



**Euro Chlor Risk Assessment for the Marine Environment
OSPARCOM Region - North Sea**

Mercury

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1. EXECUTIVE SUMMARY

Euro Chlor has voluntarily agreed to carry out risk assessment of 25 chemicals related to the chlorine industry, specifically for the marine environment and according to the methodology laid down in the EU risk assessment Regulation (1488/94) and the Guidance Documents of the EU Existing Substances Regulation (793/93).

The study consists of the collection and evaluation of data on effects and environmental concentrations. Basically, the effect data are derived from laboratory toxicity tests and exposure data from analytical monitoring programs. Finally the risk is indicated by comparing the “predicted environmental concentrations” (PEC) with the “predicted no effect concentrations” (PNEC), expressed as a hazard quotient for the marine aquatic environment.

To determine the PNEC value, three different trophic levels are considered: aquatic plants, invertebrates, fish and amphibians. PEC values are derived from monitoring in North Sea coastal waters, estuaries and sediments

Based on 21 data for fish and amphibians, 68 data for invertebrates and 35 data for algae, a PNEC for inorganic mercury of 470 ng/l was derived. Based on 11 data for fish, 9 data for invertebrates and 7 data for algae a PNEC for organic mercury of 10 ng/l was estimated. For inorganic mercury, worst case concentrations in coastal waters and estuaries found recently are up to 170 ng/l giving a safety margin up to 3 between PEC and PNEC. For organic mercury, a worst case PEC of 8.5 ng/l was calculated leading nearly to no safety margin.

Based on limited data confirmed by extrapolation from water effect levels, a PNEC sediment of 31.2 mg/kg and 1.2 mg/kg wet weight is found respectively for inorganic and organic mercury. For sediment, PEC values of 1.6 mg/kg and 0.048 mg/kg wet weight respectively for inorganic and organic mercury lead to margins of safety between 7 and 25.

Potential for secondary poisoning (if total transformation into organic mercury is considered in fish) was evaluated in large and small fish-eating predators. A lowest Tolerable Daily Intake (TDI) of 18 mg/kg b.w./d was compared with a daily intake (DI) varying from 6 to 22 µg/kg b.w. as calculated from fish monitoring data. The corresponding safety margins were estimated between 3 and 1.

In conclusion, the current monitoring data on mercury in coastal waters, estuaries and sediments do not demonstrate a significant risk to the environment although the margin of safety between PECs and PNECs are not far from 1. Trends in river waters are showing a six-fold decrease since 20 years. However, mercury levels in marine biota (fish) are mainly constant over the same period. Potential for secondary poisoning in marine fish-eating predators (birds or mammals) is also not of high concern based on current levels found in biota.

Emissions from the chlor-alkali industry were estimated to represent less than 10% of total anthropogenic emissions in Western Europe and less than 1% of total global cycle for mercury. Although the chlor-alkali industry is committed to continue mercury emissions reduction, it is unlikely that any future reductions from this source will significantly change the North Sea situation.

2. INTRODUCTION: PRINCIPLES AND PURPOSES OF EURO CHLOR RISK ASSESSMENT

Within the EU a programme is being carried out to assess the environmental and human health risks for "existing chemicals", which also includes chlorinated chemicals. In due course the most important chlorinated chemicals that are presently in the market will be dealt with in this formal programme. In this activity Euro Chlor members are cooperating with member state rapporteurs. These risk assessment activities include human health risks as well as a broad range of environmental scenarios.

Additionally Euro Chlor has voluntarily agreed to carry out limited risk assessments for 25 prioritised chemicals related to the chlorine industry. These compounds are on lists of concern of European Nations participating in the North Sea Conference. The purpose of this activity is to explore if chemicals related to chlorine industry presently pose a risk to the marine environment especially for the North Sea situation. This will indicate the necessity for further refinement of the risk assessments and eventually for additional risk reduction programmes.

These risk assessments are carried out specifically for the marine environment according to principles given in *Appendix 1*. The EU methodology is followed as laid down in the EU risk assessment Regulation (1488/94) and the Guidance Documents of the EU Existing Substances Regulation (793/93).

The exercise consists in the collection and evaluation of data on effects and environmental concentrations. Basically, the effect data are derived from laboratory toxicity tests and exposure data from analytical monitoring programs. Data are described for both inorganic and organic mercury. Where necessary, the exposure data are backed up with calculated concentrations based on emission models.

Due to mercury's potential to bioaccumulate in the environment, secondary poisoning has been examined more closely.

Finally the risk is indicated by comparing the "probable environmental concentrations" (PEC) with the "predicted no effect concentrations" (PNEC), expressed as a hazard quotient for the marine aquatic environment.

3. COMPOUND IDENTIFICATION

3.1 *Description*

CAS number	:7439-97-6 (elemental mercury)
EINECS number	:231-106-7
EC-Annex I Number	:080-001-00-0
IUPAC name	:Mercury
Molecular formula	:Hg
Molecular weight	:200.59

Mercury (Hg) is a silvery white metal, liquid at room temperature. In the environment, mercury may occur in three oxidation states: elemental (Hg^0), mercurous (Hg_2^{2+}) and mercuric (Hg^{2+}), either as inorganic mercury compounds (mercuric(II)chlorides,

hydroxides, oxides and sulphides) or organic mercury compounds. The speciation of mercury strongly depends on the pH, the redox potential and the presence of ligands, such as chloride, sulphate and humic acids. In marine waters the major form of mercury in the dissolved phase is the highly soluble and stable HgCl_4^{2-} complex (stability constant $10^{15.4}$).

3.2 *EU labelling*

According to Annex 1 of 67/548/EEC on the classification and labelling of dangerous substances and its 25th Adaptation to Technical Progress (Dir 98/98/EEC), elemental mercury is classified as toxic (T) and dangerous to the environment (N), with phrases:

R 23: Toxic by inhalation;

R 33: Danger of cumulative effect;

R50-53: Very toxic to aquatic organisms, may cause long-term effects in the aquatic environment

S 1/2: Keep locked up and out of the reach of children;

S 7: Keep container tightly closed;

S 45: In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible)

S60: This material and its container must be disposed of as hazardous waste

S61: Avoid release to the environment. Refer to special instructions/Safety Data Sheets

4. PHYSICO-CHEMICAL PROPERTIES

4.1. *Properties*

Table 1 gives the major chemical and physical properties of elemental mercury.

Table 1: Physico-chemical properties of elemental mercury (Hg^0)

Property	Value Hg^0
Molecular weight	200.59
Aspect	Silvery white metal
Melting point	-38.87
Boiling point	356.58
Density	13.546 (20°C)
Vapour pressure	0.25 Pa (25 °C)
Log Kow	
Kd (l/kg)	316,000 (1)
Water solubility (ng/l)	20-30

(1) see section 7.1.8.

4.2. *Physics and chemistry of mercury in the environment*

In order to understand the movement of mercury through the environment, some knowledge about the chemistry and physics of mercury is necessary (Tournaux, 1933; Lamure & Brusset, 1962; Pascal, 1962; Brusset, 1977; Klemm, 1960/69):

- Atomic properties: mercury is a transition metal. The reactivity of mercury is low due to the relatively low activity of its two peripheral electrons.
- Physical properties: mercury is a liquid metal at all the temperature ranges in the environment (freezing point: -39°C , boiling point: 357°C). As all metals, it has a very high surface tension. This property together with other ones (heat of adsorption, vaporisation, etc.) makes it easily adsorbed to solids where it forms microballs. It also has a great tendency to fill surface micropores. Mercury has a high sorption coefficient (K_d). Metallic mercury, as well as some of its species (e.g. dimethylmercury) have a very high volatility (high vapour pressure).
- Chemistry and reactions: mercury with its oxidation stage 2+ (HgII) exclusively forms covalent bonds. The mercurious ion (Hg_2^{2+}) is in fact a combination of Hg° and HgII . The complexes formed by HgII with various ligands are however very often ions (e.g. Hg_2^{2+} , $(\text{HgCl}_4)^{2-}$, etc.). Strong covalent binding is found with sulphur and selenium whereas weaker bonds are formed with carbon and nitrogen. In water HgCl_2 forms soluble ionic complexes ($(\text{HgCl})^+$, $(\text{HgCl}_4)^{2-}$, etc.). On the contrary HgS is highly insoluble except in sulfide concentrated solutions. The methyl mercuric complex (CH_3Hg) (I) forms mainly covalent bonds with OH^- , Cl^- or CH_3^- ,... The oxidation/reduction processes govern the mercury chemistry in the environment.

The essential chemical features of mercury in the environment are:

- Mercury salts and methyl mercury may be reduced under ambient conditions to elemental mercury.
- Elemental mercury vapour may be oxidised in the atmosphere or in water to mercury salts.
- Mercury salts and elemental mercury may be converted in biological systems to the much more toxic methylmercury series of compounds which have a high potential for bioaccumulation through food chains and which can be volatile.
- Mercuric sulphide that is formed in anaerobic sediments and soils is very insoluble and relatively unavailable to biological recycling.
- Mercury forms mainly covalent bonds with other atoms.

5. COMPARTMENT OF CONCERN BY MACKAY LEVEL I

The risk assessment presented here, focuses on the aquatic marine environment, with special attention for the North Sea conditions where appropriate. Although this risk assessment only focuses on one compartment, it should be noted that all environmental compartments are inter-related. For mercury the situation is even more complicated, because in the different environmental compartments, mercury will occur in various forms, depending on a variety of conditions. In general the pH, redox potential and the presence of ligands such as chloride, sulphate and humic acids will affect the form in which mercury occurs. Because of this differentiation of mercury species in the different environmental compartments, a Mackay level I calculation to determine the 'compartment of concern' is not useful. Below some insight in the prevalent mercury forms and their importance in the different environmental compartments will be shortly given.

In water mercury mainly occurs as inorganic mercury(II) compounds, in marine waters HgCl_4^{2-} is the major dissolved ion. In water and sediment only 0.01-10% of the mercury

is methylated. Methylation is most prevalent in sediments through the activity of sulphate-reducing bacteria, but possibly also through the presence of organic compounds. In freshwaters and marine waters most mercury (up to 95%) is bound to the suspended particles in the water. In sediment most mercury is precipitated as very stable HgS.

In soil, mercury mainly occurs as metallic mercury and inorganic mercury(II) compounds (approximately 95%) which can be reduced to the rapidly volatilizing metallic mercury. The ionic forms can be methylated up to several percent of the total mercury present, through biotic and abiotic processes. The mobility of mercury is considered low (Sloof *et al.*, 1995). Below pH 6 the sorption to clay and iron oxides no longer plays an important role and is determined by the humic fraction. At lower pH the sorption does not decrease markedly.

The atmospheric mercury is primarily elemental mercury (between 90 and 95%), divalent mercury (3 to 4%) and methylated mercury (2 to 3%). In air mercury occurs in the gaseous form, which can be transported over long distances and remain in the atmosphere for a considerable length of time. Hg can be oxidized and subsequently precipitates on soil or in surface water (see section 6.3 for more details).

6. PRODUCTION, USES, EMISSIONS AND CYCLING

6.1 Production

In 1989, the primary world production was well over 5,700 tonnes (Slooff citing Maxson *et al.*, 1991). In 1996, the total world production was estimated to be 3,260 tonnes in 8 countries although overestimation (by more than 1,000 tonnes) for the former USSR was probably done (World Bureau of Metal Statistics, 1997). Reduction of the 1997 production in Europe to about 400 tonnes per year has certainly lowered the world production to less than 2,000 tonnes. It has to be noted that mercury recovery from various applications can represent a non negligible source of mercury use.

6.2 Main Uses

Mercury is applied in various industrial processes and products: dental clinics, measuring and control equipment (e.g. thermometers, blood pressure measuring equipment etc), batteries, lamps, and the chlor alkali industry (table 2). In the chloralkali industry mercury is used as cathode in the electrolysis process to produce chlorine gas and caustic soda from a sodium chloride solution in closed cells.

**Table 2 : Usage of mercury in Europe (1985-1992)
(OECD Monograph N° 98, 1994 (a) (in tonnes/year)
and estimates for 1996**

Application	Mercury content	Quantity	Estimated quantities for 1996 (c)
Dental clinics	50% per amalgame filling	68.9	68.9
Laboratories		31.5 (b)	31.5
Measuring and control equipment (thermometers included)	1.5 g per thermometer	31.7	(31.7) or lower
Batteries <ul style="list-style-type: none"> • cylindrical • button cell - mercury oxide • alkaline • silver oxide • zinc-air 	0.025 - 0.15% 30% 0.5 - 1% 1% 1%	99.4	5-8
Lamps & switches <ul style="list-style-type: none"> • fluorescent lamps • energy saving lamps 	5-15 mg per fluorescent lamp	12.2	> 12.2
Pesticides as seed dressing		13.1	0
Chlor-alkali industry		152.4	120
Other		<44.4 (b)	(73) (d)
TOTAL		<453.6	345

(a) 10 countries considered (DK, S, N, NL, FIN, GB, F, D, CH, B)

(b) Mainly in Germany

(c) Estimation based on informal data from ALMADEN (E) and Euro Chlor Mercury balance for 1996

(d) Extrapolated value from total and known uses

6.3. Emissions and cycling

6.3.1. Mercury in the atmosphere

At a global scale, the atmosphere is the environmental compartment with the largest influence on mercury transportation and fluxes. This has been demonstrated by recent modelling studies (Petersen *et al.* 1995; Iverfeldt *et al.* 1996).

The residence time of elemental mercury in the atmosphere is estimated to be between 1.1 and 1.4 year (Slemr, 1996), which allows not only long-range transportation but also a relatively homogeneous concentration in the atmosphere around the world. This was measured to be of about 2 ng/m³ (Slemr 1996).

As there is no reliable data available on the vertical distribution of mercury in the atmosphere, it is assumed an homogeneous distribution in a realistic atmospheric layer of about 10 km height. In this case the total amount of mercury in the atmosphere is calculated to be about 10 000 t.

As described in *Appendix 3* the elemental mercury could be oxidised and then hydrolysed into the atmosphere. In those forms the mercury can be easily re-deposited either through wet or dry processes. The re-deposition is of course more important in the regions where the

concentrations in oxidants and in particulate materials are higher, i.e. mainly in the atmosphere over continental areas. The re-deposition fluxes to land are 2 to 4 times higher than those to oceanic areas.

