



# Report on mercury Emission Limit Values (ELV) and Best Available Techniques (BAT) at the Mediterranean countries

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#### 1. Introduction

In the framework of the Barcelona Convention and the Article 15 of the Protocol for the Protection of the Mediterranean Sea against Pollution from Land-Based Sources and Activities (LBS Protocol), the Mediterranean Action Plan (MAP) agreed at its meeting of 2008 in Aix-en- Provence (France) to develop an action plan on mercury for the biennium 2010-2011 in order to establish measures and deadlines for reducing mercury discharges to the marine environment.

In this context, the CP/RAC in collaboration with MEDPOL prepared a diagnosis of mercury in the Mediterranean region in order to describe the state of mercury as regards the legal framework, production, trade, use, emissions, waste, prevention and control, and identification of future challenges.

Based on this analysis, the Secretariat of the Convention produced a draft "Regional Plan for the Reduction of Mercury as part of the implementation of Article 15 of the LBS Protocol" which is currently undergoing approval by the MAP countries. As agreed in the last meeting of MEDPOL Focal Points to review Regional Plans (25-27 May 2011 in Rhodes), in article 3 of the draft Regional Plan on mercury, the measures related to the non-chloralkali industry should present the recommended ELVs in two columns, the first one reporting the ELVs currently indicated in the draft plan as a target for 2015 (50 micrograms per liter, already accepted in Rhodes) and the second one with the available state-of-the-art ELVs as targets for 2019.

This report prepared by CP/RAC in cooperation with MED POL, contains a comparative analysis on the state of the art of the BAT (Best Available Techniques) for the reduction of mercury emissions in water, associated with ELV, with the aim to define the targets which Mediterranean countries must meet by 2015 and 2019, and also summarizes the national views, information and/or experiences regarding mercury ELV associated with BAT, collected from the questionnaires sent to MED POL Focal Points and designated experts.







# 2. Scope and object

The main objective of this study is <u>to offer technical information and a comparative</u> <u>analysis ("benchmarking") on Best Available Techniques (BAT) and Associated</u> <u>Emission Limits (AEL) of mercury in water</u> for the following sectors manufacturers and / or users:

- Users of mercury and its compounds as catalysts, for example in the manufacture of polyurethane.
- Manufacture of mercury catalysts.
- Production of organic and inorganic compounds of mercury for other uses, such as laboratory reagents.
- Manufacture of batteries containing mercury.
- Non-ferrous metallurgy.
- Plants for the recycling and recovery of mercury.
- · Extraction and refining non-ferrous metals.
- · Treatment of hazardous waste containing mercury.





#### 3. International references

This chapter describes the reference information on mercury Emission Limit Values (ELV) associated with Best Available Techniques (BAT) compiled from main international organisms and consulted experts.

## 3.1 International Negotiating Committee on Mercury

The International Negotiating Committee (INC) to prepare a global legally binding instrument on Mercury has not identified nor proposed at its third session specific best available techniques and best environmental practices (BAT/BEP) with associated mercury emission limit values (ELV). In any case, articles 10 and 11 or 11 alt. of the draft text<sup>2</sup>, specifies that the Conference of the Parties shall adopt guidelines on BATs and BEPs for reducing atmospheric emissions of mercury and releases of mercury and mercury compounds to water and land. It is still to be decided in the following sessions of the negotiating Committee if these future guidelines will be compulsory or not.

The new draft of the text of the instrument presented at the INC3 considers, for emissions and releases (section G), two options: option1, separating atmospheric emissions and releases to water and land into two articles (articles 10 and 11), and option 2, addressing both emissions and releases in one article (article 11 alt). In both options, in the current draft action plans are proposed for the source categories by which each country (or alternatively only countries with significant aggregate emissions, still to be decided) should, on a mandatory or on a voluntary basis (still to be decided), reduce (and where feasible eliminate) its atmospheric mercury emissions and releases of mercury and mercury compounds to water and land.

http://www.unep.org/hazardoussubstances/Mercury/Negotiations/INC3/INC3MeetingDocuments/tabid/3487/Default.aspx

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<sup>&</sup>lt;sup>1</sup> INC3, Nairobi, October-November 2011





The considered sources of mercury releases to water and land are specified in <sup>3</sup>. For chlor-alkali production the proposed expiration date for allowable use exemption is 31 December 2020. For the rest of processes described in Annex D, no expiration date is still proposed. For the case of the acetylene-based VCM production (which uses mercury catalyst, on the contrary of the ethylene based VCM production which is mercury-free), it is still to be decided if it is an acceptable exemption until five years after the COP decides that a mercury-free acetylene-based technology for the process is available (there is a pilot project under development in China). The dental practices are considered as a source and a compulsory installation of filters are contemplated.

It is worth mentioning that option 1 specifies that Parties may cooperate in developing and implementing strategies and methodologies for achieving reductions or eliminations, including through the provision of financial and technical assistance.

#### 3.2 OSPAR Convention

The Convention for the Protection of the marine Environment of the North-East Atlantic (the 'OSPAR Convention') is the mechanism by which fifteen Governments of the western coasts and catchments of Europe, together with the European Community, cooperate to protect the marine environment of the North-East Atlantic. France and Spain are the only Mediterranean countries that are members both of OSPAR and the Barcelona Convention.

OSPAR has first developed, and is implementing, a suite of five thematic strategies to address the main threats that it has identified within its competence (the Biodiversity and Ecosystem Strategy, the Eutrophication Strategy, the Hazardous Substances Strategy,

<sup>&</sup>lt;sup>3</sup> Sources of mercury releases to water and land: (between square brackets, processes not yet decided)

<sup>1.</sup> Facilities that manufacture mercury-added products.

<sup>2.</sup> Facilities that use mercury in the manufacturing processes listed in **Annex D** (manufacturing processes not allowed under article 7): Chlor-alkali production, [Acetylene-based vinyl chloride monomer production], [production processes in which mercury or mercury compounds are used as catalysts], and [Artisanal and small-scale gold mining].

<sup>3.</sup> Facilities for mercury recovery, recycling, and reprocessing and facilities where mercury is produced as a by-product of non-ferrous metals mining and smelting, as listed in Annex A.

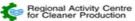
<sup>4.</sup> Artisanal and small-scale gold mining.

