
chloro-	52-54-8	Х	
benzene, 1,1'-(dichloroethenylidene)bis[4- chloro-	72-55-9	х	
stannane, hydroxytriphenyl-	76-87-9	Х	
benzenemethanol, 4-chloroalpha(4-	80-06-8	x	
phenol 2 2'-thiobis[4 6-dichloro-	97-18-7	Х	
urea, N-(4-chlorophenyl)-N'-(3,4- dichlorophenyl)-	101-20-2	X	
benzene, 1,2,4-trichloro-5-[(4- chlorophenyl)sulfonyl]-	116-29-0	х	
phosphonothioic acid, ethyl-, O-ethyl O- (2,4,5-trichlorophenyl) ester	327-98-0	х	
benzene, 1,1'-(2,2,2-trichloroethylidene)bis[4- fluoro-	475-26-3	х	
phenol, 2,4-bis(1,1-dimethylethyl)-5-methyl-	497-39-2	Х	
benzeneacetic acid, 4-chloroalpha(4- chlorophenyl)alphahydroxy-, ethyl ester	510-15-6	х	
stannylium, triphenyl-	668-34-8	Х	
2,4,6-tri-tert-butylphenol	732-26-3	Х	
benzene, 1-chloro-2-[2,2,2-trichloro-1-(4- chlorophenyl)ethyl]-	789-025-6	х	
2,5-methano-2H-indeno[1,2-b]oxirene, 2,3,4,5,6,7,7-heptachloro-1a,1b,5,5a,6,6a- hexahydro-, (1a.alpha.,1b.beta.,2.alpha.,5.alpha.,5a.beta. 6 beta. 6a alpha.)-	1024-57-3	x	
phenol 3 5-bis(1 1-dimethylethyl)-	1138-52-9	x	
benzene 1.3.5-trichloro-2-(4-nitrophenoxy)-	1836-77-7	X	
benzenamine, N-butyl-N-ethyl-2,6-dinitro-4- (trifluoromethyl)-	1861-40-1	X	
pimozide	2062-78-4	Х	
ethyl O-(p-nitrophenyl) phenyl phosphonothionate	2104-64-5	х	
phosphorothioic acid, O-(4-bromo-2,5- dichlorophenyl) O,O-dimethyl ester	2104-96-3	х	
phosphorothioic acid, O-(4-bromo-2,5- dichlorophenyl) O,O-diethyl ester	4824-78-6	х	
tetrasul	2227-13-6	Х	
carbamothioic acid, bis(1-methylethyl)-, S- (2,3,3-trichloro-2-propenyl) ester	2303-17-5	x	
[1,1'-biphenyl]-4-ol, 3,5-bis(1,1- dimethylethyl)-	2668-47-5	х	
phosphorothioic acid, O,O-diethyl O-(3,5,6- trichloro-2-pyridyl) ester	2921-88-2	Х	
benzene, 1-chloro-2-[2,2-dichloro-1-(4- chlorophenyl)ethenyl]-	3424-82-6	x	
4,7-methano-1H-indene, 4,5,6,7,8,8- hexachloro-3a,4,7,7a-tetrahydro-	3734-48-3	X	
DIDT	3972-13-2	Х	