Inputs of mercury into the atmosphere

The main sources of emissions of mercury to the atmosphere were characterised by The Expert Panel of Atmospheric Mercury Processes (1994) and defined as follows:

- Anthropogenic mercury emissions refer to the mobilisation and release of geologically bound mercury by man activities (e.g. coal combustion) with mass transfer of mercury to the atmosphere.
- Natural mercury emissions refer to the mobilisation and releases of geologically bound mercury by natural biotic and abiotic processes, with mass transfer of mercury to the atmosphere (e.g. volcanoes).
- Re-emission of mercury is the mass transfer of mercury to the atmosphere by biotic and abiotic processes from a pool of mercury that was deposited to earth's surface after initial mobilisation by either anthropogenic or natural activities.

The two last pathways are considered as mercury emission from natural surfaces and they represent a large uncontrolled area of emissions sources.

The total amount of mercury in the atmosphere is thus built from a mix of anthropogenic, natural and re-emission sources. In the frame of the realistic scenario proposed here, the inputs into the atmosphere could be estimated as follows:

Real natural sources of atmospheric mercury coming from the terrestrial compartment

- Erosion and degassing from mineralised soils is estimated to be of about 700 t/y on the basis of flux measurements, 500 t/y coming from the mercuriferous belts (Lindqvist *et al.* 1991)
- Volcanic eruptions and geothermal activities may significantly contribute to the natural emissions of mercury. The best global estimate of mercury released by volcanoes is about 830 t/y, 95% of it coming from active erupting volcanoes (Varekamp & Buseck, 1986).
- Evasion of mercury from the earth's subsurface crust occurs through faults and fractures in bedrock. This phenomenon display extreme spatial and temporal variation, but a conservative estimate of 1000 t/y is considered here. This does not take into account mercury evasion from earth's crust directly to the deep ocean (Wilken *et al.*, 1999).

Anthropogenic emissions

According to Ebinghaus *et al.* (1999), a total emission to the atmosphere from anthropogenic sources for the Western world is about 870 t/y. This estimate represents approximately 15% of the total global anthropogenic emissions. This leads to a total anthropogenic emission into the atmosphere of about 5600 t/y. However 30% of this amount is quickly redeposited at a local or regional scale, leaving about 4000 t/y globally distributed in the atmosphere.

Exchange processes, which can act as sources or sinks of atmospheric mercury. These exchanges affect the total amount of mercury and are occurring both at the air-water and the

air-soil interfaces. Before going into detail of these exchanges, the aquatic and terrestrial compartments situations will be shortly reviewed.

6.3.2. Mercury in the aquatic compartment

- *Mercury in deep ocean*

In open ocean studies, the dissolved mercury is in the range of 0.2 to 1 ng/l, with some times higher concentrations of 2 ng/l (Mason and Fitzgerald, 1996; Scheldbauer, 1998). The methylated forms represent a maximum of 10% of the total mercury, the measured concentrations varying between 0.002 and 0.12 ng/l for methyl mercury (Mason *et al.*; 1996) and from about zero (at the surface) to a maximum of 0.06 ng/l in deep water (at 2000 to 2500m depth) for dimethylmercury. In the upper layer of the ocean, the mercury is coming from atmospheric deposition in the form of reactive mercury (isolated HgII) and the observed concentration varies between <0.2 and 0.6 ng/l (Mason and Fitzgerald, 1996).

- *Exchanges with the atmosphere*

Most of the mercury deposited into the ocean from the atmosphere is in the form of HgII. This reactive form is reduced mainly to elemental mercury by biological processes. The elemental mercury is then re-emitted back to the atmosphere to be ultimately deposited on land and sequestered into surface soils. For the Northern Hemisphere, the deposition mainly occurs in mid latitude regions while the re-emission mainly occur in equatorial regions where the temperature and the biological activity are more important. These exchange fluxes between ocean surface and the atmosphere are of the order of magnitude of 3000 t/y in both directions. These exchanges take place in the mixing layer of the ocean where most of the biological activity and oceanic circulation cycles occur. The total amount of mercury present in this mixing layer is estimated to be of about 18000 t.

- *Continental margins*

The continental margins represent the interface between the open ocean and the continents. These include estuaries, inland seas, continental shelves and slopes. They are characterised by a high biological activity as well as by a high content in suspended solids.

Most of the mercury present in these areas is linked to suspended solids (Cossa *et al.* 1994 and 1996; Vandal *et al.* 1995). The observed concentrations are varying from area to area within a range of 50 to 1000 ng/kg suspended matter. The mercury enrichment in suspended particles is proportional to their organic carbon content, in particular in areas where phytoplankton is abundant. Methyl mercury generally makes up to 3% of the total mercury linked to particles.

The concentrations of dissolved mercury species in coastal waters in North Atlantic are most often less than 1 ng/l (Cossa *et al.* 1996).

- *Input into continental margins*

While in the open sea the main input of mercury is coming from the atmosphere, in continental margins, the mercury fluxes tend to be larger due to the continental run-off and riverine input.

The riverine inputs into continental margins are directly related to terrestrial concentrations of mercury as well as to the fresh water compartment. In a review paper from Cossa *et al.* 1996, it is said, on basis of existing data, that 90% of the run-off into

the continental margins are **not** under the influence of **direct** anthropogenic mercury discharges. They are coming from dissolved mercury in organic rich waters (concentration between 0.4 and 0.6 ng/l) and from rocky debris carried out by the flows. The 10 other % comes from industrialised river with a dissolved mercury concentration of about 2 ng/l. The mercury concentrations in rock debris, in organic coated particles and in particles from industrialised rivers are 20, 80 and 500 µg/kg respectively. On this basis, a mercury burden to continental margins of 940 t/y as adsorbed on particles and of 40 t/y as dissolved mercury can be estimated. It has to be pointed out that the majority of the heavily contaminated particles are discharged in the Northern Hemisphere (Europe and North America).

Like the open ocean, the continental margins are also exchanging mercury species with the atmosphere. A total exchange of about 700 t/y in both directions can be estimated (Cossa *et al.* 1996)

- *Sedimentation in continental margins*

About 95% of terrestrial particles entering the continental margins settle in near shore environment, but 10% of the total can be re-mobilised.

In sediment, the higher levels of mercury found in the upper layers do not result from increase in anthropogenic input, but from the fact that mercury is associated with iron and manganese oxides (Walsh, 1997). These can be reduced by microbiological activity, leading to upward movement of mercury in the sediment. If the iron and manganese can be re-oxidised through re-mobilisation, they can trap the mercury again. It means that the oxygen content of the water is an important factor in the immobilisation of mercury in the sediment.

6.3.3. Mercury in terrestrial compartment

In a compilation of natural and anthropogenic mercury sources by Ebinghaus *et al.* (1999), an amount of $1.5 \cdot 10^7$ t of mercury burden in the upper layer of the continents can be calculated. This leads to a background concentration of 0.05 mg/kg in agreement with the most recent literature data. It is generally accepted that the terrestrial compartment acts as a sink for mercury even if, due to re-emission, a horizontal re-distribution occurs.

- *Deposition through wet and dry precipitation*

The wet precipitation of mercury is thought to be the more important deposition process, because mercury is present in rain both in dissolved form and adsorbed on particles. In urban and industrialised areas, a major fraction of the mercury in rainfall is associated with particles (Ebinghaus *et al.* 1996; Slemr 1996; Petersen *et al.* 1995). The total mercury concentrations in precipitation are in the range of 2 to 100 ng/l in relatively remote areas, methyl mercury representing about 5% of the total (Bloom *et al.* 1988; Munthe *et al.* 1995).

- *Mercury in terrestrial waters*

The level of mercury in terrestrial waters varies considerably from place to place depending on geological characteristics and on the organic content of the water. There are positive relationships between dissolved mercury and dissolved organic carbon or between mercury adsorbed on particles and their organic content (Coquery *et al.* 1995; Quemerais *et al.* 1996). As the organic content plays an important role, there are two types of waters where high level of mercury can be observed: rivers from industrialised regions with a high COD and lakes with relatively high dissolved humic acid. The

presence of organic material can in certain conditions favour the methylation (Watras *et al.*, 1996)

6.3.4. Summary of the approach

The general global cycling of mercury as described in the section 6.3. could be summarised by proposing a global scheme of mercury burdens and fluxes as presented in Fig 1

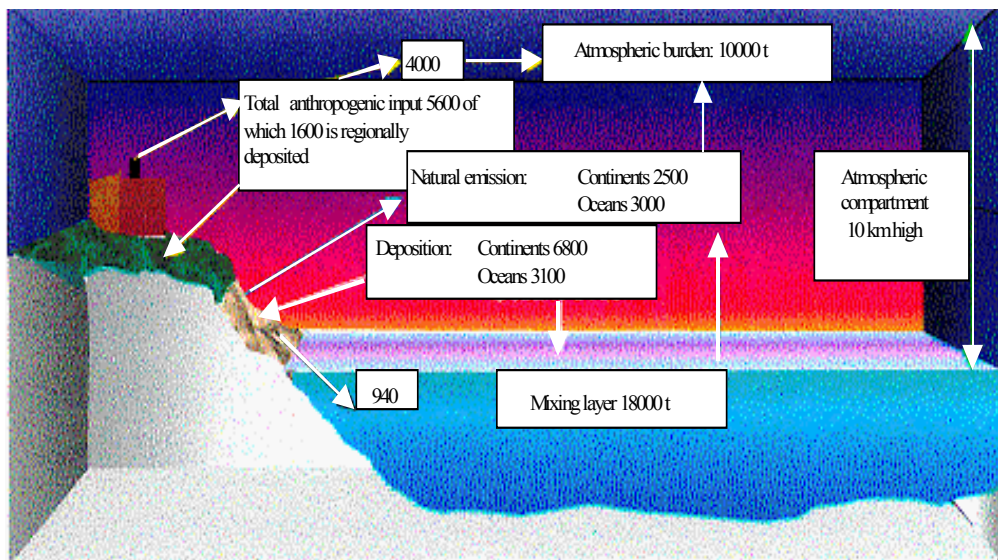


Fig 1 Global mercury cycle (Fluxes in t/y)

Emissions from the chlor-alkali industry

Emissions from the chlor-alkali industry in Western Europe are closely watched by Euro Chlor and OSPARCOM. For the specific OSPARCOM area, emissions for 1997 are reported as 8.5 tonnes mainly in air and to a less extent in products and water. Mercury losses to water amounted to 502 kg (OSPARCOM-PRAM 99/5/15, 1999).

For the same year, Euro Chlor reported total emissions of 10.5 tonnes including non-OSPARCOM regions (*Appendix 2*). A report prepared by Berdowski *et al.* (1997) mentioned air emission values for the chlor-alkali industry of 15 EU countries in 1990 as 28.4 tonnes whereas Euro Chlor air emission data represented 20.4 tonnes (2.7 g Hg/t Cl₂ capacity, 7,542,000 tonnes capacity for mercury cell process in 1990) for the same year. The difference may be explained by the inclusion of ex-GDR emissions in the Berdowski data.

In 1990, the chlor-alkali contribution represented 12.6% of the total anthropogenic air emissions of mercury in the EU (15 countries) (Berdowski *et al.*, 1997). However, the total emission level quoted by Berdowski (245 tonnes for 15 EU countries) is different from the one quoted in Pacyna (1994) (quoted in Ebinghaus, 1999) for the same year (467 tonnes for 15 EU countries). Using the Pacyna values for 1990, the chlor-alkali emissions would represent 6% of the total air emissions in the EU. No recent figures are available concerning EU total anthropogenic mercury emissions in the atmosphere.

7. EFFECT ASSESSMENT

As a first approach, this chapter only considers the following three trophic levels: aquatic plants, invertebrates and fish. The effects on other organisms are only discussed when indicated.

The evaluation of the data was conducted according to the quality criteria recommended by the European authorities (Commission Regulation 1488/94/EEC). The evaluation criteria are given in [Appendix 1](#).

7.1 Inorganic mercury

Documented data from all available sources, including company data and data from the open literature, were collected and incorporated.

A summary of all evaluated data is given in [Appendix 4a](#). In total 21 data for fish and amphibians, 68 data for invertebrates and 35 data for algae have been evaluated. Respectively 5, 29 and 1 data were considered valid for risk assessment purposes. For the respective taxonomic groups, 13, 32 and 20 should be considered with care, and 3, 7 and 15 data, respectively, were judged as not valid or not assignable for risk assessment.

The different trophic levels are reviewed hereafter. Only valid data are used for risk assessment.

7.1.1 Marine Fish

Only one marine species has been tested both in one paper giving short term and long term data. The tests are considered valid (validity 1) as they were carried out under semi-static conditions with analysis of the test concentrations. The 96h-LC₅₀ for *Fundulus heteroclitus* is 67 µg/l, the 32-d NOEC (reproduction) with the same species is 10 µg/l. Both tests were started with fertilised eggs (Sharp & Neff, 1980).

7.1.2. Freshwater Fish

Eleven acute toxicity studies are reported for 7 species with survival as endpoint. Eight of these 11 studies result in 96h-LC₅₀ -values between 124 and 282 µg/l. From these eight studies, seven have validity 2 (static and short term, no chemical analysis), whereas only one study with *Pimephales promelas* has validity 1 (flow through, concentrations analysed, Snarski & Olson, 1982). The latter 96h-LC₅₀ is 168 µg/l.

Two studies result in lower 96h LC₅₀ -values: 26 µg/l for *Poecilia reticulata* (validity 2, concentrations not analysed, Khangarot & Ray, 1987) and 33 µg/l for rainbow trout

(validity 4, reliability not assignable, Hale, 1977). One reference (Alam & Maughan, 1992) reports five LC₅₀ -values for juvenile *Cyprinus carpio* with four values ≥ 570 $\mu\text{g/l}$ and one of 160 $\mu\text{g/l}$. Although the experiment was carried out as a semi-static test and test concentrations were analysed, validity 2 is assigned as the test substance is unknown.

Three long-term studies are available for 2 species of freshwater fish. A semi-static test with the embryos and larvae of *Brachydanio rerio* (Dave & Xiu, 1991) gave a 14-day NOEC for lethality of 1 $\mu\text{g/l}$. Although concentrations were not determined by analysis, the solutions were renewed daily. The embryos were not fed after hatching and the test determined whether the median survival time was less than in the controls. Therefore, the result should be used with care (validity 2).