<sup>5.</sup> Facilities for the disposal of mercury-containing wastes.

<sup>6.</sup> Each Party shall ensure the installation of amalgam separators at dental practices within its territory at the latest by 20[xx]. The separators shall have an efficiency of no less than [xx] per cent.







the Offshore Industry Strategy and the Radioactive Substances Strategy), together with a Strategy for the Joint Assessment and Monitoring Programme, which assesses the status of the marine environment and follows up implementation of the strategies and the resulting benefits to the marine environment. These six strategies fit together to underpin the ecosystem approach.

During the 1980s and 1990s, OSPAR adopted more than 60 Recommendations and legally-binding Decisions<sup>4</sup> to regulate the main point sources (e.g. industry) and diffuse sources (e.g. products and wastes) of pollution with hazardous substances in the OSPAR area. OSPAR countries were required to implement best available techniques (BAT) and best environmental practices (BEP) and to achieve specified limit values for emissions and discharges for major industrial sources of heavy metals, organo-halogens and polycyclic aromatic hydrocarbons (PAHs). Regulated industries include: large combustion plants; the manufacturing of iron, steel, aluminium, textiles, chlorine, pharmaceuticals, organic chemicals, pulp and paper, and vinyl chloride; and the refining of crude oil. Periodic reporting shows that these measures have been broadly implemented across the OSPAR area. This work has been increasingly supported by implementation of similar EU legislation.

As for particular mercury limit values, only PARCOM Decision 85/1 on Programmes and measures of 31 December 1985 on limit values and quality objectives for mercury discharges by sectors other than the chlor-alkali electrolysis industry, establishes the limit values indicated below to be complied as from July 1989.

<sup>&</sup>lt;sup>4</sup> Relevant OSPAR decisions regarding mercury are:

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 Recommendation 85/1 on Limit Values for Mercury Emissions in Water from Existing Brine Recirculation Chlor-alkali Plants (exit of factory site).

PARCOM Decision 80/2 on Limit Values for Mercury Emissions in Water from Existing and New Brine Recirculation Chlor-alkali Plants (exit of the purification plant).

PARCOM Decision 80/1 on Environmental Quality Standard for Mercury in Organisms.

PARCOM Recommendation 89/3 on Programmes and Measures for Reducing Mercury Discharges from various sources.

PARCOM Recommendation 90/1 on the definition of the Best Available Technology for Secondary Iron and Steel Plants.

PARCOM Recommendation 92/4 on the reduction of emissions from the electroplating industry.

PARCOM Recommendation 93/2 on further restrictions on the discharge of mercury from dentistry.







Table 5. Limit values for mercury discharges by sectors other than the chlor-alkali electrolysis industry (PARCOM Decision 85/1).

Industrial sector	Limit	value
1. Chemical industries using mercury	50	μg/l effluent
catalysts:	0.1	g/t vinyl chloride production capacity
a. in the production of vinyl chloride		
b. in other processes	50	μg/l effluent
,	5	g/kg mercury processed
		3 3 3 3 3 7
2. Manufacture of mercury catalysts used in	50	μg/l effluent
the production of vinyl chloride	0.7	g/kg mercury processed
·		
3. Manufacture of organic and non-organic	50	μg/l effluent
mercury compounds (expect for products	0.05	g/kg mercury processed
referred to in point 2)		
4. Manufacture of primary batteries	50	μg/l effluent
containing mercury	0.03	g/kg mercury processed
5. Non-ferrous metal industry	50	μg/l effluent
a. Mercury recovery plants		
b. Extraction and refining of non-ferrous	50	μg/l effluent
metals		
6. Plants for the treatment of toxic wastes	50	μg/I effluent
containing mercury		

Regarding the electroplating industry, PARCOM Recommendation 92/4 considers technical measures to treat specific in-plant waste water streams that are particularly hazardous (e.g. cadmium, mercury, chlorinated solvents). The maximum concentration of mercury in specific waste water streams is 50 µg/l.





# 3.3 European IPPC Bureau (EIPPCB)

The Integrated Pollution Prevention and Control Bureau (IPPC) of the Institute for Prospective Technological Studies (IPTS) of the European Commission's Joint Research Centre (JRC) was set up to organise an exchange of information between Member States and Industry on Best Available Techniques (BAT), associated monitoring and developments in them.

The IPPC Bureau produces reference documents on Best Available Techniques, called BREFs, which are the main reference documents used by competent authorities in Member States when issuing operating permits for the installations that represent a significant pollution potential in Europe. In this sense, the Proposal for a Directive of the European Parliament and of the Council on Industrial emissions declares in its article 15 that "the competent authority shall set emission limit values that do not exceed the emission levels associated with the best available techniques as described in the BAT reference documents (BREFs)."

In the international context, the European information exchange on best available techniques is considered to be an EU contribution to the global process initiated in 2002 at the World Summit on Sustainable Development so that non-EU countries can also reap the benefits of this ambitious work.

Considering the sectors and subsectors covered by the scope this work, it has been difficult to distinguish mercury Emission Limit Values (ELV) for such sectors and subsectors. Hence, information collected from the IPPC Bureau experts has been classified according to two main IPPC sectors: chemical industry and non-ferrous metals industry.

#### 3.3.1 Chemical industry

In the latest adopted series of BREFs regarding the chemical sector, BAT-Associated Emission Levels (AELs) for Hg emissions to water exist in the reference document on **'Large volume organic chemical industry'** or LVOC BREF (EC, 2003a) as **50 µg/I** (as a daily average). This value is reported to be for waste water emissions for the whole LVOC sector and it refers to tributary streams after dedicated pre-treatment and before final treatment.