phosphorothioic acid, O-(2,5-dichloro-4-	18181_70_0	Y	
iodophenyl) O,O-dimethyl ester	10101-70-9	^	
strobane	8001-50-1	Х	
stannane, tricyclohexylhydroxy-	13121-70-5	Х	
distannoxane, hexakis(2-methyl-2-	13356 08 6	Y	
phenylpropyl)-	13330-00-0	^	
3,5-dioxa-6-aza-4-phosphaoct-6-ene-8-nitrile,	1/1816 18 3	Y	
4-ethoxy-7-phenyl-, 4-sulfide	14010-10-3	^	
phenol, 2,6-bis(1,1-dimethylethyl)-4-(1-	17540 75 0	v	
methylpropyl)-	17540-75-9	^	
phosphonothioic acid, phenyl-, O-(4-bromo-	21600-00-5	x	
2,5-dichlorophenyl) O-methyl ester	21003-30-3	~	
phosphorodithioic acid, O,O-diisooctyl ester	26999-29-1	Х	
propanoic acid, 2-(2,4,5-trichlorophenoxy)-,	10308-13-1	x	
2-butoxyethyl ester		~	
1H-imidazole, 1-[2-(2,4-dichlorophenyl)-2-	22916-47-8	x	
[(2,4-dichlorophenyl)methoxy]ethyl]-	22010 11 0	~	
benzenamine, N-(cyclopropylmethyl)-2,6-	26399-36-0	x	
dinitro-N-propyl-4-(trifluoromethyl)-	20000 00 0		
4-piperidinol, 1-[4,4-bis(4-fluorophenyl	26864-56-2	Х	
phosphorothioic acid, O,O,O-tris(4-	64131-85-7	х	
nitropnenyi) ester	00000 45 5	X	
benzoic acid, 2-[(2,6-dicnioro-3-methylp	29098-15-5	X	
	36065-30-2	Х	
honzonomino NI (2 phonyl 4 5			
benzenamme, n-[3-prienyi-4,3-	27002 02 0	v	
thiazolidinylidenel	37093-02-0	^	
henzoic acid 5 (2.4 dichlorophenoxy) 2			
nitro- methyl ester	42576-02-3	Х	
2 2 5-endo 6-exo 8 9 10-			
heptachloronorbornane	51775-36-1	Х	
sibelium	52468-60-7	Х	
benzenepropanamine, N-methylgamma[4-	50000 70 7	V	
(trifluoromethyl)phenoxy]-, hydrochloride	56296-78-7	X	
oxirane, 2-(3,5-dichlorophenyl)-2-(2,2,2-	50120 00 2	v	
trichloroethyl)-	30130-00-2	^	
benzene, 1-[2-(2-chloroethoxy)ethoxy]-4-	65025-28-2	x	
(1,1,3,3-tetramethylbutyl)-	00920-20-2	^	
hydramethylnon	67485-29-4	Х	
cyclopropanecarboxylic acid, 3-(2-chloro-			
3,3,3-trifluoro-1-propenyl)-2,2-dimethyl-,	68085-85-8	Х	
cyano(3-phenoxyphenyl)methyl ester			
furo[3,4-b]pyridin-7(5H)-one, 5-[4-			
(diethylamino)-2-ethoxyphenyl]-5-(1-ethyl-2-	69898-41-5	Х	
methyl-1H-indol-3-yl)-			
flucythrinate	70124-77-5	Х	
morpholine, 2,6-dimethyl-4-(C10-13)-alkyl-	81412-43-3	Х	
propanoic acid, 2-[4-[[3-chloro-5-			
(trifluoromethyl)-2-pyridinyl]oxy]phenoxy]-, 2-	87237-48-7	Х	
etnoxyethyl ester			
propaquizatop	111479-05-1	Х	
2,4-Dichlorophenoxyacetic acid (2,4-D)	94/5/		X
	120365		X
(aichiotptop)		1	