A flow-through study with *Pimephales promelas* (Snarski & Olson, 1982) examined growth and reproduction over an exposure period of 41 weeks, and also the survival and growth of the progeny after a further 30 days. Based on measured concentrations, there was no effect on the survival, growth and reproduction of the parent fish at 0.5 $\mu\text{g/l}$. However, the authors reported a significantly lower growth at the next lower (and lowest) concentration tested (0.26 $\mu\text{g/l}$), with an apparent effect (not tested statistically) on the number of reproducing females. The growth of the progeny after 30 days was reported to be slightly, but significantly, affected at 0.5 $\mu\text{g/l}$ (3.3% length effect, 10.7% weight effect). However, again, a considerably greater effect was recorded at 0.26 $\mu\text{g/l}$, with only 50% survival and a 26% weight reduction. Due to this lack of a clear concentration-response relationship, it is uncertain whether any effects at 0.26 $\mu\text{g/l}$ were attributable to mercury. For the purposes of this risk assessment, the observed NOEC of 0.5 $\mu\text{g/l}$ for the parent generation is considered valid with restrictions (validity 2). The NOEC for the progeny is considered to be ≤ 0.5 $\mu\text{g/l}$ but is not valid since neither the NOEC nor LOEC are certain.

The same authors (Snarski & Olson, 1982) also separately tested for the effects on growth of *Pimephales promelas* over a 60-day exposure period using *Artemia* as food. The NOEC was 1.02 $\mu\text{g/l}$ which was considered valid. They also carried out the same study using dry trout starter food. Growth of the controls was much reduced compared with those fed *Artemia*, and the accumulation of mercury was not concentration-related; the results were not considered reliable. A later study, by the same laboratory (Spehar & Fiandt, 1986), determined the effects on growth of *Pimephales promelas* after exposure for 32 days under flow-through conditions with analysis of the solutions. The NOEC was 0.63 $\mu\text{g/l}$, which was considered valid.

Therefore, the lowest valid long-term NOEC is 0.5 $\mu\text{g/l}$, for growth and reproduction of *Pimephales promelas* after 41 weeks (Snarski & Olson, 1982).

7.1.3. Marine Invertebrates

For marine invertebrates 7 experiments on 5 crustaceans species are reported with EC/LC₅₀ endpoints. Six 96h-LC₅₀ studies are considered valid, ranging between 10 and 680 $\mu\text{g/l}$. The lowest LC₅₀ of 10 $\mu\text{g/l}$ for *Acartia tonsa* should be considered with care (validity 2, static but short-term, not analysed, test substance unknown, Sosnowski & Gentile, 1978), but some other low values confirm this result: LC₅₀ is 15.3 $\mu\text{g/l}$ for *Penaeus indicus* (validity 1, flow-through, concentrations analysed, McClurgh *et al.*, 1984) and 30 $\mu\text{g/l}$ for

P. merguensis at 35°C (validity 1, semi-static, concentrations analysed, Denton & Burdon-Jones, 1982). The latter study clearly illustrates the influence of test conditions: a 10°C lowering of temperature reduces the toxicity by a factor of ten. A reduction of the salinity from 35 to 20 ‰ increases the toxicity for this species by more than a factor of two (Denton & Burdon-Jones, 1982).

In short-term studies, the sensitivity of other marine invertebrates such as polychaetes (4 species) and molluscs (9 experiments, 6 species), seems to be comparable to crustaceans. The lowest LC₅₀ are for the molluscs *Crassostrea* 5.6 to 12 µg/l (4 experiments, embryos and larvae, 48h to 12 d) and for *Mytilis edulis* where the 48h-EC₅₀ is 5.8 µg/l. The 96h-LC₅₀ for polychaetes varies between 14 and 90 µg/l. The majority of these studies is considered valid with validity 1 and 2.

Six long-term studies are reported for 5 crustacean species, with NOEC values ranging between 0.5 and 6 µg/l. The lowest valid NOEC is 0.8 µg/l which is the result of two independent experiments with *Mysidopsis bahia*. In both experiments the life cycle was studied for effects on reproduction and mortality in a flow-through system. Concentrations were analysed in both tests (validity 1, Gentile *et al.*, 1982, Lussier *et al.*, 1985).

Also in longer-term studies, crustaceans seem to be as sensitive as the other tested marine taxa: protozoa (1 species), hydrozoa (1 species), worms (2 species) and molluscs (5 experiments, 4 species). The 112-d NOEC (reproduction) for the mollusc *Crepidula fornicata* is 0.25 µg/l (validity 1, semi-static test, concentrations analysed, Thain, 1984). Five other valid NOECs are between 1 and 10 µg/l.

7.1.4. Freshwater invertebrates

EC/LC₅₀ studies are reported for 6 species. The 48h-EC₅₀ for *D. magna*, *D. pulex* and *Ceriodaphnia reticulata* ranges between 2.9 and 9.6 µg/l (4 experiments, validity 2, static test but short-term, concentrations not analysed, standard test methods, Khangarot & Ray, 1987b, Elnabarawy *et al.*, 1986). The lowest value is 1 µg/l, a 96h-LC₅₀ for *Crangonyx pseudogracilis* (validity 2, static test but short term, concentrations not analysed, Martin & Holdich, 1986).

Valid data are available for insects, snails and nematodes (6 experiments for 3 species). The EC/LC₅₀ values vary from 29 to 440 µg/l.

Eight studies report on the long-term toxicity for crustaceans. The lowest NOEC for reproduction is 0.62 µg/l for *Hyaella azteca* (validity 2, semi-static test, concentrations analysed, test substance unknown, Borgmann, 1993), whereas the highest NOEC is 18 µg/l for *Cyclops* sp. One study on *Daphnia magna* (Enserink *et al.*, 1991) was identifying a LOEC at 7 µg/l. A calculated NOEC was derived by using a factor of 3.2 (interval between concentrations tested) (validity 2) The same authors also used mixed aged *Daphnia magna* in a non standard system in which the population was allowed to increase freely. Using a modelling approach of Kooyman *et al.* (1983), an EC10 for the population yield is reported as 0.072 µg/l but this is not considered as valid

Other freshwater invertebrates like Protozoa and Molluscs were studied (6 experiments for 3 species). The lowest NOEC (7d, survival) is 30 µg/l, observed for the mollusc *Viviparus bengalensis*. NOECs (growth) for Protozoans vary between 34 and 775 µg/l. All values are considered valid (validity 2) but should be considered with care.

7.1.5. Marine Algae

For marine algae, EC/LC50 values are reported in three studies for 9 species. The lowest is a 5d-EC50 (growth) of 10 µg/l for a diatom, *Ditylum brightwellii*, (validity 2, nominal concentrations, Canterford and Canterford, 1980). The remaining values are for the sporelings of macroalgal species (seaweeds), for which the 48h-LC50 values ranged from 1750 to 8000 µg/l (Boney, 1971; Boney and Corner, 1959), based on nominal concentrations. However, the exposure duration (probably 1 day) is not certain from the publications, which describe a variety of different experimental designs, and the results are considered validity category 4 (not assignable).

Eight studies report NOECs/LOECs for 12 species of algae. Seven studies were classified as validity 2 (to be used with care) either because the result was based on nominal, rather than measured concentrations, or because only an effect, not a NOEC, was determined. A NOEC was reported on the growth of *Dunaliella tertiolecta* after 18 days at 330 µg/l (Portmann, 1972) based on nominal concentrations. No detectable effect was reported for the growth of *Skeletonema costatum* after 144 hours exposure to 1 µg/l in static, batch cultures (Rice *et al.*, 1973) with approximately 50% inhibition at 5 µg/l. The same authors showed similar results in a flow-through (“chemostat”) test system, but the mercuric chloride was added as a pulse to the system and allowed to decline with the input of new solution. *Skeletonema costatum* was also used to determine effects on net oxygen evolution over 4 hours (Zingmark and Miller, 1973). Slight (approximately 13%) inhibition was observed at 1 µg/l (the lowest concentration tested) but no information statistical significance was reported; this has been assumed to represent a LOEC (validity 2). The same authors show a NOEC of 1 µg/l for *Amphidinium carterae* after 4 hours exposure, but approximately 15% inhibition after 24 hours. These results for *Skeletonema costatum* are in general agreement with another study showing growth inhibition of approximately 40% after 7 days at 5 µg/l for this species (Berland *et al.*, 1977); again, lower concentrations were not tested. Similarly, the growth of *Isochrysis galbana* was inhibited by 15% (growth rate, days 2 to 3 of a 13-day study) at a measured concentration of 0.77 µg/l, with approximately 32% inhibition at 5.1 µg/l (Davies, 1974), although statistical comparisons with the control were not reported.

The growth of five species of intertidal brown macroalgae (seaweeds) was investigated in a flow-through system over an exposure period of 11 days (Stromgren, 1980). NOECs ranged from 0.9 to 9 µg/l, the most sensitive species being *Fucus serratus*; however, the next highest concentration was 5 µg/l, at which the final growth inhibition for this species was approximately 15%. Another study with a brown macroalga, *Laminaria saccharina*, testing the development of the microscopic zoospore stage, reported a NOEC of 1 µg/l (LOEC of 5 µg/l) after 14 days (Thompson and Burrows, 1984).

The remaining study (Sick and Windom, 1974) employed 3 micro-algal species exposed to a radioactive isotope of mercury (²⁰³Hg) at concentrations of 0.02 to 0.35 µg/l in static cultures for 5 days. Analyses of the cells and culture medium showed that 80% or more of the mercury was lost from the system after 24 hours. The results are considered not valid for a number of reasons. The only data for growth of the algae are given graphically as “population size”, described as being calculated from cell counts that are not reported. It is not clear whether a control was tested, since control data are not shown and the population sizes are stated to be calculated by comparison of the growth with that at the lowest added concentration of 0.02 µg/l, stated to be “ambient”. No statistical significance or variability

is quoted. From the graph, it would appear that population size was reduced by at least 25% at 0.04 µg/l for *Carteria sp* and *Dunaliella tertiolecta*, and at 0.06 µg/l (NOEC 0.04 µg/l) for *Nitzschia closterium*. The result for *Dunaliella* is in marked contrast to the NOEC of 330 µg/l described above for the same species (Portmann, 1972) and the effect concentrations are 1 to 2 orders of magnitude lower than others reported for marine algae. In view of the described uncertainties, the study has been assigned validity 3.

The lowest NOEC (0.9 µg/l, validity 2) for *Fucus serratus* is slightly higher than the lowest apparent LOEC (approximately 15% inhibition) of 0.77 µg/l for *Isochrysis galbana* (Davies, 1974). Although the statistical significance of this LOEC was not reported, it is proposed that, because the apparent inhibition was 15%, a conservative estimate of the overall NOEC for marine algae is provided by dividing this by a factor of two, giving a NOEC of 0.4 µg/l.

7.1.6. Freshwater Algae

A standard toxicity test for freshwater algae has recently been published (Chen *et al.*, 1997). The US EPA method (static test) was used to determine the 96-hour EC50 to *Selenastrum capricornutum*, and compared with a dynamic “chemostat” exposure of the same species over 96 hours. The EC50 values were 9 and 27 µg/l for the static and dynamic tests, respectively. The results were based on nominal concentrations and are therefore considered validity 2. One 33d-EC50 value is reported for another standard test organism, *Chlorella vulgaris*, which is 1030 µg/l (cell division, validity 2, Rosko *et al.*, 1977).

NOEC or LOEC values are reported for ten algae species, with exposure periods varying between 2 and 33 days. The lowest values are reported by Bringmann *et al.*: the toxicity threshold (TT,~LOEC) in an 8d-test with *Microcystis aeruginosa* is 5 µg/l (validity 2, nominal concentrations, growth, Bringmann *et al.*, 1978).

Values are reported for five more species which vary between 70 and 500 µg/l. All tests should be considered as static tests, but this is common practice in testing on micro-algae. The test substance concentrations have been analysed in only one of these tests.

7.1.7. PNEC for the aquatic environment

The evaluation of the available toxicity data for aquatic organisms does not support the hypothesis that freshwater and marine organisms have different sensitivities for inorganic mercury salts. Therefore, both freshwater and marine toxicity data have been used to determine PNEC values. The derivation of a PNEC value has been done by different methods which are detailed below.

7.1.7.1 Safety factor approach

This approach is the traditional one recommended by the TGD.

The lowest data for each trophic level are presented in *Appendix 5*. There are EC/LC₅₀ - values for more than the three trophic levels of the base-set and there are long-term NOECs for many more than three species from the three trophic levels, including the standard and many non-standard test organisms. The calculated PNEC based on long-term studies on 3 different species from three different trophic levels and using a safety factor of 10 is 0.025 µg/l. However this approach does not take into account the potential natural background of

mercury. It is agreed that the TGD methodology should be adapted specifically for inorganics and metals (TGD, 1996).

7.1.7.2 RIVM approach

RIVM calculated a maximum permissible addition (MPA) based on Aldenberg and Slob (1993) of 0.23 µg/l for both marine and freshwater species (Crommentuijn *et al.*, 1997). The background concentration is thought to correspond to 0.01 µg/l for freshwater and 0.0025 µg/l for marine water in the Netherlands. The data used were not selected based on the validity criteria used in this report.

7.1.7.3 Euro Chlor approach

Euro Chlor has also used the statistical approach of Aldenberg and Slob (1993) but only using studies with a validity 1 or 2. In this case the model calculation leads to a **PNEC value of 0.47 µg/l** (see details in *Appendix 6*) or **470 ng/l**.

It should be noted that the PNEC_{aqua} does not take into account the hazards related to secondary poisoning.

7.1.8. Effect assessment for sediment

The TGD (1996) does not give a clear guidance as to how to evaluate sediment toxicity. Under environmental conditions the major part of inorganic mercury in aquatic ecosystems will be sorbed to sediment particles, either suspended or settled. This sorbed fraction is generally assumed to have limited or no bioavailability for aquatic organisms. It is also regularly observed that sediment dwelling organisms are equally sensitive to toxicants in general as water column organisms, as stated in the TGD (1996).

7.1.8.1. Direct assessment

For inorganic mercury a large number of aquatic toxicity data are available, as described in 6.2, allowing a detailed evaluation of aquatic effects. Therefore it can be expected that the risk ratio (PEC/PNEC) as determined for the aquatic compartment will be similar for sediment dwelling organisms, assuming that exposure will be mainly via the waterphase, as based on the equilibrium partitioning method (TGD, 1996). One secondary reference (Gaudet *et al.*, 1995) refers to a Canadian data bank where data are available. As the primary source of information is not accessible, the data mentioned could not be checked and validated. Because no original data on sediment dwelling organisms were available, the chronic toxicity of inorganic mercury tested as HgCl₂ in sediment to *Chironomus riparius* in a 28 day test was determined (Thompson *et al.*, 1998, see also *Appendix 8* for key data). In this test the time to first emergence, time to 50% emergence and percentage emergence of larvae after 28 days were tested and gave a NOEC of 1000 mg Hg/kg dry weight (nominal), corresponding to 930 mg Hg/kg dry weight (measured). Toxic effects were only observed at the highest tested concentration (1800 mg/kg dw nominal, corresponding to 1600 mg/kg dw measured) with only 5% of the larvae emerging as adults, compared with 98% in the control. At this sediment concentration the concentration in the overlying water at the start was approximately 6 µg/l of total mercury, while at the end all concentrations were below 1 µg/l. This is consistent with the aquatic toxicity data found in literature where

long term NOEC's were found around 1 µg/l and shorter term EC₅₀ values of higher than 1 µg/l. This shows that the results are consistent with the hypothesis that the main exposure is via the waterphase, which supports the view that the sorbed fraction does not pose an additional risk to the aquatic ecosystem.