The final treatment of the waste waters from the chemical sector are dealt within the reference document on 'Common waste water and waste gas treatment/management systems in the chemical sector' or CWW BREF (EC, 2003b). The BREF considers the following BATs and BEPs for streams containing heavy metals:







- -segregate waste water as far as possible
- -treat the segregated waste water streams at source before mixing with other streams (Table 1)
- -facilitate further elimination of heavy metals in a final WWTP as a polishing step, with subsequent treatment of sludge, if necessary

For heavy metals, the LVOC BREF gives the following specific BATs (Table 1, resumed and adapted to mercury from original)







Table 1. Treatment Techniques associated with BATs for Heavy Metals

	Precipitation/sedimentation or air flotation/filtration	<u>lon exchange</u>	Nanofiltration (NF)/ Reverse Osmosis (RO)
Purpose	Transferring dissolved heavy metal compounds to insoluble compounds and separating them from the waste water stream	Replacement of heavy metal ions in the aqueous phase by other ions from ion exchange resin	Separation of heavy metal ions by membrane permeation.
Application	Removal of heavy metals from waste water streams, preferably for higer concentrations.	Solutions containing heavy metal ions with low concentrations.	Achieving high grade of purity
Consumables	Precipitation agent Flocculant/coagulant Energy for pumps	Regeneration liquid Fouling suppressors Energy	Chemicals for cleaning Energy 1-3 Kwh/m3
Cross-media effects	Disposal of sludge	Regeneration returns high concentrations of heavy metal solutions (recovery or disposal)	Concentrate needs further treatment, e.g. ion exchange
% pollutant removal	Dependent on production process		Hg >90 with NF Hg close to 100 with RO
Achievable Emissions Levels	Dependent on production process		Very low (near to zero with RO)





Different strategies or combination of technologies can be chosen to achieve the desired ELV depending on the origin of the waste stream:

- Removal of a single heavy metal species from inorganic waste water matrix
- Removal of a heavy metal mix from inorganic waste water matrix
- Removal of heavy metals from organic waste water matrix with tendency for formation of metal complexes, e.g. dye agents.

A proposal of  $0.01-0.84 \mu g/l$  ELV was made as reported in the adopted CWW BREF (2003, pg.294) but there was no consensus on this at the time.

As for the review of the CWW BREF (EC, 2009a), **Mr. Serge Roudier, Head of the European IPPC Bureau,** provided some information on this current process. According to him, Hg emissions to water have been reported in the questionnaires that have been submitted by **central waste water treatment plants (WWTPs**). Out of 63 questionnaires that have been filled in, 26 of them reported Hg values in their effluents, the average emissions were reported to be less than  $2 \mu g/I^5$ . **The plants that tended to be close to 2**  $\mu g/I$  were indirect dischargers, i.e. the releases are treated by a WWTP before final discharge point.

The following pre-treatment and treatment operations (carried out at the installation(s) from which the waste waters originate or at the central WWTP) have been reported in the mentioned questionnaires:

- Precipitation and filtration.
- · Ion exchange.
- Activated carbon.
- Activated sludge systems combined with sludge incineration.

Based on the data gathered from the central WWTPs, Mr. Roudier advice is that the value of 5  $\mu$ g/l Hg proposed for the year 2019 by the Regional Plan is in the higher range of what has been reported so far to IPPC Bureau.

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<sup>&</sup>lt;sup>5</sup> The exceptions reported as yearly averages were:

<sup>• 1</sup> questionnaire reported average effluent Hg emission as <20  $\mu$ g/l but this WWTP has a chlor-alkali production on the chemical site.

<sup>1</sup> questionnaire reported average effluent Hg emission as <10 μg/l but this WWTP had only 4 spot samples to derive this yearly average value.

<sup>• 1</sup> questionnaire reported average effluent Hg emission as 5  $\mu$ g/l but this is an indirect discharger and discharges to a municipal WWTP.





The 'Manufacture of organic fine chemicals' or OFC BREF (EC, 2003c) affirms that the usual measure applied to prevent heavy metals dilution and sludge contamination/emission is the pre-treatment of the concentrated waste water streams by means such as ion-exchange, precipitation/filtration, and reactive extraction.

Data on a site where heavy metals are used extensively, e.g. for metallisation, and the created waste water streams also contain heavy metal complex compounds is reported. Waste water streams are treated individually in order to remove the heavy metal content, including a step for the destruction of metal complex compounds where required. Treatments reported are precipitation and filtration and destruction of heavy metal complex compounds with  $Na_2S_4O_4$ , (sodium hydrosulphite) precipitation and filtration: The resulting value for the total effluent (before the biological WWTP) is 4  $\mu$ g Hg/l (yearly average).

#### 3.3.2 Non-ferrous Metals industries

In the adopted reference document on 'Non-ferrous Metal Industry' or NFM BREF (EC, 2001) a BAT-AEL of less than 10 µg Hg/I for the general production of lead and zinc including different process steps in primary and secondary lead and zinc production is reported.

Regarding processes to produce mercury, which include producers of copper, lead and zinc who produce mercury from the scrubber systems prior to sulphuric acid plants and secondary mercury production from the treatment of dental amalgam and lamps, both adopted and draft document of the NFM BREF (EC, 2001 and EC, 2009b) state that emissions to water of 50  $\mu$ g/l are easily achievable with a basic generic treatment of adjusting pH with lime and precipitation with a flocculant, provided that solids are removed efficiently.

According to these references, mercury can be specifically removed from aqueous effluents by precipitation as mercury sulphide, although no figures are given of the emissions reached with this method. Sodium sulphide is used as the regent and the pH of the effluent is controlled. Mercury sulphide is not soluble and is precipitated. Activated carbon is also used to remove final traces of mercury from effluents and, in some cases sand filters are used to better remove solids. Sludges and spent carbon from primary mercury production are returned to the furnaces.

For primary and secondary copper production, a general BAT-AEL of 50  $\mu$ g Hg/I can be found in the adopted BREF, with a basic treatment of adjusting pH with lime and precipitation with a flocculant.







For precious metals production, a BAT-AEL of 10 µg Hg/I can be found in the adopted NFM BREF and the current draft of the NFM BREF.

According to the consulted expert, Mr. Rainer Remus (Institute for Prospective Technological Studies, JRC - European Commission), in the current draft of the revised BREF, BAT-AELs for Hg emissions into water are included for primary and secondary copper production, refractory metals production, ferro-alloys production and for nickel and cobalt production. In all cases a BAT-AEL of 10 - 50 µg Hg/l has been included; however, it is possible that these data will be omitted or modified in the next NFM draft.

# 3.4 Umweltbundesamt (German Federal Environment Agency -UBA)

In Germany, each discharge, wherever it is located, has to comply with the Federal Water Act (Wasserhaushaltsgesetz, WHG). Regulations of the WHG cover waste water streams generated by industrial processes. Water protection legislation in Germany is implemented by the Ordinance on Waste Water (Abwasserverordnung - AbwV, 17 June 2004) and by general administrative regulations concerning minimum requirements to be met by discharges, irrespective of the quality of the receiving medium.