2,6-Dichlorobenzonitrile	1194656	X	
1,2-Dibromoethane	106934	X	
2-Methyl-4-chlorophenoxyacetic acid (MCPA)	94746	X	
2-Methyl-4-chlorophenoxypropanoic acid	00050	×	
(MCPP)	93652	X	
Acrylonitrile	107131	X	
Aldicarb	116063	X	
Amitrol	61825	X	
Aramite	140578	X	
Azinphos-ethyl	2642719	X	
Azinphos-methyl	86500	X	
Bentazone	25057890	X	
Carbazole	86748	X	
Carbofuran	1563662	X	
Chlordimeform	6164983	X	
Chlorpicrin	76062	X	
Cumatos	56724	X	
Cvanazine	21725462	X	
Demeton	57749	X	
Dibutyltin salt (all)	n a	X	
	62737	X	
Dibudrazinagulahata	12464907		
Dimotheata	60515		
Dimethoate	00010		
Dinused		X	
Disultoton	298044	X	
	148185	X	
Diuoron	330541	X	
Drins	n.a.	X	
Fenitrothion	122145	X	
Fenthion	55389	X	
Fluoroacetic acid and derivatives	7664393	X	
Foxim	14816183	X	
Hexazinone	51235042	X	
Isoproturon	34123596	X	
Kelevan	4234791	Х	
Linuron	330552	X	
Malathion	121755	X	
Metabenzthiazuron	1929880	Х	
Metazachlor	67129082	Х	
Methalachlor	51218452	Х	
Methamidophos	10265926	Х	
Metoxuron	19937596	Х	
Mevinphos	7786347	Х	
Monolinuron	1746812	X	
Morfamquat	4636833	X	
Omethoate	1113026	Х	
Oxydemeton-methyl	301122	X	
Paraguat	2074502	X	
Parathion	56382	X	
Parathion-methyl	298000	X	
Pesticides (agriculture, horticulture and forestry)	n.a.	x	
Propachlor	1918167	x	
	1010107		
Propanil	709988		Х
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Pyrazone (chloridazon)	1698608		Х
Pyrethroids, synthetic	n.a.		Х
Simazine	122349		Х
Thiabendazole	148798		Х
Triazophos	24017478		Х
Trichlorfon	52686		Х
Other organic and inorganic compounds			
Ormania Nitra non Commoundo			
Organic Nitrogen Compounds			
Nitrobenzenes	00050		X
	98953		X
1,3-Dinitrobenzene	99650		X
4-Nitro-1-isopropyibenzene	1817476		X
Halogenated Nitrobenzenes	00044		X
2-Chloronitrobenzene	89214		X
3-Chloronitrobenzene	88733		Х
4-Chloronitrobenzene	121733		х
Chlorodinitrobenzene (mixed isomers)	25567673		Х
1-Chloro-2,4-dinitrobenzene	97007		Х
Dichloronitrobenzene (all isomers)	27900750		Х
1-Fluoro-4-isocvanatobenzene	1544689		Х
Toluenes			
alpha.alpha.alpha-Trifluoro-2- nitrotoluene	384225		Х
alpha.alpha.alpha-Trifluoro-3- nitrotoluene	98464		Х
alpha,alpha,alpha-Trifluoro-3-nitro-4-	402540		х
alpha.alpha.alpha-Trifluoro-4- nitrotoluene	402540		Х
Chloroaminotoluene (chlorotoluidine, all isomers)			X
Chloronitrotoluene (all isomers)	25567684		Х
2.3-Dinitrotoluene	602017		X
benzene, 1-methyl-2.4-dinitro-	121142	Х	X
Anilines			
4-Aniline	106478		x
Chloroanilines	100110		
2 4-Dichlorophenoxy-4-aniline	14861177		X
2-Chloroaniline	95512		X
Dichloroaniline (all isomers)	27134276		X
3 4-Dichloroaniline	95761	x	X
3-Chloroaniline	108429	~	X
4-Chloro-2-nitroaniline	121879		X
benzenamine 23456-pentachloro-	527-20-8	x	<u>л</u>
	527-20-0	<u>л</u>	
Dichlorodiaminodinhenyl	1331/71		Y
[1 1'_hinhenvl]-4 4'_diamine 3 3'_dichloro_	91_94_1	X	X
	51-54-1	<u>л</u>	~
pyrimido[5,4-d]pyrimidine, 2,6-dichloro-4,8-di- 1-piperidinyl-	7139028	x	
benzamide, 2,3,5-trichloro-N-(3.5-dichlo	2277-92-1	Х	
9,10-anthracenedione, 1-amino-2-bromo-4-	128-83-6	v	
[(4-methylphenyl)amino]-		X	
1,4-pentanediamine, N4-(6-chloro-2-	69-05-6	Х	