Above mentioned observations indicate that the sorbed fraction as such is not bioavailable and therefore not toxic, with toxic effects exerted only via the waterphase. Nevertheless, for risk assessment purposes it was attempted to derive a PNEC_{sediment}, which can be compared with a PEC_{sediment} which is calculated from the mean total aquatic concentration (chapter 8.3). From the sediment test mentioned above a PNEC can be extrapolated by assigning a safety factor to the chronic NOEC determined in the test. Again the TGD does not give clear guidance to what safety factors to be used, but considering the large number of toxicity data, including chronic data, available for the aquatic toxicity it is considered safe to apply a safety factor of 10 to the lowest NOEC which was 1000 mg Hg kg⁻¹ dry weight (nominal) (930 mg Hg/kg dry weight measured), which would give a **PNEC_{sediment} of 93 mg Hg/kg dry weight or 31.2 mg Hg/kg wet weight**, based on the measured NOEC.

7.1.8.2. Indirect assessment

PNEC_{sediment} for inorganic mercury can also be calculated according to TGD methodology (equation 54). The value of Log K_d is derived from Coquery *et al.* (1995) in different coastal zones and Leermakers (1998) in the North Sea. The reported values are ranging from 4.6 to 6, most of the values being around 5.5, which is used in the calculation presented hereafter. In a recent study on sediment at Brixham Environmental Laboratory (Thompson *et al.*, 1998, see also [Appendix 8](#)) experimental K_d values have been obtained ranging between 155 000 and 696 000, leading to log K_d between 5.19 and 5.84 confirming the realistic character of the choice of 5.5 as log K_d value.

$$PNEC_{\text{sediment}} = K_{\text{sed-water}} * PNEC_{\text{water}} / RHO_{\text{sediment}}$$

Where: $K_{\text{sed-water}} = F_{\text{solid}} * K_d * RHO_{\text{solid}}$
 Where: F_{solid} is the volume fraction of solid in sediment, set at 0.2 (m³/m³)
 RHO_{solid} is the density of the solid phase set at 2.5 (kg/l)
 $K_d = 316000$

Thus, $K_{\text{sed-water}} = 158000$

And $RHO_{\text{sediment}} = 1.3 \text{ kg/l}$ and $PNEC_{\text{water}} = 0.00047 \text{ mg/l}$.

The PNEC_{sediment} is calculated to be 57 mg/kg wet weight (148 mg/kg dry weight based on the TGD sediment wet:dry ratio of 2.6). This estimated value is in agreement with the experimental value of 31.2 mg/kg wet weight indicated in the sediment test on *Chironomus riparius* described in section 7.1.8.1. and justifies, *a posteriori*, the assessment factor of 10 applied to the NOEC value.

7.1.9. Fish-eating predators

No data are available on the toxicity of elemental mercury to fish eating predators. Fish eating predators feed on substrate that may contain mercury of which 70 to 90% is

organic mercury (see mercury speciation in fish, Slooff *et al.*, 1995). Therefore, assessment of effects of inorganic mercury to fish-eating predators is not deemed relevant.

7.2. Organic mercury (methyl mercury)

A summary of all data for *methyl mercury* is presented in *Appendix 4b*. In total 11 data for fish, 9 data for invertebrates and 7 data for algae have been evaluated. Respectively 6, 1 and 0 data were considered valid for risk assessment purposes. For the respective taxonomic groups, 4, 8 and 2 should be considered with care, and 1, 0 and 5 data, respectively, were judged as not valid or not assignable for risk assessment.

7.2.1. Marine fish

Only one acute toxicity study is reported for marine fish (Sharp & Neff, 1982). This examined the effects on the survival of newly-fertilised embryos of *Fundulus heteroclitus* under static test conditions with analysis of the solutions, and was considered valid. The 96h-LC₅₀ was 51 µg/l.

7.2.2. Freshwater fish

Seven LC₅₀-values are reported for 2 species of fish. The lowest 96h-LC₅₀ is 24 µg/l for fry of *Salmo gairdneri*, with a higher value (42 µg/l) for larger fingerlings (Wobeser, 1975). The tests were semi-static (daily renewal) without analysis and the result should be used with care (validity 2). For the same species, under similar test conditions (validity 2), a 96h-LC₅₀ of 31 µg/l is also reported (Matida *et al.*, 1971). Three other values are long-term 45d-LC₅₀-values, with *Oncorhynchus kisutch*, ranging between 54 and 71 µg/l with validity 1 (Devlin & Mottett, 1992). In a study with *Trichogaster trichopterus* (validity 2, concentrations not analysed) the 96h-LC₅₀ was 89.5 µg/l (Roales & Perlmutter, 1974).

Five chronic studies are available for 4 species of freshwater fish. One is a secondary source (Mount, 1974) and there was insufficient information to validate the study (validity 4). The remaining four tests are considered valid (validity 1) as the tests were carried out under semi-static or flow-through test conditions and the test concentrations were analysed. The lowest NOEC (growth) is 0.08 µg/l (Christensen, 1975) in a two generation test with *Salvelinus fontinalis*.

7.2.3. Marine invertebrates

Crustaceans

Two studies report LC₅₀ values for marine crustaceans. Both were static tests based on nominal concentrations (validity 2). The lowest 96h-LC₅₀ is 150 µg/l for *Gammarus duebeni* (Lockwood & Inman, 1975). The other was a 48h-LC₅₀ of 1400 µg/l for *Artemia salina* (Corner & Sparrow, 1957).

Other invertebrates

Only one short-term EC₅₀ value is found: the 1h-EC₅₀ for the mollusc *Perna perna* is 50 µg/l (validity 2, not a standard criterion: filtering rate, no analysis but very short term, Watling & Watling, 1982).

The only long-term test with a marine invertebrate is also for a mollusc: the 32d-NOEC for *Mytilus edulis* is 0.3 µg/l (validity 1, growth, flow-through but no analysis of concentrations, Pelletier, 1988).

7.2.4. Freshwater invertebrates

Crustaceans

One short-term test is available using *Daphnia pulex*. The 48h-LC₅₀ is 5.7 µg/l, the 96h-LC₅₀ is 1.8 µg/l; the 8d-LC₅₀ was reported to be >1 µg/l (validity 2, static, not analysed, Tian-yi & McNaught, 1992). In a long term test by the same authors the 30d-NOEC was 0.1 µg/l (validity 2, reproduction and growth in three consecutive generations, semi-static, concentrations not analysed, Tian-yi & McNaught, 1992).

Other invertebrates

In a short-term test, the protozoan *Tetrahymena pyriformis* was relatively insensitive compared to *D. pulex*. The 6h-LC₅₀ is 168 µg/l (validity 2, concentrations not analysed but very short term, Thrashner & Adams, 1972). In the same study the NOEC(growth) was 14 µg/l.

The number of cells of another protozoan, *Poterochromonas malhamensis* was reduced by approximately 50% at 2 µg/l (LOEC). A very sensitive criterion for the flatworm *Dugesia dorotocephala* was fissioning (regeneration) with a 14d-NOEC of 0.03 µg/l (validity 2, semi-static, concentrations not analysed, not a standard test or standard criterion, Best *et al.*, 1981).

7.2.5. Marine plants, including algae

Two studies are available for three marine species. The lowest test concentration causing effect is 0.5 µg/l for the marine brown algae *Laminiaria saccharina*. At this concentration the cell number of sporelings was reduced with 43% (validity 2, semi-static, concentrations not analysed Thompson & Burrows, 1984). LOEC values are reported for two other species for *Dunaliella tertiolecta* and *Phaeodactylum tricornutum* (Overnell, 1975) based on inhibition of photosynthesis (oxygen evolution). However the exposure period was only 10 minutes, followed by an unspecified period during which oxygen evolution was measured, and the results were considered not valid

7.2.6. Freshwater plants, including algae

Four studies are available for freshwater algae. The LOEC (2 µg/l) was also the approximate EC50 for growth of *Poterochromonas malhamensis* in a static test based on nominal concentrations (validity 2) (Röderer, 1983). An inhibitory effect on the growth of *Coelastrum microporum* was reported at 3 µg/l, but no duration was given and the test was considered not valid (Holderness *et al.*, 1975). Similarly, Matson *et al.*, (1972) found a reduction of total lipids in *Ankistrodesmus braunii* at 1000 µg/l, but no time period was specified; they also reported an effect on *Euglena gracilis* but the study employed extracted chloroplasts; both results were considered not valid.

7.2.7. PNEC for aquatic organisms

The evaluation of the available toxicity data for aquatic organisms does not support the hypothesis that freshwater and marine organisms have different sensitivities for organic mercury salts. Therefore, both freshwater and marine toxicity data have been used to determine PNEC values. The derivation of a PNEC value has been done by different methods which are detailed below.

7.2.7.1 Safety factor approach

This approach is the traditional one recommended by the TGD.

The lowest data for each trophic level are presented in [Appendix 5](#). There are EC/LC₅₀ values for more than the three trophic levels of the base-set and there are long-term NOECs for many more than three species from the three trophic levels, including the standard and many non-standard test organisms. The calculated PNEC based on long-term studies on 3 different species from three different trophic levels and using a safety factor of 10 is 0.003 µg/l.

7.2.7.2 RIVM approach

RIVM calculated a maximum permissible addition (MPA) based on Aldenberg and Slob (1993) of 0.01 µg/l for both marine and freshwater species (Crommentuijn *et al.*, 1997). The data used were not selected based on the validity criteria used in this report.

7.2.7.3 Euro Chlor approach

Euro Chlor has also used the statistical approach of Aldenberg & Slob (1993) but only using studies with a validity 1 or 2. In this case the model calculation leads to a **PNEC value of 0.01 µg/l** (see details in [Appendix 6](#)) or **10 ng/l**.

It should be noted that the PNEC_{aqua} does not take into account the hazards related to secondary poisoning.

7.2.8. Effect assessment for sediment

No specific data are available for effects of methyl mercury on sediment organisms. At the end of the test run with inorganic mercury (Thompson *et al.*, 1998), the sediment from the top, middle and bottom concentrations was analysed for methylmercury. The mean measured values ranged from 0.2 to 0.3% of the nominal total mercury concentration. Methylmercury in the control sediment was below the detection limit (0.001 mg/kg) of the method. From these results, it can be stated that a NOEC for methyl mercury is higher than 0.6 mg/kg wet weight (0.2% of 312 mg Hg/kg wet weight).

By using the same equation as for inorganic mercury (section 7.1.8.2.), as recommended by the TGD, the PNEC value for methylmercury in sediment could be calculated according to:

$$\text{PNEC}_{\text{sediment}} = K_{\text{sed-water}} * \text{PNEC}_{\text{water}} / \text{RHO}_{\text{sediment}}$$

With $K_{\text{sed-water}} = 158000$, (from $K_d = 316000$, section 7.1.8.2), $\text{RHO} = 1.3 \text{ kg/l}$ and $\text{PNEC}_{\text{water}} = 0.00001 \text{ mg/l}$, the value of **PNEC_{sediment} is calculated as 1.22 mg/kg wet weight.**

7.2.9. Fish-eating predators

For fish eating predators, the effects of organic mercury will be addressed in more detail because of predominant organic speciation of mercury in their feed.

Fish-eating predators feed on substrate that may contain mercury of which 70 to 90% is organic mercury (see mercury speciation in fish, Slooff *et al.*, 1995).

No data are readily available on fish-eating predator birds (gull's, tern's, etc.). In the literature however, field observations are mentioned that indicate that in certain fish-eating avian species (divers, sea eagle, fish eagle), intoxications and reproductive impairment were noted after eating fish that contained methylmercury at concentrations of 0.2 to 0.7 mg/kg (Slooff *et al.*, 1995).

In the otter, a fish eating predatory mammal, 2 mg/kg feed, as methylmercury hydroxide, caused neurological symptoms when fed for 181 days. No NOEC was determined (O'Connor, 1980).

However, due to the lack of accurate data on the effects of organic mercury on fish eating predators under well controlled conditions, no PNEC can be calculated for this species.

In its Report to Congress on mercury, the US-EPA calculated a Reference Dose (**Rfd**) for aquatic wildlife based on a three generations study in mallard ducks exposed to « methyl mercury dicyandiamide » and on a subchronic study in mink exposed to mercury contaminated fish. (US-EPA mercury report, 1997 volume VII, chapter 3-3). EPA extrapolated the following values :

Rfd aquatic mammals: 18 µg/kg b.w./d

Rfd aquatic avian species: 21 µg/kg b.w./d

As a worst case approach, the PNEC aquatic predators (or Tolerable Daily Intake, TDI) can then be set to 18 µg/kg b.w./d. even if the uncertainty factors used by EPA (factor ± 3) to derive these TDI are substantially lower than those recommended by the TGD for a similar availability of data (Factor of ± 50 to 100).

7.3. Bioaccumulation

Mercury is able to bioaccumulate easily in organisms. The property of a compound to accumulate in organisms from water is expressed in a bioconcentration factor (BCF), which is the quotient of the compound in the organism (on the basis of fresh or dry weight) and the concentration of the compound in water: $BCF = C_{organism}/C_{water}$. The BCF can also be determined by measuring the uptake and elimination rate constants, which is the OECD recommendation method. When BCF is greater than 1, bioconcentration occurs.

7.3.1. Bioaccumulation in fish

In fish BCF values of 1,800-5,700 l/kg (*Raja clavata*, *Pimephales promelas*, *Oncorhynchus mykiss*) have been selected on a basis of an exposure duration of at least 4 weeks and a maximum exposure concentration of 1 µg/l (no state of equilibrium was reached even after 30 days of exposure) (Slooff *et al.*, 1995).

In the report from the third OSPAR workshop on ecotoxicological assessment criteria which had been held at The Hague during the 25 and 29 November 1996 (OSPAR, 1996), the very well known data from Pentreath (1976) giving a BCF value equal to 36,665 l/kg fresh weight for inorganic mercury in marine fish species thornback ray (*Raja clavata* L.) has been extracted and the geometric mean BCF for all fish species available given is 3,030 l/kg fresh weight.