According to the Ordinance on Waste Water (Abwasserverordnung - AbwV, 17 June 2004), for mercury from plants other than chloralkali electrolysis, the following requirements<sup>6</sup> shall apply:

(1) Subject to the provisions of paragraphs (2) to (5) below, a requirement of **50 µg/l** in the 2-hour composite sample or qualified random sample shall apply to mercury (Hg).

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<sup>&</sup>lt;sup>6</sup> The requirements refer to the waste water in the effluent from the plant or operating unit in which the substances or their compounds are used, prior to blending with other waste water. If the waste water is treated outside of the plant or operating unit in a waste water treatment plant designed to treat waste water contaminated with the specified substances or their compounds, then the levels stated shall refer to the waste water in the effluent from this waste water treatment plant.

<sup>&</sup>lt;sup>7</sup> Random sample shall refer to a single sample taken from a waste water flow.

Composite sample shall refer to a sample which is taken continuously over a given period, or a sample consisting of several samples taken either continuously or discontinuously over a given period and blended.

Qualified random sample shall refer to a composite sample of at least five random samples taken over a maximum period of two hours at intervals of no less than two minutes, and blended.







- (2) For the use of catalysts containing mercury, a requirement of 0.1 g/t of production capacity<sup>8</sup> shall apply to vinyl chloride production, and a requirement of 5 g/kg of mercury used in other branches of production.
- (3) For the production of catalysts containing mercury for use in vinyl chloride production, a requirement of 0.7 g/kg of mercury used shall apply.
- (4) For the production of mercury compounds other than the products cited in paragraph (3) above, a requirement of 0.05 g/kg of mercury used shall apply.
- (5) The requirements cited in paragraphs (2) to (4) above refer to the usage capacity for mercury over 24 hours on which the water discharge licence is based.

For **chemical industry**, the following requirements apply to waste water prior to blending<sup>9</sup> with other waste water (qualified random sample or 2-hour composite sample):

- (I) 50 µg/I referring to waste water flows from the manufacturing, further processing or application of these substances.
- (II) 1 µg/I referring to waste water flows not originating from the manufacturing, further processing or application of these substances but which are nevertheless contaminated with such substances below the concentration levels in (I).

For biological treatment of waste (qualified random sample or 2-hour composite sample) and treatment of waste by means of chemical and physical processes (CP facilities) and processing of used oil (random sample) a mercury limit of 50 µg/l apply to waste water prior to blending with other waste water.

For battery production the requirements for mercury (qualified random sample or 2-hour composite sample) are 50 µg/l and 0.03 kg/t referring to waste water prior to blending with other waste water.

For production and casting of the non-ferrous metals, lead, copper, zinc and byproducts as well as the production of semi-manufactured goods a mercury limit of 50 µg/I (qualified random sample or 2-hour composite sample) apply to waste water prior to blending with other waste water.

Waste water from cooling systems for the indirect cooling of industrial processes is excluded from these requirements and the same Ordinance on Waste Water (Abwasserverordnung – AbwV, 17 June 2004) establish related provisions. **Discharges** 

<sup>&</sup>lt;sup>8</sup> Production-specific load level shall refer to the load level (e.g. m³/t, g/t, kg/t) in relation to the production capacity on which the water discharge licence is based.

<sup>&</sup>lt;sup>9</sup> Blending shall refer to the merging of waste water flows from different origins.





from cooling systems of industrial processes must not contain mercury compounds (qualified random sample or 2 hours composite sample).

Reports on Best Available Techniques (BAT)<sup>10</sup> in zinc and lead production (DFIU, 1999a) and copper production (DFIU, 1999b) published by UBA describe related German Candidate BAT for waste water treatment supporting the abovementioned legal requirements.

Usually, contaminated water generated by the non-ferrous metal industry is characterised by the presence of elevated metal concentrations (for example, mercury) as well as suspended solids. So the end of pipe treatment techniques used in the plants should be selected in order to minimise the concentration of these pollutants in final effluent discharges to the aquatic environment. The treatment of the waste water of the whole facility is usually done in a central waste water treatment plant but depending on the site specific conditions plants can be connected to an urban waste water system where the end of pipe treatment is applied. Because of different pollutant loads, the effectiveness of the end of pipe treatment may be improved by separating cooling water, surface runoff water from roofs and roadways and stockyard as well as process water or by use and reuse of water in decades depending from the demands for the water to be used.

If the treatment is carried out at the plant site, the waste water from the different production plants is usually brought together in a collecting tank where oil, grease and plastics are removed mechanically. The subsequent treatment is based on **chemical precipitation and neutralisation, sedimentation and filtration or centrifugation** as described in Table 2.

http://www.umweltbundesamt.de/nachhaltige-produktion-anlagensicherheit-e/publikationen/index.htm.





Table 2. Main devices for waste water treatment in non-ferrous metal industry (DFIU, 1999a).

Process step	Principle	Device	Remark					
Precipitation and neutralisation	Chemical precipitation: forming of insoluble complexes by addition of precipitants, adjustment of pH.	Precipitation reactor, tanks.	To remove heavy metals, hydroxides and sulphides are used as precipitants; ferric sulphate may be used to eliminate the surplus sulphide.					
Solids separation	<b>Sedimentation:</b> Settling due to gravity, often use of additional flocculants.	Clarifier, two compartment tank, cyclators.	Flocculants: polymers.					
Polishing step	Filtration	Gravity filter.						
Precipitate dewatering	Filtration, centrifugation	Belt filter, vacuum filter (rotary drum filter), filter press, cyclone.	Dewatered sludge is recycled to the metal production process or dumped.					

# 3.5 Flemish Institute for Technological Research (VITO)

The Centre for Best Available Techniques is hosted by VITO (the Flemish Institute for Technological Research which provides policy-relevant information and support to Regional, National and European governments). This BAT-centre collects, evaluates and distributes information on available environmentally friendly techniques. For the preparation of this report, the **expert Ms. Caroline Polders** has been consulted.