methoxy-9-aziridinyl)-N1,N1-diethyl-,			
dihydrochloride			
methane, nitro-	75-52-5	Х	
1.4-benzenediamine, N.N'-di-2-naphthalenvl-	93-46-9	Х	
benzenamine. 4.4'-	129-73-7		
(phenylmethylene)bis[N.N-dimethyl-		X	
benzenamine 44'-methylenebis[N N-diethyl-	135-91-1	X	
1 4-benzenediamine N N'-bis(1-etbyl-3-	139-60-6		
methylpentyl)-		X	
2-nanhthalenamine NN-bis(2-chloroethyl)-	494-03-1	x	
4-(dimethylbutylamino)dinhenylamin	793-24-8	X	
	1606-67-3	X	
1-octanesulfonamide N-ethyl-	1000-07-3	X	
$1 1 2 2 3 3 4 4 5 5 6 6 7 7 8 8 8_{-}$	1601_00_2	x	
[1, 1, 2, 2, 3, 3, 4, 4, 3, 3, 3, 0, 0, 7, 7, 3, 0, 0, 0]	1031-33-2	~	
1 4 benzenediamine N (1 4 dimethylpentyl)			
N' phopyl	04/01/3081	Х	
honzonomino 4.4' mothylonohio[NL (1			
mothyloropyl)	5285-60-9	Х	
henzenemine 4.4' methylenehie[2.6 diethyl	12600.25.0	V	
Denzenamine, 4,4 - metnylenebis[2,6-dietnyl-	13680-35-8	X	
9,10-anthraceneolone, 4,8-diamino-2-(4-	15114-15-5	X	
etnoxypnenyi)-1,5-dinydroxy-			
methanone, (2-butyl-3-benzoturanyl)[4-[2-	40774 00 4	V	
(dietnylamino)etnoxyj-3,5-dilodopnenyij-,	19774-82-4	X	
1,3,5-triazine-2,4,6(1H,3H,5H)-trione, 1,3,5-	26603-40-7	X	
tris(3-isocyanatomethylphenyl)-			
benzenamine, 4-(2,6-diphenyl-4-pyridinyl)-	29312-59-2	X	
N,N-dimethyl-			
[1,1'-biphenyl]-4,4'-diamine, N,N'-bis(2,4-	29398-96-7	X	
dinitrophenyl)-3,3'-dimethoxy-			
2-anthracenecarboxamide, 1-amino-N-(3-			
bromo-9,10-dihydro-9,10-dioxo-2-	52740-90-6	X	
anthracenyi)-9,10-dinydro-9,10-dioxo-			
3,3'-(ureylenedimethylene)bis(3,5,5-	56525-54-7	X	
trimethylcyclohexyl) diisocyanate			
1,4-benzenediamine, N,N,N'-tris(1-	64381-97-1	x	
methylpropyl)-			
methylium, tris[4-(dimethylamino)phenyl]-,			
salt with 3-[[4-	65294-17-9	x	
(phenylamino)phenyl]azo]benzenesulfonic	00201110	~	
acid (1:1)			
benzenesulfonic acid, 2-amino-, (1-	68015-60-1	x	
methylethylidene)di-4,1-phenylene ester	00010 00 1	~	
2-butanone, O-[[[[1,3,3-trimethyl-5-[[[[(1-			
methylpropylidene)amino]oxy]carbonyl]amino	68083-48-7	X	
]cyclohexyl]methyl]amino]carbonyl]oxime			
astemizole	68844-77-9	Х	
1,2-Ethanediamine	33855479		Х
2,4,6-Trichloro-1,3,5-triazin (cyanuric	108770		
chloride)	100770		Х
4,4'-diaminodiphenyl (benzidine)	92875		Х
5-Isoxazolamine	14678058		Х
Cyanoguanidine	461585		Х