Comparison of the mean dissolved mercury of 0.019 µg/l in European water (see section 8.1.1) with the mean mercury concentration in fish of 115 µg/kg (see section 8.2.1.) gives a BCF of 6,050 l/kg fresh weight.

It is noted that a part of the total amount of mercury in fish can be present as methyl mercury. Methylation of inorganic mercury in fishes takes place both externally and internally: externally by bacteria in the mucous membrane on the skin and internally in the intestines (Jernelöv, 1972; Romijn *et al.*, 1991). So the quantity of methyl mercury in these animals is not only a result of the uptake of methyl mercury from water and food, but come also from a transformation by the microorganisms present on the fish slime. However, according to season, temperature, fish species, this rate of transformation of mercury in methyl mercury can be nil or superior to 80% in the worst case (Jernelöv, 1972).

The methyl mercury BCF values for fish ranged between 4,300 l/kg and 35,000 l/kg. According to Slooff *et al.* (1991), it seems that the comparison with BCF-values with inorganic mercury clearly indicates that in fish methyl mercury (geometric mean of the data set is equal to 8,100 l/kg) is accumulated to a greater extent than is inorganic mercury (geometric mean of the data set is 3,030 l/kg) whereas for OSPAR (1996) it seems that the geometric mean of the data set are close 3,030 l/kg (inorganic mercury) compared with 3,640 l/kg (methyl mercury).

7.3.2. Bioaccumulation in Molluscs

Slooff *et al.* (1995) gives inorganic mercury BCF values of 190-5,300 l/kg for molluscs. In the OSPAR report (1996), a geometric mean BCF of 1,750 l/kg (fresh weight) has been calculated for mussels (*Mytilus edulis*). This value can be recalculated to soft parts dry weight using a correction factor of 0.134 (dry weight/fresh weight) as defined by Haenen *et al.* (1993) giving a BCF of 13,061 l/kg dry weight.

Comparison of the mean dissolved mercury of 0.010 to 0.170 µg/l in north Sea estuaria (see section 8.1.3.) with the mean mercury concentration in marine molluscs of 4-100 µg/kg (see section 8.2.2.) gives a BCF of 24-2500 l/kg fresh weight.

It seems that BCF values for molluscs for organic mercury (3,500 l/kg) are higher than the BCFs for inorganic mercury.

7.3.3. Bioaccumulation in other invertebrates and plants

Values of inorganic mercury BCF in invertebrates taken from the literature ranged between:

- 517-670 l/kg for worms
- 330-2,400 l/kg for crustaceans
- 140-12,600 l/kg for insects
- 870 l/kg for algae (*Croonmonas salina* and *Oedogonium* sp.)
- 18-150 l/kg for aquatic plants.

(all on fresh weight basis, reviewed by Slooff *et al.*, 1995)

Comparison with the BCF values for organic mercury generally indicates a higher accumulation of methyl mercury. For aquatic plants organic mercury BCF-values of 8 l/kg to 2,950 l/kg (fresh weight basis) have been determined applying to the whole plant or to the floating and/or emerged parts (Slooff *et al.*, 1995). However, when comparing BCF values of inorganic and organic mercury, no conclusive evidence that methyl mercury is accumulated in aquatic plants to higher extent than inorganic mercury has been shown (Slooff *et al.*, 1995).

Invertebrates have shown a higher organic mercury BCF value than for inorganic mercury with values ranging from 110 l/kg to 1,800 l/kg for worms 24,900 l/kg to 70,700 l/kg for crustaceans and 2,500 l/kg to 8,500 l/kg for insects (on fresh weight basis, Slooff *et al.*, 1995). In the OSPAR report (1996) a BCF of 13,333 l/kg is given. This value recalculated to soft parts dry weight with the same correction factor as above defined by Haenen *et al.* (1993) gives a BCF = 99,500 l/kg. The geometric mean BCF for all mollusc is 5,490 l/kg fresh weight and 40,970 l/kg dry weight (OSPAR, 1996). In their paper, Slooff *et al.* (1995) said that an organic mercury BCF value 20 to 35 fold higher than those for inorganic mercury has been observed in comparable test with *Daphnia magna*.

7.3.4. Conclusions

Although the BCF for inorganic and organic mercury are respectively higher than 100 and 1000, the PNEC calculation for the water compartment will be based only on long-term toxicity tests as recommended by the TGD.

Mercury can be persistent in the field and lead to biomagnification which is an accumulation along the food chain with an increase in concentration in subsequent trophic levels. Mercury, and methylmercury in particular, can also be accumulated to a large extent from food, specially since there is generally no environmental-chemical equilibrium between the various compartments (soil, water, organism), which leads to higher mercury levels under field conditions than expected on the basis of the theoretical BCF-values. This should be taken into account for higher trophic levels (secondary poisoning).

7.4. Persistence

Observations show that Total Gaseous Mercury mainly composed of Hg^0 species is ubiquitous in the atmospheric media. The global lifetime of Hg^0 would be of the order of 1 year. This lifetime is long enough to authorise long range transport. Wania and Mackay (1996), using a model of partitioning of semi-volatile organic compounds described in Bidleman (1988) were able to classify compounds as a function of the sub-cooled liquid vapour. On that basis four classes of compound mobility have been defined. Owing to that model, compounds with vapour pressure higher than 1 Pa should stay in the gas phase. The Hg^0 species has a vapour pressure of 0.24 Pa (Slooff *et al.*, 1995) and therefore a deposition process by condensation cannot be excluded in polar regions. This aspect has been studied by Mackay *et al.* (1995) where they compare the behaviour of mercury with hexachlorocyclohexane. The relationship between temperature and the fraction of mercury adsorbed on atmospheric particulates show that at - 40°C, about 50 % of atmospheric mercury would be in condensed form. This work suggests that mercury may behave similarly to compounds now classified as POP (Persistent Organic Pollutant) and may deposit in the coldest regions of earth by condensation process. This would have to be confirmed by further modelling work.

7.5. Conclusion

It can be concluded from the above data that mercury is a persistent, toxic and bioaccumulable chemical. Its potential for secondary poisoning (food-chain biomagnification) and for long-range transport, makes it a high priority chemical for emission control. However, due to its natural occurrence, mercury will remain ubiquitous in the environment.

8. EXPOSURE ASSESSMENT

8.1. Regional scenario

To apply the global scenario (Wilken *et al.*, 1999) described under section 6.3. to a regional scale for the North Sea, it is proposed here to follow a similar type of reasoning. The following hypotheses have been made:

- The background levels in sea and in soil are supposed to be the result of the global scenario
- The additional inputs to the region are coming from regional input.
- As described in the global scenario, only 30% of the air emissions in a region are re-deposited at a local or regional level, the remaining 70% being globally distributed.
- The inputs from river water to the sea are based on the measured concentrations in the rivers going into it. As a worst case, the distributions of mercury concentrations in many rivers surrounding the North Sea have been used to estimate a regional distribution of mercury concentrations in water entering the sea. In such an approach an additional safety factor corresponding to the dilution of the rivers into the sea is included in the PEC estimates.
- A similar approach is made for estimating the mercury concentration in the sediment, most of the available data being measured in fresh water sediment or in estuarine areas.
- As said in the global approach, most of the mercury input into the continental margins through water is coming from suspended solids, but more than 90% of this input settle through sedimentation not very far from the coast, making the coastal areas and the estuaries the more sensitive part of the marine environment.

8.1.1. Mercury concentrations measured in river water and estuaries

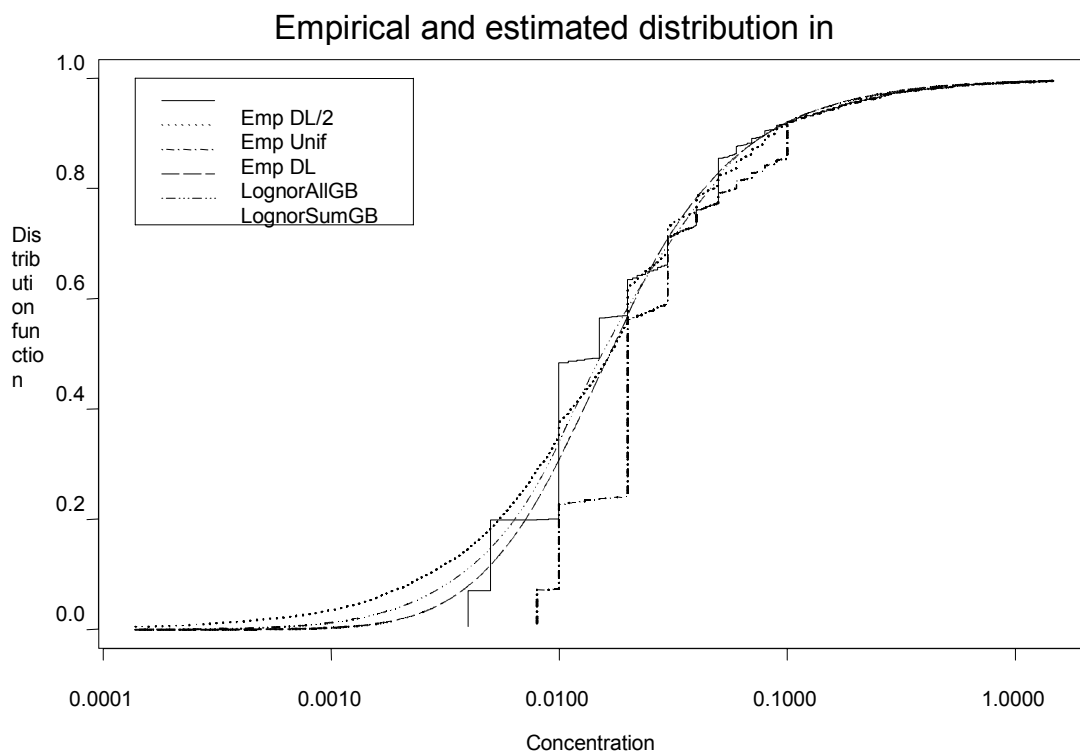
The prioritisation of hazardous chemicals is under discussions both under the EU Water Framework Directive (June 1998) and under the OSPAR DYNAMEC process (OSPAR Dyanec process, 1998). In these contexts, monitoring data base have been established by the Fraunhofer Institute in Schmalenberg Fraunhofer Instiute (March 1999), to evaluate mean concentrations of chemicals in the aquatic environment (water and sediment). A statistical in depth analysis of the data corresponding to mercury has been performed (Govaerts, B, Vanden Eeckhout, P, June 1999) and the results of this analysis are briefly presented here.

- The data have been collected in the period 1994-1997 in different European countries (B, D, F, I, NL, S and UK). More than 10 000 measures of total mercury as well as 17800 measures of elemental mercury have been evaluated for water and more than 3000 data for sediment.

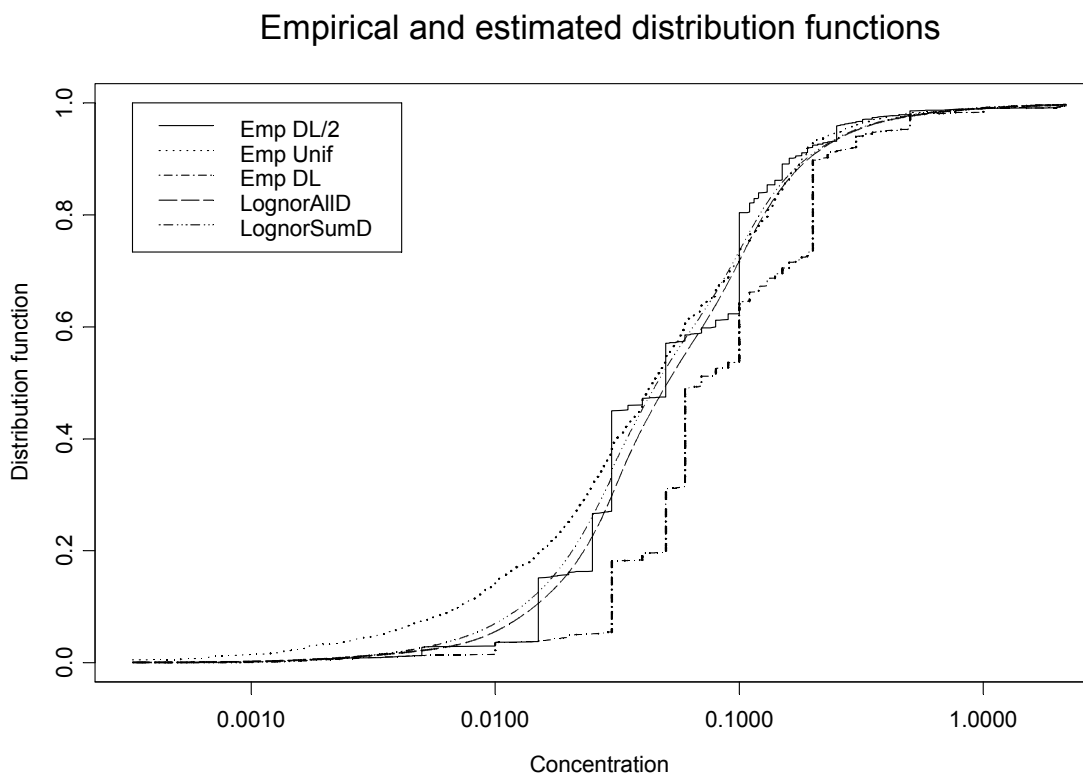
- It appears that the experimental distributions of concentration obtained at each different location (220 measurement sites) can be well represented by a log-normal distribution. The parameters of the distributions have been adjusted based on the maximum likelihood estimation for censored data, due to the existence of data under the detection limits.
- The information coming from different locations have been merged to get a consistent estimation of the regional distribution. As a first approximation, all the location have been given the same weight, but the analysis could be extended to take into account geographical information (river flows for example). This aggregated distribution is compared to the empirical one on a regional basis.

The empirical distributions of the total mercury concentrations in water ($\mu\text{g/l}$) are given hereafter for two countries: UK and Germany (continuous lines in Fig 2 and 3).

Region UK: Figure 2 (concentrations in $\mu\text{g/l}$)



Region Germany: Figure 3 (concentrations in $\mu\text{g/l}$)



In the UK, the 95 percentile values are 0.155 µg/l and 0.170 µg/l for the estimated and empirical distributions respectively. For Germany, the values are 0.301 and 0.250 µg/l respectively.

The distributions presented above have been adjusted taking into account all experimental data. It means that even very peculiar local situations have been considered. In a regional approach these special cases are not representative. Therefore a statistical filter has been applied to the data to eliminate the locations where the mean is higher than 10 times the median value. Moreover, all the measures under the detection limit (DL) have been replaced by DL/2, which is a classical statistical approach corresponding to log normal distribution in each location. The validity of this approach is confirmed by the curves (dotted lines) presented in Fig 2 and 3, and by other studies (OSPAR Document DYN-INT(2) 99/1/4-E and S. Uhlig).