#### 3.5.1 Chemical industry

The VITO study "BATs for wastewater treatment in the Large Volume Organic Chemistry (LVOC) industry" (Polders, 2008), gives recommendations with respect to BAT-associated emission levels for this sector and with respect to further research. The study gives data from discharges into surface waters of 20 chemical companies. The concentration of mercury in the wastewater of these companies varies from 1 to 10  $\mu$ g Hg/l.







Appendix 5.3.2 of the Order of the Flemish Government of 1 June 1995 (VLAREM II) concerning the sectorial discharge conditions for industrial waste water sets the current mercury Emission Limit Levels valid for the industrial sectors in Flanders (Table 3). The VITO study recommends to discard these emission limit values which specifies permit conditions of discharge, because they are " out of date and not in line with the Best Available Technologies any longer".

Table 3. Limit values for mercury discharges by sectors other than the chlor-alkali electrolysis industry (VLAREM II, Appendix 5.3.2).

	Mercury (µg/l)
Pharmaceutical industry	150
Other laboratories	150
Lacquer, paint, printing inks and pigments (production)	1
Non ferrous-metal (production and processing)	50
Cleaning by the internal washing of receptacles in which substances were stored or transported	1
Paper and cardboard factories and pulp mills	< reporting limit
Landfills	150
Textiles (fibres, yarn, wool, fabrics, knitted work, plaiting, textile goods and similar products)	20

<sup>&</sup>quot;Reporting limit": the value below which a component is reported as unquantifiable ("<"). This is equivalent to at least the limit of determination.

#### 3.5.2 Non-ferrous Metals industries

Contrary to chemical sector, the BAT study on the non-ferrous metals (NFM) industry<sup>11</sup>, which was based on the NFM BREF (EC, 2001), concludes that the Flemish legislation,

<sup>&</sup>lt;sup>11</sup> BBT voor de non-ferronijverheid. Gent. Academia Press.





as well as the current environmental performance of the installations are in line with the BAT-requirements from the BREF. To further improve upon the environmental performance of the Flemish industry, more stringent emission limit values are suggested for water pollution, in particular mercury and other heavy metals.

# 3.6 Instituto Andaluz de Tecnología (IAT) – Andalusian Technology Institute

IAT provided technical assistance to the Ministry of Environment of Andalucía for the granting of Emission Limit Values to metal production and processing facilities. IAT collected both legal reference values and limit values associated with Best Available Techniques for air emissions and wastewater discharges of such facilities (DGPC, 2006). For the preparation of this study, **experts Ms. Eva Pérez and Mr. Victor Vazquez** have been consulted.

The BATs identified through the study are:

- Neutralization and/or precipitation.
- Solid separation.
- Discharge, recycling or recovery of treated water.
- Sludge dewatering and management.

Table 4 summarizes limit values collected for the purpose of the study.

http://www.emis.vito.be/sites/default/files/pagina/non-ferro\_volledig.pdf.







**Table 4.** Reference Limit Values and Best Values Achieved for mercury discharges for non-ferrous metals industry (DGPC, 2006).

Dis	scharges to pub	lic sea or land d	lomain (ug/l)	
		rence Limit Value		Reference Limit
	Monthly	Daily	Punctual	Value <sup>13</sup>
Non-ferrous metals sector	50	200-100	200-100	50
Discharges to	o public surface	water domain c	or sewer systen	ns (µg/l)
	Refe	rence Limit Value	es <sup>14</sup>	Reference Limit Value <sup>15</sup>
	Monthly	Daily	Punctual	
Non-ferrous metals sector	100	50	50	50

#### 3.7 World Bank

In 1999, the World Bank published the Pollution Prevention and Abatement Handbook (World Bank Group, 1999), which was specifically designed to be used in the context of the World Bank Group's environmental policies. The Handbook provides detailed guidelines to be applied in the preparation of World Bank Group projects. It covers almost 40 industrial sectors and represents the state-of-the-art thinking on how to reduce pollution emissions levels that are normally achievable through a combination of cleaner production and end-of-pipe treatment.

The emission guidelines for each of the industrial sectors present emissions levels normally acceptable to the World Bank Group in making decisions regarding provisions of World Bank Group assistance.

A mercury maximum value of 10  $\mu$ g/l is established for for direct discharge to surface waters in the metal and chemical sectors.

<sup>&</sup>lt;sup>12</sup> Decree 14/1996 of Andalucia.

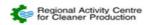
<sup>&</sup>lt;sup>13</sup> Ordinance on Requirements for the Discarge of Waste Water into Waters, 17 June 2004. Federal Ministry for the Environment (Germany), Nature Conservation and Nuclear Safety.

<sup>&</sup>lt;sup>4</sup> Spanish Royal Decree 849/1986.

<sup>&</sup>lt;sup>15</sup> Ordinance on Requirements for the Discarge of Waste Water into Waters, 17 June 2004. Federal Ministry for the Environment (Germany), Nature Conservation and Nuclear Safety.







This emission level is considered to be consistently achieved by well-designed, welloperated, and well-maintained pollution control systems. Dilution of effluents to achieve these guidelines is unacceptable.

All of the maximum levels should be achieved for at least 95% of the time that the plant or unit is operating, to be calculated as a proportion of annual operating hours.

## 3.8 United States Environmental Protection Agency (EPA)

The U.S. Clean Water Act (CWA) requires states to compile a list of water bodies that do not fully support beneficial uses such as aquatic life, fisheries, drinking water, recreation, industry or agriculture. These inventories characterize as fully waters supporting, impaired, or in some cases threatened for beneficial uses.

The Total Maximum Daily Load (TMDL) is a regulatory term in CWA describing a value of the maximum amount of a specific pollutant that a body of water can receive while still meeting water quality standards. In the case of the states of the North-East Region 16 of the U.S., an initial target fish mercury concentration of 0.3 ppm is fixed, being the current level 1.14 ppm (90th percentile). This reduction factor (RF) fixes the water quality goal. Then the base year mercury loadings are calculated from the following sources:

- -Area of the Region: 307,890 Km2
- -Point source load (PSL) (wastewater discharge data from industrial permits): 141 Kg/year
- -Modeled anthropogenic atmospheric deposition (Anthropogenic Nonpoint Source Load): 4,879 Kg/year
- -Natural Nonpoint source load atmospheric deposition: 1,627 Kg/yr

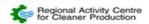
This gives a Total Source Load of 6,647 Kg/yr, and the loading goal as (TSL\*(1-RF)) = 1,749 Kg/year, which represents the maximum load of mercury to achieve a desired target of 0.3 ppm of mercury in fish tissue.