Cyclohexylamine	108918		Х
Diethylamine	109897		Х
Dimethylamine	124403		Х
N,N-Diphenylamine	122394		Х
Organic oxygen compounds			
1.3-Dichloro-2-propanol	96231		Х
2 2-Dichloropropionic acid	75990		X
2-Chloroethanol	107073		X
2-Ethyl-1-bexanol	104767		X
2-propanol 1-(tert-dodecylthio)-	67124-09-8	X	<i>x</i>
3.5.5-Trimethyl-1-bexanol	3452979	Χ	X
his(2-Chloroisopropyl)ether	108601		X
butanovi chloride 4-[2.4-bis(1.1-	100001		Χ
dimethylpronyl)nbenoxyl-	50772-29-8	Х	
Chloroacetic acid	70118		X
Decanol	112301		X
Diphonovymethanal (carbonic acid, diphonyl	112301		^
ester)	102090		Y
Diphonylothor	101949		X
	101040		A V
	100090		
	20000177		A V
	27238942		X
	70000		X
	76039		X
Trichloroethanal (chloral)	302170		X
Phthalate Ester			
o-Phthalic acid	90193763		X
Butylbenzylphthalate	85687	Х	Х
Dibutylphthalate	84742	Х	Х
Diethylhexylphthalate	117817	Х	Х
Di-n-octylphthalate	117840	Х	Х
Diethylphthalate	84662		Х
Phthalates, other			Х
1,2-benzenedicarboxylic acid, diisooctyl ester	27554-26-3	Х	Х
1,2-benzenedicarboxylic acid, bis(2-	84-69-5		
methylpropyl) ester	04-03-0	Х	Х
Organic Ester			
neodecanoic acid, ethenyl ester	51000-52-3	Х	
propanoic acid, 2-[4-(2,2-			
dichlorocyclopropyl)phenoxy]-2-methyl-, ethyl	52179-28-9		
ester		Х	
2-propenoic acid, (pentabromophenyl)methyl	59447-55-1	x	
ester	00447 00 1	Χ	
2-propenoic acid, 2,2,3,3,4,4,5,5,6,6,7,7,7	559-11-5	x	
Tridecafluroroheptyl Ester	555-11-5	Λ	
Organophosphate			
phosphoric acid, 2-ethylhexyl diphenyl ester	1241-94-7	Х	
phosphoric acid, isodecyl diphenyl ester	29761-21-5	Х	
Cresyldiphenylphosphate	26444495		Х
Tris(2,3-dibromo-1-propyl)phosphate	126727		Х
Tributylphosphate	126738		X
Tricresylphosphate	1330785		X
Trioctylphosphate	78422		Х
Triphenylphosphate	115866		X