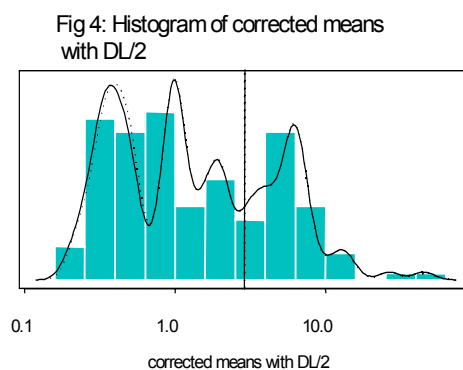
On this basis, for river waters in Europe, the empirical mean values for all countries (about 500 locations) are 120 ng/l for total mercury and 19 ng/l for dissolved mercury (measured after filtration on 0.45 µm filter).

In the marine environment, **estuaries** are generally considered as the more sensitive locations. It is known that mercury has a very poor solubility in water and is mainly transported in an adsorbed form on the particulate fraction (Coquery *et al.*, 1997, UNEP, 1998). According to Slooff *et al.* (1995), the background concentration of dissolved mercury in the North Sea and the Wadden Sea is in the range of 0.5 to 3 ng/l. In estuaries, concentrations ranging from 10 to 170 ng/l of dissolved mercury have been observed. For example, measured values of 112 ng/l in front of the Scheldt estuary, (sampling point 150, Leermakers, 1998), from <10 to 170 ng/l in North Sea and Wadden Sea (Sloof *et al.*, 1995), and from 50 to 90 ng/l in the Rhine estuary (WRc report survey, 1998) have been reported. According to Coquery *et al.* (1995) salinity has practically no influence on the dissolved fraction of mercury. This is confirmed by the Leermakers (1998) results. Details are available in Appendices 9 and 10.

Several publications by Bayens (1992-1996-1998) on the Scheldt estuary in Belgium and The Netherlands reported variations of dissolved methylmercury between 0.01 and 0.120 ng/l in the winter and between 0.08 and 0.6 ng/l in summer and autumn. These values correspond to about 30 to 50% of the total methylmercury concentration, leading to a worst case estimation of the total methylmercury in Scheldt estuary of about 1.8 ng/l.

8.1.2. Mercury in sediment

The total mercury concentration in three countries (D, F and NL) have been combined to give the empirical density function presented hereafter (Fig. 4). All the data have been considered, the statistical outliers having not been removed (Govaerts, B., Vanden Eeckhout, P, 1999).



This analysis gives mean values in sediment of 0.83 mg/kg in The Netherlands, 4.3 mg/kg in France, 2.200 mg/kg in Germany and an overall mean of 2.9 mg/kg. The overall 95 percentile value is about 8 mg/kg (all values expressed per kg dry weight sediment). If, as in the TGD, a thermodynamical partition equilibrium is assumed between the dissolved mercury and the mercury adsorbed in sediment, a mean partition coefficient at a regional level can be estimated by comparing the 0.019 $\mu\text{g/l}$ level for dissolved mercury and the 2.9 mg/kg level for mercury in sediment. The partition coefficient can be calculated according to methodology presented in [Appendix 11](#). A value of about 300,000 is obtained which is in good agreement with the values published in the literature and with the K_d value used to estimate $\text{PNEC}_{\text{sediment}}$ in section 7.1.8.

A mean approach is justified at a regional level due to the large possible variations in the partition coefficient from place to place, in Europe. It is indeed well known that the partition coefficient between dissolved and adsorbed mercury is a function of the water salinity and organic content.

Additional data reported in the literature are presented in [Appendix 9](#). They are all compatible with the distribution of concentration described above.

In Wadden Sea, Slooff *et al.* (1995) reported values of 0.3 to 0.6 mg/kg dry weight, (corresponding to about 0.06 to 0.12 mg/kg wet weight), with background level of 0.1 to 0.2 mg/kg dry weight. The mean value of mercury concentration in sediment in coastal zone of the Irish Sea according to the WRc survey report (1998) is 117 $\mu\text{g/kg}$ dry weight, (corresponding to 23 $\mu\text{g/kg}$ wet weight). Calculated from Coquery *et al.* (1997), the mercury levels in Loire and Seine estuaries are respectively 20 and 200 $\mu\text{g/kg}$ wet weight. A statistical analysis of the COMMPS database of mercury concentrations in freshwater river sediments shows (see section 8.1.2.) that the mean value is 2.9 mg/kg dry weight and the 95 percentile of the distribution is about 8 mg/kg dry weight (corresponding to 1.6 mg/kg wet weight). These values are about one order of magnitude higher than the values reported in coastal areas. This may correspond to an apparent dilution by a factor of 10 of sediment due to tidal mixing effect. These observations are compatible with the data presented in the RIVM report (Sloof *et al.*, 1995), where values of 2-3 mg/kg dry weight are reported in freshwater harbours sediment.

According to Bayens (1992-1996-1998), the total methylmercury concentrations in sediment vary between 4 and 10 $\mu\text{g/kg}$ representing 1 to 1.5% of the total mercury.

8.1.3. Temporal trends

Total mercury concentrations in UK river waters have been collected by WRc (1998) over the period between 1974 and 1995. This database has been statistically analysed using the Sen's estimator approach (Sen, 1968) to define temporal trends. This analysis concludes to a rapid decrease of the mean concentrations from about 600 ng/l in 1974 to about 245 ng/l in 1984. A decrease rate from 250 to 100 ng/l is observed between 1984 and 1994. If this decrease rate is slower, it is however fully statistically significant.

Even if this information is essentially limited to UK, a recent OSPAR document (April 1999) confirms this trend for the OSPAR area. The current concentrations in European rivers (and consequently in the sea) could then be lower than the levels reported here on the basis of existing data.

8.1.4. Levels in continental margins

In the monitoring data used at the regional level, all emission sources are included both natural and anthropogenic ones. As stated in Section 6.4 of this report, the contribution of the European chlor-alkali industry is limited to a small percentage of total anthropogenic emission (less than 10%) and even lower when including natural inputs.

It has to be pointed out that, according to a recent study of Coquery *et al.* (1997) on the Seine and Loire estuaries, "the riverine dissolved mercury inputs to the adjacent coastal waters have been estimated to be half of the corresponding atmospheric deposition". If this observation could be generalised to the other rivers of the OSPAR area, the atmospheric contribution to the continental margins could correspond to a maximum additional 38 ng Hg/l. The hypothesis under this estimate is based on the Coquery *et al.* (1997) observation reported above and on the conservative assumption that the volume of the continental margin water is identical to the total volume of the rivers considered. Such an estimation leads to a mercury concentration in continental margins of about 60 ng/l which is quite compatible with the measured values reported under Section 8.1.1.

According to Bayens (1998), the contribution of the Scheldt estuary to the flows parallel to the coast is less than 2%, indicating a dilution factor of about 50.

8.2. Concentration in biota

In a Draft Assessment Report presented at OSPAR-MON meeting in Copenhagen on February 23-27, 1998, time trends analyses from 1983 to 1991 have been carried out on measured concentration of mercury in marine organisms (blue mussels and fish). It appears that, "all but one of the time series analyses, revealing significant information on trends, show downward trends". Interestingly "the fish muscle tissue data sets generally show concentrations close to or slightly above the OSPAR Background Reference concentrations (BCR) values (ratios <2)".

8.2.1. Concentration in fish

On the basis of the data collected by WRc (1998) over the period 1978-1995 in different countries (B, DK, NL, S, UK) the mean value of the concentration of mercury in fish muscle over the whole period of time is of 115 µg/kg and the 90 percentile is of 220 µg/kg, both expressed in wet weight.

In a recent UBA report (1998), concentrations of methyl mercury in muscle of *Zoarces viviparus* of 112 ± 5 µg/kg wet weight in Watten Meere and of 43 ± 1.5 µg/kg in Ostsee have been reported.

Additional data obtained in marine fish in various North Sea areas (WRc and UBA reports) are reported in Appendix 9. The values vary between 5 to 180 µg/kg wet weight of fish muscle. When available, the concentrations in methyl mercury are also given. It amounts between 80 and 95% of the total mercury.

8.2.2. Concentration in molluscs

In marine molluscs, concentrations of mercury between 4 and 100 µg/kg wet weight for the whole organism have been reported (WRc, 1998 and UBA, 1998). When reported, the fraction of methyl mercury is less than 50% (see Appendix 9).

8.2.3. Concentration in marine mammals

Over the period 1988-1992, the concentrations of mercury have been measured in liver of marine mammals and vary between 3 and 100 mg/kg wet weight (WRc, 1998). The 90 percentile calculation on more than 200 observation over this period is 98.4 mg/kg wet weight. There is no time trend observable over this period. Similar values have been recently observed by Siebert *et al.* (1999). They indicated that the total mercury burden in these species can reach concentrations of mercury up to 450 mg/kg dry weight in liver tissues (corresponding to about 150 mg/kg wet weight) and up to 400 mg/kg dry weight in muscle (corresponding to about 112 mg/kg wet weight) (see Appendix 9).

8.2.4. Concentration in seabirds

Niecke *et al.* (1998) reported measured concentrations of mercury in the feathers of sea eagles in the Mecklenburg-Vorpommern region (Germany) over the last century. The values increased from 8 mg/kg in 1900 to 20 mg/kg in 1990 and then decreased down to 11 mg/kg over the past decade. They also indicated that the observed concentrations are lower in the Ostsee coastal area than in the rest of the region. The reported values are said to be lower than the concentrations leading to poisoning symptoms (see Appendix 9).

Another field study (Oehme *et al.*, 1981) indicated that lethal poisoning of sea eagles by methyl mercury occurs at concentrations from 45 to 133 mg/kg in liver or from 45 to 306 mg/kg wet weight in kidney. Borg *et al.* (1969) reported a lethal concentration of 200 mg/kg wet weight liver for the same species.

9. RISK ASSESSMENT CONCLUSION

9.1. Inorganic Mercury

9.1.1. Water

According to data detailed under section 7.1., the toxicity levels of mercury towards fresh water and marine water organisms are very similar. The overall conclusion of this study leads to a PNEC value of 470 ng/l in aquatic compartment.

Considering the highest observed concentration for total mercury in **coastal areas** as a **worst case**, (170 ng/l in the North Sea and Wadden Sea), the PEC/PNEC ratio is calculated to be $170/470 = 0.36$, which gives a safety margin of about 3. Using the dissolved mercury fraction would increase this safety margin by a factor of 10 at least.

9.1.2. Sediment

A PNEC was derived from a *Chironomus riparius* study as 31.2 mg/kg wet weight. A PEC of 1.6 mg/kg wet weight was derived from a whole set of freshwater data over Europe.

Even if the freshwater sediment is considered as the **worst case**, without taking into account the dilution in estuaries of contaminated particles by less contaminated suspended solids coming from the sea, the PEC/PNEC ratio is $1.6/31.2 = 0.05$, giving a margin of safety of about 20.

9.2. Methyl mercury

9.2.1. Water

Considering that methylmercury represents, in a very reasonable worst case, 5% of the total dissolved mercury (Wilken, 1999) and that the highest total mercury concentration found in both North Sea and Wadden Sea is 170 ng/l, a total methylmercury concentration of $(170 \times 5/100) = 8.5$ ng/l is calculated as a **worst case** PEC value. This should be compared to the methylmercury PNEC value of 10 ng/l, leading to a PEC/PNEC ratio of $8.5/10 = 0.85$ and to a safety margin of 1.2. This margin would be increased by a factor 10 at least if the dissolved fraction is taken into account.

Considering the measured values of total methylmercury in Scheldt estuary are lower than 1.8 ng/l (see § 8.1.1), the worst case approach presented here is very conservative.

9.2.2. Sediment

According to Slooff *et al.* (1995), only 0.01 to 10% of the total mercury present in water and sediment is methylated. Experimental values obtained by Coquery *et al.* (1997) in Loire estuary (France) indicate that, depending on the compartment considered, methylmercury to mercury ratio are 0.2, 0.2 and 2.9% for sediment, fluid mud and marine water respectively. In its review, Wilken (1999) indicates that “methylmercury generally make up to 3% of the

total mercury linked to particles in continental margin areas". In Elbe sediment, data presented in the UBA report (1998) indicates a ratio of methylmercury to total mercury between 0.4 and 0.6%.

As indicated in the section 9.2 above, the 95 percentile of the total mercury concentration distribution in sediment is 8 mg/kg dry weight (corresponding to 1.6 mg/kg wet weight). Considering that 3% of this total mercury is methylated, a concentration of methyl-mercury of $(1.6 \times 0.03) = 0.048$ mg/kg wet weight can be estimated as a typical, conservative PEC value. If the highest reported level of methylation (10%) is used, a conservative worst case PEC value of 0.16 mg/kg wet weight is obtained.

This worst case approach is very conservative compared to the measured values of methylmercury in sediment of Scheldt estuary (4 to 10 µg/kg).

A worst case PNEC sediment derived from PNEC water is calculated as 1.2 mg/kg wet weight.

By comparing this value with the conservative typical and worst case PEC values estimated here above, safety margins of 25 and 7 respectively are obtained.

9.3. **Secondary poisoning in aquatic predators**

Since aquatic predators are mainly exposed to mercury through fish-feeding, it is assumed that they are essentially exposed to the organic forms of mercury.

The RIVM (Slooff *et al.* 1995) document does not propose a clear PNEC approach for aquatic predators. The discussion presented in section 7.2.9. leads however to a reference dose or a tolerable daily intake (TDI) for aquatic predators of 18 µg/kg b.w./d.

Assuming a daily fish intake by marine predators of approximately 5% of their body weight for large predators (large sea mammals), the daily mean exposure to organic mercury is calculated to be contained in 50 g fish per kg body weight predators. This corresponds about to a mean daily intake (DI) value of 6 µg/kg body weight and a 90 percentile DI value of 11 µg/kg body weight predators. For smaller marine predators (sea birds, gull, tern, ...) the daily intake of feed may reach up to 10% of the bodyweight. By analogy, the daily exposure will then reach a mean of 12 µg/kg body weight and a 90 percentile of 22 µg/kg body weight.

The mean DI/TDI ratios will then be for large predators $6/18 = 0.3$ and for smaller predator $12/18 = 0.7$. If the 90 percentile values are considered the DI/TDI ratios are $11/18 = 0.61$ and $22/18 = 1.2$ for large and small predators respectively.