The necessary reductions were divided into 3 phases, 1998-2003, 2003-2010 and 2010 on. The Phase III timeline and goal is set following re-evaluation of mercury emissions, deposition and fish tissue concentrations in 2010. To meet the reduction required in phase III, major air point sources will be addressed through the application of more stringent

<sup>&</sup>lt;sup>16</sup> States of Massachussets, New Hampshire, New York, Rhode Island, Vermont, Maine, Connecticut







control technology requirements and/or emission limits, economically and technically feasible/achievable.

It's worth mentioning that Northeast states recommend EPA implement plant-specific MACT (Maximum achievable Control Technology) limits for mercury under Section 112(d) of the Clean Air Act (Standards of performance for existing sources; remaining useful life of source) to control U.S power plants mercury emissions by 90% by costeffective and available technologies.<sup>17</sup>

<sup>17</sup> New England Interstate Water Pollution Control Commission. Northeast Regional Mercury Total Maximum Daily Load. Working document. 2007







#### 4. MAP countries contributions

In order to collect national views, information and/or experiences regarding mercury ELV associated with BAT, a brief questionnaire (see Annex) was sent to MEDPOL Focal Points and designated experts to identify the existence of the industrial sectors covered by this report in their countries and, either the approval of mercury ELV proposed for 2019 (5 μg/l) or the proposal of more appropriate ELV.

Twelve Mediterranean countries have provided information on the existence of such industrial sectors in their countries and their opinion on mercury ELV target proposed for 2019, eleven responses were provided by MEDPOL Focal Points and one by a national expert (Lebanon).

From a regional point of view, most industrial sectors included in the questionnaire have been identified in at least one Mediterranean country except for some specific processes of the chemical industry considered as mercury users (acetaldehyde production, vinyl acetate production, production of the cube (1-amino anthrachion) and the use of mercury intermediates for the production of other mercury compounds) which have been identified by none of the countries which responded the questionnaire.

As for the proposed mercury ELV for 2019:

- Nine out of the twelve countries have indicated their approval of the ELV 5 μg/l for 2019.
- Two other countries, France and Turkey, have proposed less stringent ELV for 2019:
  - France has proposed to keep the ELV for 2015 until 2019 (50 µg/l) except for the treatment of mercury containing wastes in which an ELV of 30 µg/l is proposed.
  - o Turkey proposes to keep the ELV 50 µg/l in the chemical industry (producers) and to reduce it to 10 µg/l for batteries industry, non-ferrous metals industry and waste treatment.
- Morocco has considered that it is necessary to assess the compliance of ELV for 2015 (50 μg/l) before establishing ELV targets for 2019.

All questionnaire responses are shown in Table 6.







**Table 6.** Summary of questionnaire responses from MEDPOL Focal Points (in grey, values that disagree with proposed ELV).

		NIA & GOVINA	СҮРІ	RUS	FRA	NCE	ISRA	AEL	ITA	ιLY	LEBA	NON	MAI	_TA	IOM	NACO	SYF	RIA	TUN	IISIA	TUR	KEY
	Sector identified? (Y/N)	ELV proposed for 2019	Sector identified? (Y/N)	ELV proposed for 2019	Sector identified? (Y/N)	1	Sector identified? (Y/N)	ELV proposed for 2019		ELV proposed for 2019												
CHEMICAL INDU	ISTRY	(USERS	5)																			
Use of mercury catalysts in the manufacture of polyurethane elastomers	Υ	5	N	5	Z	N.A.		5		5	N	5	Ν	5	N	5	N	5		5	N	
Acetaldehyde production with mercury- sulphate (HgSO4) as catalyst	N	5	N	5	?	50		5		5	N	5	N	5	N	5	N	5		5	N	
Vinyl acetate production with Hg catalysts	N	5	N	5	?	50		5		5	N	5	N	5	N	5	N	5		5	N	







		NIA & GOVINA	СҮР	RLIS	FRA	NCE	ISR	ΔFI	ITA	ΙV	LEBA	NON	MA	ΙΤΔ	MO	NACO	SYF	RΙΔ	TUN	ΙΙΣΙΔ	TUR	(FV
	Sector identified? (Y/N)		Sector identified? (Y/N)		Sector identified? (Y/N)	ELV proposed for 2019	Sector identified? (Y/N)	ELV proposed for 2019	Sector identified? (Y/N)	ELV proposed for 2019	Sector identified? (Y/N)	ELV proposed for 2019	Sector identified? (Y/N)	ELV proposed for 2019	Sector identified? (Y/N)	ELV proposed for 2019	Sector identified? (Y/N)	ELV proposed for 2019	Sector identified? (Y/N)	ELV proposed for 2019		ELV proposed for 2019
Production of the cube (1-amino anthrachion) colours/pigments with Hg catalyst	N	5	N	5	?	50		5		5	N	5	N	5	Z	5	N	5		5	Z	
Use of mercury intermediates for production of other mercury compounds	N	5	N	5	?	50		5		5	Ν	5	N	5	N	5	N	5		5	N	
Use of mercury intermediates in the pharmaceutical industry	Y	5	N	5	?	50		5		5	N	5	N	5	N	5	Y	5		5	N	
CHEMICAL INDU	JSTRY (	(PRODU	JCERS)	)																		
Manufacture of mercury catalysts	N	5	N	5	?	50	N	5		5	N	5	N	5	N	5	N	5		5	Y	50
Manufacture of organic and non-organic mercury compounds	N	5	N	5	?	50	N	5		5	N	5	N	5	Ν	5	N	5		5	Y	50