Trixylenylphosphate	25155231		Х
Drugs / Pharmaceuticals			
chlorpromazine	50-53-3	X	
1.4-pentanediamine. N(4)-(7-chloro-4-	50-63-5		
quinolinyl)-N(1),N(1)-diethyl-, phosphate (1:2)		x	
1.4-pentanediamine. N4-(7-chloro-4-	54-05-7		
quinolinyl)-N1,N1-diethyl-		x	
10H-Phenothiazine, 2-chloro-10-[3-(4-methyl-	58-38-8		
1-piperazinyl)propyl]-		X	
1-Piperazineethanol, 4-[3-[2-(trifluoromethyl)-	69-23-8		
10H-phenothiazin-10-yl]propyl]-		X	
1-Piperazineethanol, 4-[3-[2-(trifluoromethyl)-	146-56-5		
10H-phenothiazin-10-yl]propyl]-,			
dihydrochloride		X	
10H-phenothiazine, 10-[3-(4-methyl-1-	440-17-5		
piperazinyl)propyl]-2-(trifluoromethyl)-,			
dihydrochloride		X	
trifluperidol	749-13-3	Х	
1.2-Ethanedisulfonic acid, compd. with 2-	1257-78-9		
chloro-10-[3-(4-methyl-1-piperazinyl)propyl]-			
10H-phenothiazine (1:1)		X	
10(9H)-acridinepropanamine, N,N,9,9-	4757-55-5		
tetramethyl-, [R-(R*,R*)]-2,3-			
dihydroxybutanedioate (1:1)		X	
niflumic acid	4394-00-7	Х	
10(9h)-acridinepropanamine, n,n,9,9-	4757-55-5		
tetramethyl-		X	
[1,1'-biphenyl]-2,2'-diol, 5,5'-dichloro	10331-57-4	X	
1H-imidazole, 1-[2-(2,4-dichlorophenyl)-2-	22832-87-7		
[(2,4-dichlorophenyl)methoxy]ethyl]-,			
mononitrate		X	
clotrimazole	23593-75-1	Х	
1-butanone, 4-[4-(2,3-dihydro-2-thioxo-1	57648-21-2	Х	
benzamide, N-[5-chloro-4-[(4-	57808-65-8		
chlorophenyl)cyanomethyl]-2-methylphenyl]-			
2-hydroxy-3,5-diiodo-		X	
4H-imidazo[1,5-a][1,4]benzodiazepine, 8-	59467-70-8		
chloro-6-(2-fluorophenyl)-1-methyl-		X	
1-octanesulfonamide, N-ethyl-	67969-69-1		
1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-			
heptadecafluoro-N-[2-(phosphonooxy)ethyl]-,			
diammonium salt		X	
Hormones			
17-Ethynylestradiol	57-63-6	Х	X
Diethylstilbestrol	56-53-1	Х	Х
Mestranol	72-33-3	X	Х
Oestradiol	50-28-2	Х	X
Oestron	53-16-7	Х	X
Diosgenin	512-04-9	X	
Pregn-4-ene-3.20-dione. 17-I(1-			
oxohexyl)oxyl-	630-56-8	X	
Inorganic compounds			
Hypochlorite, sodium-	7681529		X

Annex B. EU, OSPAR and HELCOM legal references adopting ELVs.

a) European Union

- **Directive 2000/60/EC** of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy.
- **Directive 76/464/EEC** of 4 May 1976 on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community
- **Council Directive 82/176/EEC** of 22 March 1982 on limit values and quality objectives for mercury discharges by the chlor-alkali electrolysis industry.
- **Council Directive 84/156/EEC** of 8 March 1984 on limit values and quality objectives for mercury discharges by sectors other than the chlor-alkali electrolysis industry.
- **Council Directive 83/513/EEC** of 26 September 1983 on limit values and quality objectives for cadmium discharges.
- **Council Directive 84/491/EEC** of 9 October 1984 on limit values and quality objectives for discharges of hexachlorocyclohexane.
- Council Directive 86/280/EEC of 12 June 1986 on limit values and quality objectives for discharges of certain dangerous substances included in List I of the Annex to Directive 76/464/EEC.
- **Council Directive 88/347/EEC** of 16 June 1988 amending Annex II to Directive 86/280/EEC on limit values and quality objectives for discharges of certain dangerous substances included in List I of the Annex to Directive 76/464/EEC
- **Council Directive 90/415/EEC** of 27 July 1990 amending Annex II to Directive 86/280/EEC on limit values and quality objectives for discharges of certain dangerous substances included in list I of the Annex to Directive 76/464/EEC
- **Council Decision 2006/507/EC** of 14 October 2004 concerning the conclusion, on behalf of the European Community, of the Stockholm Convention on Persistent Organic Pollutants.
- Council Decision Décision 2004/259/CE of 19 February 2004 concerning the conclusion, on behalf of the European Community, of the 1988 Protocol to the 1979 Convention on Long Range Transboundary Air Pollution on Persistent Organic Pollutants.
- **Communication COM(2001)593 final** from the Commission to the Council, the European Parliament and the Economic and Social Committee of 24 October 2001. Community strategy for dioxins, furans and polychlorinated biphenyls.

b) HELCOM Recommendations

 HELCOM Recommendation 27/1, adopted 8 March 2006, on Limitation of Emissions into Atmosphere and Discharges into Water from Incineration of Waste.