The values used to estimate the TDI for top predators are relatively conservative, since a recent survey in marine mammals from North Sea and Baltic sea waters (Siebert *et al.*, 1999) indicated that **even for levels up to 150 mg/kg wet weight, no histopathological effects attributable to acute or chronic mercury poisoning could be detected**. A correlation was however observed between total mercury concentration in the organisms and its nutritional state but parasitic infestation was a confounding factor in this study.

Moreover, the above discussion is in agreement with the general conclusion of the 3rd OSPAR workshop on Ecotoxicological Assessment Criteria (1996) which indicate a lowest

NOEC value for mammals of 220 $\mu\text{g}/\text{kg}$ food and for birds of 250 $\mu\text{g}/\text{kg}$ food. These values in food correspond to or are higher than the 90 percentile of the concentration observed in marine fish in the North Sea, indicating that the RfD used for estimating the TDI is conservative.

9.4. Conclusion

Based on PEC or DI derived from monitoring data the different PEC/PNEC or DI/TDI ratios show that at present time, mercury **as a general pollutant from different sources** is not a threatening environmental problem in the North Sea area. The chlor-alkali industry is contributing to less than 10% of the total anthropogenic air and water mercury emissions in Europe. Further mercury emissions reduction will not rapidly improve the current North Sea situation. This statement is confirmed by the fact that over the period 75-95, the drastic reduction of mercury emissions from European chlor-alkali plants did not modify significantly the concentration levels observed in marine fish as shown in WRC database (see Fig.5 and 6 hereafter)

Fig 5 : Mercury Fish Muscle Wet weight Marine waters UK

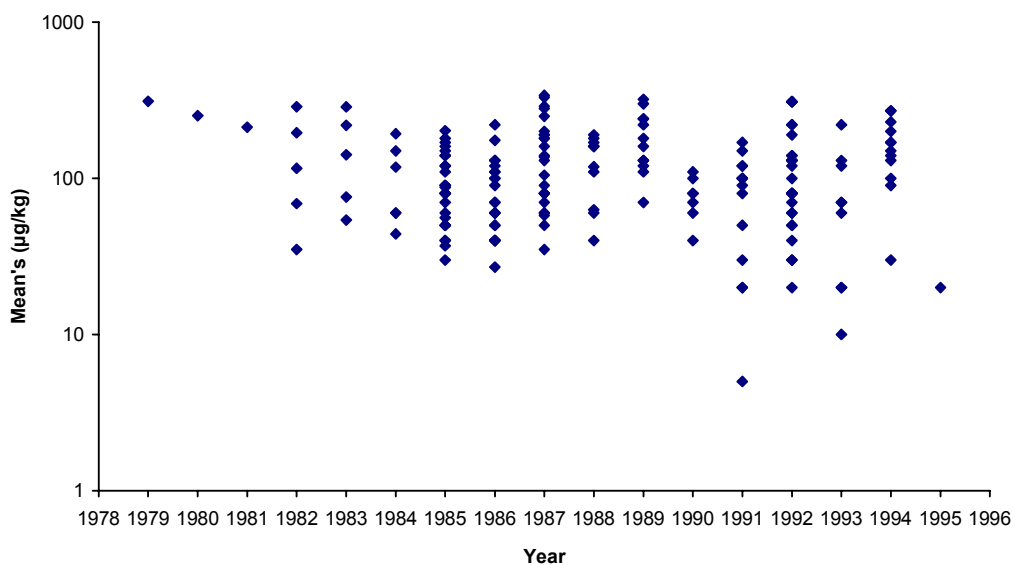
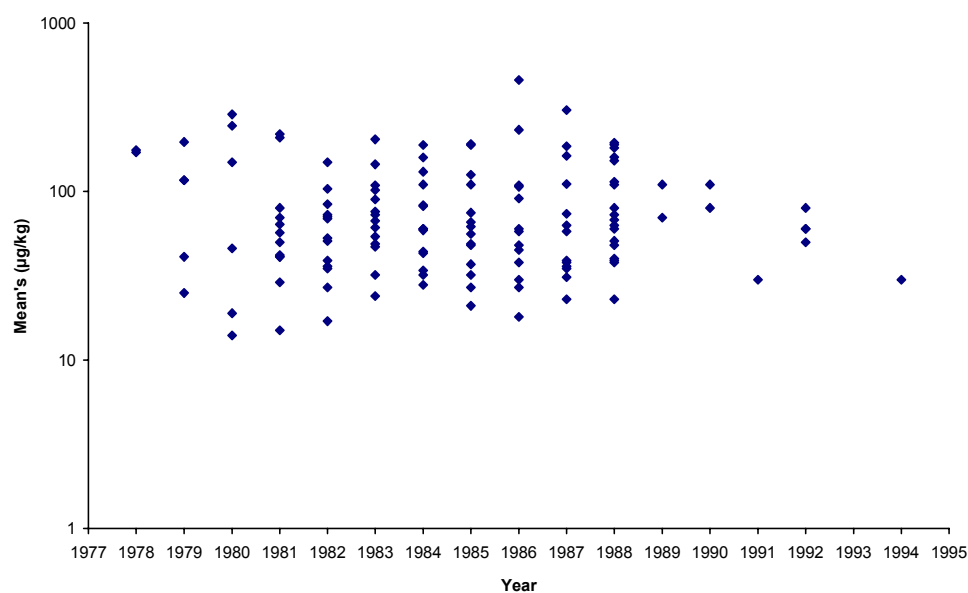


Fig 6 : Mercury Fish Muscle Wet weight Coastal waters North Sea



Calculation of PEC/PNEC ratios for mercury in the regional scenario

Inorganic Mercury			
	PEC	PNEC	PEC/PNEC
Aquatic organisms			
- estuaries and coastal areas <u>worst case</u>	170 ng/l	470 ng/l (dissolved fraction)	0.36
- sediment <u>worst case</u>	1.6 mg/kg wet weight	31.2 mg/kg wet weight	0.05
Organic Mercury			
	PEC	PNEC	PEC/PNEC
Aquatic organisms			
- marine water <u>worst case</u>	8.5 ng/l	10 ng/l (dissolved fraction)	0.85
- sediment typical	0.048 mg/kg wet weight	1.2 mg/kg wet weight	0.04
- sediment worst case	0.16 mg/kg wet weight		0.13
Aquatic predators	DI	TDI	DI/TDI
- marine mammals typical	6 µg/kg b.w./d	18 µg/kg b.w./d	0.33
- marine mammals worst case	11 µg/kg b.w./d	18 µg/kg b.w./d worst case	0.61
- sea birds typical	12 µg/kg b.w./d		0.7
- sea birds worst case	22 µg/kg b.w./d		1.2

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10.2 References for ecotoxicity data

See Appendices 7a and 7b

APPENDIX 1

Environmental quality criteria for assessment of ecotoxicity data

The principal quality criteria for acceptance of data are that the test procedure should be well described (with reference to an official guideline) and that the toxicant concentrations must be measured with an adequate analytical method.

Four cases can be distinguished and are summarized in the following table (according to criteria defined in IUCLID system).

Table : Quality criteria for acceptance of ecotoxicity data

Case	Detailed description of the test	Accordance with scientific guidelines	Measured concentration	Conclusion: reliability level
I	+	+	+	[1] : valid without restriction
II	±	±	±	[2] : valid with restrictions; to be considered with care
III	insufficient or -	-	-	[3] : invalid
IV	the information to give an adequate opinion is not available			[4] : not assignable

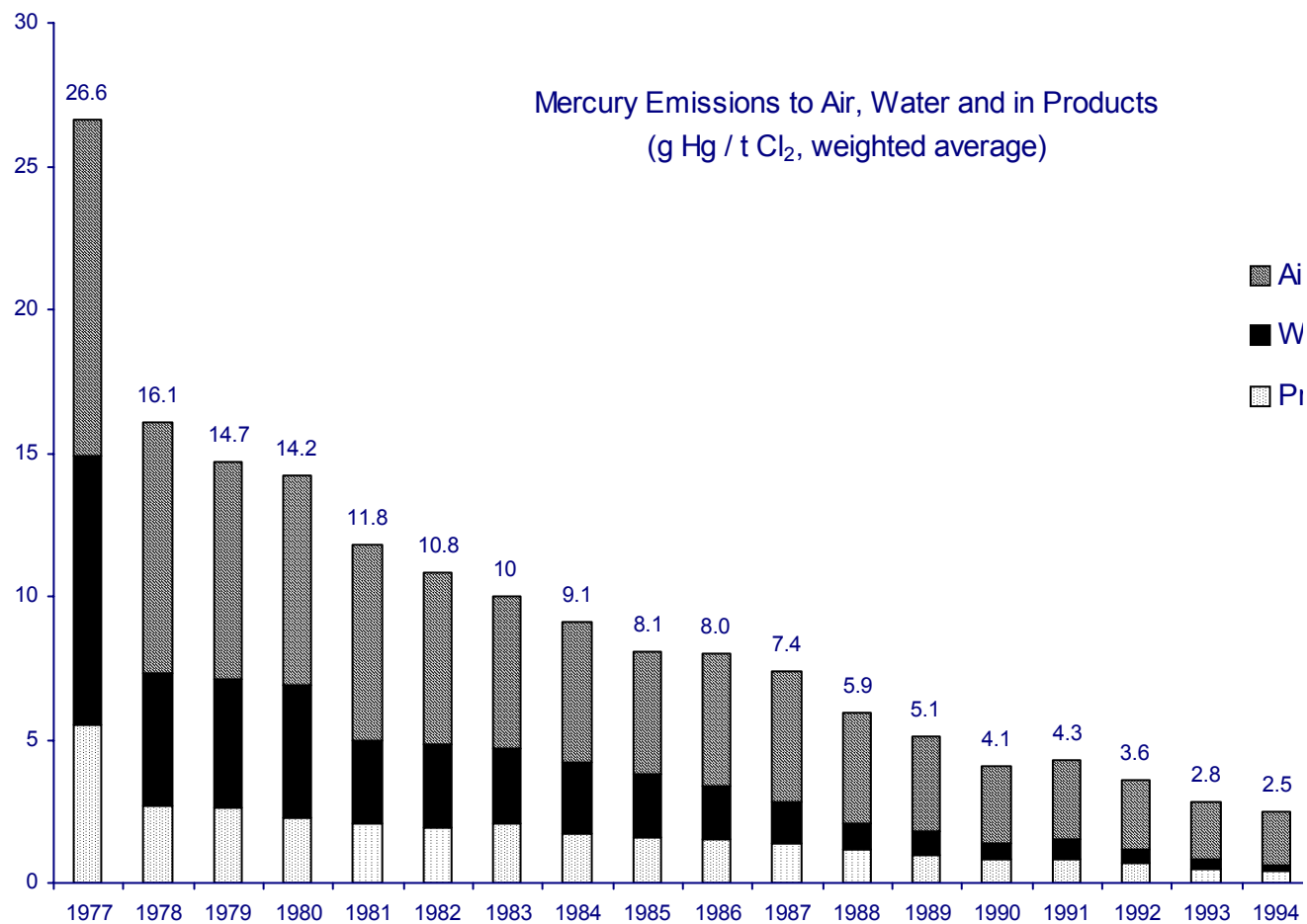
The selected validated data LC50, EC50 or NOEC are divided by an assessment factor to determine a PNEC (Predicted No Effect Concentration) for the aquatic environment.

This assessment factor takes into account the confidence with which a PNEC can be derived from the available data: interspecies- and interlaboratory variabilities, extrapolation from acute to chronic effects,...

Assessment factors will decrease as the available data are more relevant and refer to various trophic levels.

APPENDIX 2

Mercury Emissions 1977-1997
Euro Chlor: W. Europe



ATMOSPHERIC CHEMISTRY OF MERCURY.

Because of its high vapour pressure, mercury is easily emitted to the atmosphere. The understanding of the atmospheric chemistry of this element is difficult because of a complex speciation, the role of the aqueous phase in the atmosphere, the role of particulate and the cycling of mercury between surface and the atmosphere.

1. Emissions

The flux of mercury from the earth surface to the atmosphere is mainly occurring by elemental mercury (Hg^0). (Nriagu, 1988, Lindqvist, 1991, Slemr *et al.*, 1985)

1.1. Natural sources

The sources of natural origin generally listed for atmospheric mercury sources are volatilisation of elemental mercury Hg^0 from soil, vegetation, from surface waters and volcanic eruption (OECD, 1994). However it is important to point out that part of the mercury emitted from natural surfaces can come from anthropogenic mercury previously deposited. The natural emission has been estimated between 2700 and 6000 tonnes/year. (OECD, 1994). In a recent review of emission estimates O. Lindqvist (1991) indicates old estimations of up to 30 000 tonnes/year for natural emissions and recent estimates from Pacyna and Nriagu in 1988 giving a much smaller value of 3000 tonnes/year.

Recent estimation of Hg^0 emission from forest indicate a significant source, of the same order as for soils (Lindberg *et al.*, 1996). This leads to a total estimation of continental emissions ranging between 1400 and 3200 tonnes/year. Using an estimated flux of Hg from ocean of 2000 tonnes/year as quoted in (Lindberg *et al.*, 1996) and (Schroeder & Munthe, 1998) and an average value for continental emissions of 2300 tonnes/year this would total in about 4300 tonnes/year of natural Hg^0 emission which is significantly higher from previous estimations. As stated above it remains difficult to know what part of this emission value would come from previously deposited mercury from anthropogenic origin.

1.2. Anthropogenic emissions

The different anthropogenic activities leading to atmospheric emission of mercury have been extensively reviewed in different reports. The OECD report (1994) indicates the value of 3600 tonnes/year estimated by Nriagu and Pacina. Lindqvist (1991) estimates a value of about 4500 with a possible range of 3000 to 6000 tonnes/year.

Recently an inventory of world wide anthropogenic emission of mercury was published by Pirrone *et al.* (1996). Between 1983 and 1992 the reported emissions vary between 1861 tonnes/year in 1983, peak at 2288 tonnes/year in 1989 and then slow down to 2199 tonnes/year in 1992. This last emission is smaller than the previously reported numbers.

1.3. Comparison between anthropogenic and natural emissions

On the basis of the above numbers it could be said that natural emissions could be from the same order to larger by a factor of 2 than anthropogenic emissions. However, as said above

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mercury is recycled from soil and water to Hg^0 which return to the atmosphere. Part of the mercury emitted to the atmosphere from soil and water probably comes from the pool of mercury which has been accumulated since preindustrial times.

It could be suggested taking into account the uncertainty above that natural and anthropogenic emissions are of the same order.