		VIA &	0.15																			
	HERZE	GOVINA	CYPI		FRA		ISR		ITA		LEBA		MAI		MON	NACO	SYF	l	TUN		TUR	
	Sector identified? (Y/N)	ELV proposed for 2019	Sector identified? (Y/N)	ELV proposed for 2019	Sector identified? (Y/N)	ELV proposed for 2019	Sector identified? (Y/N)	ELV proposed for 2019	Sector identified? (Y/N)	ELV proposed for 2019	Sector identified? (Y/N)	ELV proposed for 2019	Sector identified? (Y/N)	ELV proposed for 2019	Sector identified? (Y/N)	ELV proposed for 2019	Sector identified? (Y/N)	ELV proposed for 2019	Sector identified? (Y/N)	ELV proposed for 2019	Sector identified? (Y/N)	ELV proposed for 2019
BATTERIES IND	BATTERIES INDUSTRY																					
Manufacture of batteries containing mercury	Y	5	N	5	?	50	N	5		5	Y	5	N	5	N	5	Υ	5		5	Y	10
NON-FERROUS	METAL	INDUS	TRY																			
Non ferrous metal industry: mercury recovery plants	N	5	N	5	?	50	Y	5		5	N	5	N	5	N	5	N	5		5	Υ	10
Non ferrous metal industry: extraction and refining of non- ferrous metals	Z	5	N	5	?	50		5		5	Ν	5	Z	5	Z	5	N	5		5	Υ	10
WASTE TREATM	IENT																					
Plants for the treatment of toxic wastes containing mercury	N	5	N	5	Υ	30		5		5	N	5	Υ	5	N	5	N	5		5	Υ	10







		NIA & GOVINA	СҮРІ	RUS	FRA	NCE	ISR	ΑEL	ITA	ALY	LEBA	NON	MAI	_TA	MON	IACO	SYF	RIA	TUN	IISIA	TUR	KEY
	Sector identified? (Y/N)	ELV proposed for 2019	Sector identified? (Y/N)	ELV proposed for 2019	Sector identified? (Y/N)	ELV proposed for 2019	Sector identified? (Y/N)	ELV proposed for 2019	Sector identified? (Y/N)	ELV proposed for 2019	Sector identified? (Y/N)	ELV proposed for 2019	Sector identified? (Y/N)	ELV proposed for 2019	Sector identified? (Y/N)	ELV proposed for 2019						
Other sectors													Υ	5								

The specific comments provided by some of the countries are included below:

**Bosnia and Herzegovina:** environmental Law and relevant Rulebooks, which are in force at the moment in Bosnia and Herzegovina, do contain neither limit range, nor industry specific limit value for mercury emission. Therefore, there is a single limit value for mercury emission applicable to all industries on the territory of Bosnia and Herzegovina.

France: the value of 50 μg/l appears in French regulations as the ELV applicable to all "classified installations for environmental protection" subject to authorization.

Italy: the national legislation states a limit emission value in superficial waters (including marine coastal waters), as  $\leq$  5 µg/L (Dlgs 152/2006). Nevertheless, the legislation doesn't specify the type of industrial sector producing Hg emission.

**Lebanon:** questionnaire completed by Dr. Ali Yaacoub, Director of the Lebanese Cleaner Production Center.

Malta: other sectors: public sewer.







Morocco: the adoption of new limits requires the prior assessment of the status of implementation of the objectives set for 2015. Is that all countries can achieve these goals by 2015? What are the means to do so? Are available for all countries, both the north and south of the Mediterranean? It is necessary that all parties respect the limit values laid down in 2015 before moving to new standards for 2019.

Internationally, developing countries have repeatedly stressed that the commitments of the future convention on mercury, remain dependent on the establishment of a financial mechanism capable of helping countries to implementing the various provisions of the Convention. And at this stage, targets are not yet discussed.

Syria: Syrian Standard 3474/2009 for "Allowable treated water to be drained to an aqueous environment" determines a mercury ELV of 5 µg/l.

Tunisia: Values are acceptable because:

The discharge standards in the maritime public domain in Tunisia set the emission limit value of mercury to 1 µg / l. It should be noted that the current standard does not consider the type of activity.

It should be noted that this standard is being reviewed; concerning this parameter the proposed emission limit into the public maritime domain is 5 µg / I, which corresponds to the ELV proposed for 2019.

Turkey: sectors considered as identified in Turkey (Y) in the questionnaire are the ones listed in Annex I of the By-law on Control of Pollution by Dangerous Substances in Water and its Environment (Official Gazette No. 26005, dated 26 November 2005). The sectors considered as not identified (N) are the ones not considered by Turkish Legislation.

A national project on Implementation of By-law on Control of Pollution by Dangerous Substances in Water and its Environment will be implemented near future. Until the outputs of the national project and technical and scientific research are gathered, the limit values in the by-law will be valid.







#### 5. Conclusions

#### 5.1 International references

International references consulted provided scarce and dispersed information on BAT-Associated Emission Levels (AELs) for Hq emissions to water from the sectors scoped by this report. Most consulted references reported to have difficulties when trying to translate BAT-associated emission values to sectorial emission limit values because of the heterogeneity of the considered industrial sectors. Emission levels are considered to be very specific to each process and are difficult to define and quantify without a detailed study.

#### Chemical industry

BAT-Associated Emission Level (AEL) for Hg emissions to water according to LVOC BREF is 50 µg/l (as a daily average). This value refers to tributary streams after dedicated pre-treatment and before final treatment.

According to the CWW BREF (2003) the BATs for heavy metals at installations from which the waste waters originate are: Precipitation/sedimentation or air flotation, filtration, lon exchange, nanofiltration and reverse osmosis. In the current draft of CWW BREF, reported Hq emissions to water are less than 2 µg/l. The pre-treatment and treatment operations at WWTP reported are: precipitation and filtration, ion exchange, activated carbon and activated sludge systems combined with sludge incineration. According to these data, the value of 5 µg/l Hg proposed for the year 2019 by the Regional Plan is in the higher range of what has been reported so far to IPPC Bureau.

According to OFC BREF, an example site where waste water streams are treated individually in order to remove the heavy metal content by precipitation and filtration and destruction of heavy metal complex compounds with Na<sub>2</sub>S<sub>4</sub>O<sub>4</sub> (sodium hydrosulphite), precipitation and filtration, the resulting value for the total effluent before the biological WWTP is 4 µg Hg/I (yearly average).

OSPAR emission limit values (1985) for mercury discharges by sectors other than the chlor-alkali electrolysis industry are considered by PARCOM Decision 85/1. For the different chemical subsectors, a single ELV is established at 50 µg/l.