- **HELCOM RECOMMENDATION 25/1,** adopted 2 March 2004, Elimination of PCBs and PCTs.
- **HELCOM RECOMMENDATION 23/12,** adopted 6 March 2002, Reduction of Discharges and Emissions from Production of Textiles.
- **HELCOM RECOMMENDATION 23/11,** adopted 6 March 2002, Requirements for discharging of waste water from the chemical industry.
- HELCOM RECOMMENDATION 23/7, adopted 6 March 2002, <u>Reduction of</u> discharges and emissions from the metal surface treatment.
- HELCOM RECOMMENDATION 23/6, adopted 6 March 2002, <u>Reduction of</u> emissions and discharges of mercury from chloralkali industry.
- HELCOM RECOMMENDATION 18/2, adopted 12 March 1997, Offshore Activities.
- **HELCOM RECOMMENDATION 17/6,** adopted 12 March 1996, Reduction of Pollution from Discharges into Water, Emissions into the Atmosphere and Phosphogypsum out of the Production of Fertilizers.

c) OSPAR Decisions and Recommendations

- PARCOM Decision 80/2 on Limit Values for Mercury Emissions in Water from Existing and New Brine Recirculation Chloralkali Plants (exit of the purification plant).
- **PARCOM Decision 81/1** on Limit Values for Existing Waste Brine Chlor-Alkali Plants.
- **PARCOM Decision 81/2** on Limit Values for Existing Brine Recirculation Chlor-Alkali Plants (exit of the factory site).
- PARCOM Decision 82/1 on New Chlor-Alkali Plants Using Mercury Cells.
- **PARCOM Recommendation 85/1** on Limit Values for Mercury Emissions in Water from Existing Brine Recirculation Chlor-Alkali Plants (exit of factory site).
- PARCOM Decision 85/1: Programmes and Measures of 31 December 1985 on Limit Values and Quality Objectives for Mercury Discharges by Sectors other than the Chlor-alkali Industry
- **PARCOM Decision 85/2**: Programmes and Measures on Limit Values and Quality Objectives for Cadmium Discharges.
- **PARCOM Recommendation 92/3** Concerning Limitation of Pollution from New Secondary Steel Production and Rolling Mills.
- **PARCOM Decision 92/3** on the Phasing Out of PCBs and Hazardous PCB Substitutes.
- PARCOM Recommendation 92/2 Concerning Limitation of Pollution from New Primary Iron and Steel Production Installations (Spain lifted its reservation in 2003).

- **PARCOM Recommendation 92/4** on the Reduction of Emissions from the Electroplating Industry (Spain lifted its reservation in 2003).
- PARCOM Recommendation 92/8 on Nonylphenol-Ethoxylates.
- PARCOM Recommendation 93/1 on the Limitation of Pollution from Existing Primary Iron and Steel Production Installations (Spain lifted its reservation in 2003)
- **PARCOM Recommendation 94/5** on Best Available Techniques and Best Environmental Practice for Wet Processes in the Textile Processing Industry.
- **PARCOM Decision 95/1** on the Phasing Out of Short-Chained Chlorinated Paraffins.
- **PARCOM Recommendation 97/1** Concerning Reference Values for Effluent Discharges for Wet Processes in the Textile Processing Industry.
- **OSPAR Recommendation 98/2** on Emission and Discharge Limit Values for Existing Aluminium Electrolysis Plants.
- **OSPAR Decision 98/4** on Emission and Discharge Limit Values for the Manufacture of Vinyl Chloride Monomer (VCM) including the Manufacture of 1,2-dichloroethane (EDC). Consolidated text.
- **OSPAR Decision 98/5** on Emission and Discharge Limit Values for the Vinyl Chloride Sector, Applying to the Manufacture of Suspension-PVC (s-PVC) from Vinyl Chloride Monomer (VCM). Consolidated text.
- **OSPAR Recommendation 2002/1** on Discharge Limit Values for Existing Aluminium Electrolysis Plants.
- OSPAR Recommendation 2000/3 on Emission and Discharge Limit Values for the Manufacture of Emulsion PVC (e-PVC) from Vinyl Chloride Monomer. Consolidated text.