According to VITO, the ELVs established in the Order of the Flemish Government of 1 June 1995 (VLAREM II) for the chemical industry are out of date and should no be used any more.

The German Ordinance on waste water (Abwasserverordnung – AbwV, 17 June 2004) establishes a mercury limit of 50  $\mu$ g/I for chemical industry and plants using mercury other than chloralkali electrolysis.

According to World Bank Handbook, a mercury maximum value of 10  $\mu$ g/l is consistently achieved by well-designed, well-operated, and well-maintained pollution control systems.

#### **Battery manufacturing**

OSPAR emission limit value for the manufacture of batteries containing mercury is 50 µg/l.

The **German Ordinance on waste water** (Abwasserverordnung – AbwV, 17 June 2004) establishes a mercury limit of **50 µg/l** for **battery production**.

No other emission limit values have been identified for this sector and references regarding non-ferrous metals industries should not be used for this purpose.

#### Non-ferrous metals industry (NFM)

According to NFM BREF (EC, 2001) a **BAT-AEL** of less than 10  $\mu$ g Hg/I for the general production of lead and zinc including different process steps in primary and secondary lead and zinc production is reported.

Regarding processes to produce mercury, emissions to water of 50  $\mu$ g/l are considered to be easily achievable provided that solids are removed efficiently.

In general, for primary and secondary copper production, refractory metals production, ferro-alloys production and for nickel and cobalt production, **BAT-AELs for Hg emissions** into water are in the range of 10 - 50 µg Hg/l; however, it is possible that these data will be omitted or modified in the next NFM draft.

OSPAR emission limit values for mercury discharges by sectors other than the chloralkali electrolysis industry are considered by PARCOM Decision 85/1 which were to be complied as from July 1989. For the different non-ferrous metal subsectors, a limit value of **50 µg/I** is established.





According to VITO, Flemish legislation and current environmental performance of the installations are in line with the NFM BREF. However, more stringent emission limit values are suggested for mercury water pollution.

According to the references compiled by IAT, reference limit value for non-ferrous metals industry is 50  $\mu$ g/l. BAT associated to such mercury limit values are neutralization and/or precipitation, solid separation, discharge, recycling or recovery of treated water and sludge dewatering and management.

The German Ordinance on waste water (Abwasserverordnung – AbwV, 17 June 2004) establishes a mercury limit of 50  $\mu$ g/I for production and casting of the non-ferrous metals, lead, copper, zinc and by-products as well as the production of semi-manufactured goods.

According to World Bank Handbook, a mercury maximum value of 10  $\mu$ g/l is consistently achieved by well-designed, well-operated, and well-maintained pollution control systems in the NFM industry.

#### **Mercury waste treatment**

OSPAR emission limit value for mercury waste treatment is 50 µg/l.

No other emission limit values have been identified for this sector and no other references should be used for this purpose.

The German Ordinance on waste water (Abwasserverordnung – AbwV, 17 June 2004) establishes a mercury limit of 50  $\mu$ g/I for biological treatment of waste and treatment of waste by means of chemical and physical processes (CP facilities) and processing of used oil







#### 5.2 MAP countries contributions

Twelve Mediterranean countries have provided information on the existence of the industrial sectors considered by the scope of this report in their countries and their opinion on mercury ELV target proposed for 2019.

Most industrial sectors have been identified in at least one Mediterranean country except for some specific processes of the chemical industry considered as mercury users (acetaldehyde production, vinyl acetate production, production of the cube (1-amino anthrachion) and the use of mercury intermediates for the production of other mercury compounds) which have been identified by none of the countries which responded the questionnaire.

As for the proposed mercury ELV for 2019, nine out of the twelve countries have indicated their approval of the ELV 5 µg/l for 2019. Two other countries, France and Turkey, have proposed less stringent ELV for 2019 and Morocco has considered that it is necessary to assess the compliance of ELV for 2015 (50 µg/l) before establishing ELV targets for 2019.







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# **Annex: Questionnaire to MEDPOL Focal Points**





In order to set mercury emission limit values (ELV) to water by 2019 for other sectors than chlor alkali, we will appreciate if you check the following table and include/correct the information concerning your country where appropriate (column in grey are ELV for 2015 already agreed):

En vue de définir des valeurs limites d'émission de mercure (VLE) dans l'eau provenant de secteurs autres que des chlorures alcalins, nous apprécierons que vous vérifiez le tableau suivant et que vous incluez / corrigiez les informations concernant votre pays, (les colonnes en gris sont les valeurs limites d'émission pour 2015 déjà acceptées):

	Sector	Emission Limit	Emission Limit	Agree?
Industrial sector	identified in	Value (ELV)	Value (ELV)	(Y/N)
muusinai secioi	your country?	for 2015	proposed for 2019	Comment
	(Y/N)	(µg/l)	(µg/l)	
Chemical industry (users)				
Use of mercury catalysts in				
the manufacture of		50	5	
polyurethane elastomers				
Acetaldehyde production with				
mercury-sulphate (HgSO4) as		50	5	
catalyst				
Vinyl acetate production with		50	5	
Hg catalysts		30	3	
Production of the cube (1-				
amino anthrachion)		50	5	
colours/pigments with Hg		30	3	
catalyst				
Use of mercury intermediates				
for production of other		50	5	
mercury compounds				
Use of mercury intermediates		50	5	
in the pharmaceutical industry		30	3	
Chemical industry (producers	5)			







	Sector	Emission Limit	Emission Limit	Agree?
		Value (ELV)		(Y/N)
Industrial sector		` ,	, ,	` '
	your country?		proposed for 2019	Comment
	(Y/N)	(µg/l)	(µg/l)	
Manufacture of mercury		50	5	
catalysts		00		
Manufacture of organic and				
non-organic mercury		50	5	
compounds				
Batteries industry				
Manufacture of batteries				
containing mercury		50	5	
Non ferrous metal industry				
Non ferrous metal industry:			_	
mercury recovery plants		50	5	
Non ferrous metal industry:				
extraction and refining of non-		50	5	
ferrous metals				
Waste treatment	1		1	
Plants for the treatment of				
toxic wastes containing		50	5	
mercury				
Other:				

#### Notes:

Measured at the final discharge point after treatment.

Values are yearly averages of 24-hours mixed samples