2. Atmospheric concentrations

Most of measurements published so far report values for total gaseous mercury (TGM) in remote areas and rural areas ranging between 1 and 4 ng/m^3 . Mercury appears to be widely present in atmosphere in Northern and Southern hemispheres Slemr *et al.* (1985) have measured concentrations of TGM varying roughly between 1.6 and 2.2 ng/m^3 between -30 and $+30^\circ$ of latitude in marine air. Concentrations however vary with location i.e. between marine and continental air where values are closer to 4 ng/m^3 . Recently Slemr *et al.* (1995) indicated values measured for the northern hemisphere in the southern Germany of 2.3 ng/m^3 and 1.79 ng/m^3 in marine air. In urban air concentrations can be a lot higher. A value of 8.94 ng/m^3 is reported in Slemr *et al.* (1985). Values ranging between 20 and 50 ng/m^3 are reported in the OECD report (1994). In polluted area the TGM atmospheric concentration can reach very high values i.e. up to 100 ng/m^3 and more.

Species	Atmospheric concentration ng/m^3 or % of TGM
Total gaseous mercury TGM	1- 4 (Lindqvist, 1991, EPA, 1997) 1.6-2.2 (Slemr <i>et al.</i> , 1985), marine air 3.45 (Slemr <i>et al.</i> , 1985), rural 8.94 (Slemr <i>et al.</i> , 1985), urban 2.8-3.2, Nordic Countries, (Iverfeldt, 1991). 2.3 Southern Germany,(Slemr <i>et al.</i> , 1995) 1.79, Marine air,Northern Hemisphere (Slemr et al, 1995) 1.18, Marine air, Southern Hemisphere (Slemr <i>et al.</i> , 1995) 1.93-4.05 (Lindberg 1998) 2.2-4.1 (Lindberg & Stratton, 1998) 20-50, (Lindqvist, 1991), industrial
Hg^{II}	0.05-0.15 (3-5%) (Stratton & Lindberg, 1995) 0.03-0.163 (Lindberg, 1998) 0.1 (3%) (Lindberg & Stratton, 1998)
Methyl mercury compounds	<0.01 (5%), marine air (Slemr <i>et al.</i> , 1985) 0.41 \pm 0.31 (14%)
Dimethyl mercury	< 0.02, marine air (< 2%) (Slemr <i>et al.</i> , 1985) <0.05, rural (< 2%) (Slemr <i>et al.</i> , 1985) 1.67 \pm 1.16 (20%), urban (Slemr <i>et al.</i> , 1985)

Measurements carried out by Slemr *et al.* (1985) where made between 1977 and 1979 and the authors consider that some increase of the atmospheric concentration took place over that period but at the limit of statistical significance. More recently measurements made at the Wank mountain (Southern Germany) and during the Polarstern cruise show a decreasing trend of the TGM concentration with -22% between 1990 and 1994.

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The major part of TGM is identified as elemental mercury Hg^0 . The proportion is generally higher than 80 %. In remote area the proportion is likely to be higher than 95 %. In polluted area dimethyl mercury (DMM) and monomethyl mercury (MMC) also represent unusually high proportions. In remote area TGM would be composed of roughly 95 % of Hg^0 and 5 % composed of particulate Hg and organic forms of mercury species.

Recently the presence of Hg^{II} forms have been observed in the gaseous phase representing 3 to 5 % of TGM (Stratton & Lindberg, 1995; Petersen *et al.*, 1998) although it was stated in previous work that it has not been detected in gaseous phase (Lindqvist, 1991).

3. Concentrations in rain water

Lindqvist reports ranges of observed Hg concentrations from 1 to 100 ng/l as extremes with a background range of 1 to 25 ng/l in Nordic countries. Concentrations reported in the United States vary between 11 and 130 ng/l. Mean values are reported between 35 and 57 ng/l. (EPA, 1997).

Slemr *et al.* (1985) report values ranging between 2.9 to 14.3 ng/l for reactive Hg and in urban continental areas 13.2 ng/l for reactive Hg and 25 to 55 ng/l for total Hg.

Wet deposition values have been reported in OECD (1994) and EPA(1996) reports respectively ranging 5 to 10 $\mu\text{g}/\text{m}^2/\text{yr}$ and 4.4 to 44 $\mu\text{g}/\text{m}^2/\text{yr}$ for different locations in the US. Estimate of current total deposition rates ranging from 7 to 12.5 $\mu\text{g}/\text{m}^2/\text{yr}$.

4. Speciation of mercury in the atmosphere

4.1. Hg^0

The major part of TGM (Total Gaseous Mercury) is composed of elemental mercury Hg^0 . It is emitted as such by natural surfaces by volatilisation process and by anthropogenic activities. Available data would tend to indicate that it represents roughly 95% of atmospheric mercury on a global basis.

4.2. Hg^{II}

Recently analytical work was able to confirm the presence of Hg^{II} species in the gaseous phase. These species form the part of atmospheric mercury called reactive atmospheric mercury (RGM) which is highly soluble and can be rapidly dry or wet deposited at the surface (Lindberg & Stratton, 1998). It is probably mainly constituted of $HgCl_2$ and $Hg(OH)_2$. The sources of RGM is likely to be mainly direct anthropogenic emission like for example combustion processes.

4.3. Monomethyl mercury compounds (MMC) and dimethyl mercury (DMM)

MMC and DMM species are detected both in remote and urban area. As shown in table of section 2 their fraction of TGM strongly vary between remote and urban area being very small in the former and significant in the latter. MMC and DMM are produced by natural biological methylation processes. The high concentration in urban area also indicate anthropogenic direct or indirect production of that compound.

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4.4. Particulate mercury

Slemr *et al.* (1985) have measured mean concentration of particulate bound mercury in marine atmosphere of the northern and southern hemisphere were 0.013 ± 0.018 ng Hg/m³ and 0.007 ± 0.004 ng Hg/m³ respectively.

Most frequently observed particulate bound mercury contribution to TGM were in the range between 0 and 0.2% in marine air and 0.9 % in continental location (Slemr *et al.*, 1985).

5. Fate of mercury species in the atmosphere

5.1. Homogeneous gas phase

Hg⁰

The only identified homogeneous gas phase reaction which could lead to the oxidation of elemental mercury is its reaction with ozone to form HgO:



A first attempt to quantify the rate constant of that reaction gave a value ranging between $4.2 \cdot 10^{-19}$ and $1.7 \cdot 10^{-18}$ cm³ molec⁻¹ S⁻¹ and corresponding lifetimes ranging between 2 and 25 days. A recent measure of that rate constant shows that this reaction is slower. The previous higher rate constant could be due to wall losses effects not taken into account.

The recent rate constant measured is: $3 \pm 2 \cdot 10^{-20}$ cm³ molecule⁻¹ S⁻¹. The life time of atmospheric Hg⁰ associated with that process can be calculated at about 1.4 years for tropospheric concentrations of ozone of the order of 30 ppbv.

Hg^{II}

As said in the previous section atmospheric Hg^{II} species are likely to be rapidly deposited because of their high solubility in comparison with Hg⁰. For example the solubility of HgCl₂ is about 10⁶ times higher than Hg⁰ as can be deduced from their Henry's law constants (Schroeder & Munthe, 1998). Both wet and dry deposition processes have been shown to occur rapidly for those species. (Lindberg & Stratton, 1998)

DMM

In the atmosphere and in the gaz phase dimethyl mercury could undergo decomposition by reactions with radicals like Cl[•], OH[•] and NO₃[•]. In the case of the reaction with NO₃[•] the products formed are HgO and CO₂ (Sommar *et al.*, 1997). The lifetime of this species is likely to be of the order of 1 day.

Methyl mercury forms are formed by abiotic and biotic methylation processes. Dimethyl mercury would be the species preferably emitted to the atmosphere because of its volatility.

APPENDIX 3**5.2. Aqueous phase reactions**

The heterogeneous interaction of atmospheric mercury with aerosols and clouds is considered to be the main process for its atmospheric removal. This is supported by the very high concentrations observed in rain water of Hg^{II} species. The mechanism proposed by Munthe *et al.* (Slemr *et al.*, 1985; Fitzgerald *et al.*, 1991, Schroeder & Munthe, 1998) is rather complex and involves several mercury species. The mercury species present in the gas phase are Hg⁰, HgCl₂, HgO and particulate Hg. HgO is produced by the oxidation of Hg by ozone. Those four species are interacting with atmospheric water in different ways. Particulate Hg is likely to be physically scavenged by the atmospheric water and remains as such in the cloud droplet. The other three species are in a first step going to be solubilised according to the Henry law and will be solubilised in the aqueous phase and further react depending on their nature. The reaction of Hg⁰ with ozone in aqueous phase has been shown to rapidly form HgO that is further converted Hg⁺⁺ (Munthe, 1992; Pleijel & Munthe, 1995). The rate constant measured in Munthe (1992) is in the range of 10⁷ to 5 10⁸ M⁻¹ S⁻¹. The ozone concentration is calculated in Munthe (1992) using the Henry constant of 1.3 10⁻² M atm⁻¹. For a concentration of 30 ppbv the concentration would be 3.9 10⁻¹² mole/l. The corresponding lifetime of Hg⁰ in aqueous phase would then be about 40 minutes ($\tau = 1/k(O_3)$) which shows that this reaction is quite rapid. Reactions of Hg⁰ with other species like OH radicals in the aqueous phase are also considered. The oxidation of Hg⁰ leads to the formation of Hg^{II} soluble species which could also adsorb on particulates contained in the aqueous aerosol. Soluble Hg^{II} and adsorbed species are then removed from the atmosphere by the normal precipitation process.

It is important to note that in spite of the rapid transformation of Hg⁰ in aqueous phase by reacting with ozone, its overall rate of removal from the atmosphere is governed by its solubility in water. Also, competition is taking place between oxidation of Hg⁰ species in Hg^{II} and further reduction of Hg^{II} back in Hg⁰ by S^{IV} from SO₂ dissolution in atmospheric water (Munthe, 1992). This overall mechanism of atmospheric mercury species interactions with cloud water has been used as the basis for recent modelling work (Petersen *et al.*, 1995, 1998) which is in broad agreement with observed Hg^{II} concentrations in precipitations. This process could be the main removal process of mercury from the atmosphere. If mercury is dry deposited in its elemental form it can be reemitted to the atmosphere if it is not meanwhile converted to Hg^{II} inorganic species by any surface or soil processes.

5.3. Discussion on the removal process of mercury species from the atmosphere

The global burden of mercury in the atmosphere can be derived from atmospheric concentration. Assuming a global volume of the atmosphere of 3 10¹⁸ m³ on the basis of a surface of the earth of about 5 10¹⁴ m² and 6000 m for the atmosphere height (at one atm pressure) one can calculate that one ng/m³ correspond to a burden of 3000 tonnes. Assuming an average concentration between 1 and 4 ng/m³ i.e. 2.5 ng/m³ it gives a global atmospheric burden of 7500 tonnes of mercury species, most of it being in the form of Hg⁰. Slemr *et al.* (1985) have calculated an atmospheric burden of about 6000 tonnes.

Residence time for atmospheric mercury ranging between 0.5 and 2 years have been estimated (Lindqvist, 1991). In their paper, Slemr *et al.* (1985) indicate their previous work where they

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calculated a residence time of about 0.9 year for atmospheric mercury from an analysis of differences between southern and northern hemispheres concentrations. Assuming steady state this would mean a global emission of about 6000 tonnes per year. A flux of mercury from wet deposition was calculated to be comprised between 5 and 8000 tonnes/year (Slemr *et al.*, 1985). Deposition numbers listed above are ranging between 5 and 12.5 $\mu\text{g}/\text{m}^2/\text{yr}$. Assuming a value for the earth surface of $5 \cdot 10^{14} \text{ m}^2$, one $\mu\text{g}/\text{m}^2/\text{yr}$ correspond to a deposition flux of about 500 tonnes. The global flux derived would then be comprised between 2500 and 6250 tonnes per year. Similar type of calculation carried out by Lindqvist gave a value of 7500 tonnes (Lindqvist, 1991).

If one assume that the global background rain water concentration of mercury is between 1 and 25 ng/l, assuming an average rain fall worldwide of 75 cm and using the earth surface value above, one calculates that 1 ng/l represent 375 tonnes of deposited flux. The global flux would then be comprised between 375 and 9375 tonnes/year.

The numbers derived for emission, atmospheric burden and lifetime are very broadly consistent with the emission numbers of 7500 tonnes for natural and anthropogenic emissions listed by Lindqvist (1991).

The wet deposition seems to be the major process for removal of atmospheric mercury as it is shown by mercury concentration in rain water and as explained above in the discussion on aqueous phase mechanisms.

6. Comparison between Industrial and pre-industrial levels of mercury

Pre-industrial deposition rate estimations of mercury have been listed for two places in the US (EPA, 1997). For Minesota 3.7 and 12.5 $\mu\text{g}/\text{m}^2/\text{y}$ and in Northern Wisconsin 7 and 24.5 $\mu\text{g}/\text{m}^2/\text{y}$ respectively for pre-industrial and present times. Present deposition rate are roughly 3 times the estimated pre-industrial one. If one would assume that the atmospheric lifetime of mercury in the pre-industrial atmospheric condition would be the same as for present conditions and assuming stationary state the pre-industrial atmospheric burden would have to be of the order of 2000 tonnes and the global average atmospheric concentration about 0.6 to 0.7 ng/m^3 . However the pre-industrial atmosphere concentrations of ozone and SO_2 which are playing an important role in the atmospheric removal process of mercury were much lower and this could modify the mercury atmospheric lifetime and consequently the atmospheric mercury burden. This aspect still requires examination.

7. Transport and deposition of mercury species in the atmosphere

7.1. Hg^0

Observations show that TGM mainly composed of Hg^0 species is ubiquitous in the atmospheric media. The global lifetime of Hg^0 would be of the order of 1 year. This lifetime is long enough to authorise long range transport. This transport has been shown to occur at European scale (Petersen *et al.*, 1995) but one may expect the possibility of long range transport at greater scales on the basis of the lifetime and observations.

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The main process for atmospheric mercury deposition has been shown to be wet deposition involving a mechanism of Hg^0 oxidation in aqueous phase.

It is also interesting to consider if the Hg^0 species itself could be deposited like a semivolatile compounds because of its physical properties.

Wania and Mackay (1996), using a model of partitioning of semi-volatile organic compounds described in Bidleman (1988) were able to classify compounds as a function of the sub-cooled liquid vapour. On that basis four classes of compound mobility have been defined. Owing to that model, compounds with vapour pressure higher than 1 Pa should stay in the gas phase. The Hg^0 species has a vapour pressure of 0.24 Pa (Slooff *et al.*, 1995) and therefore a deposition process by condensation cannot be excluded in polar regions. This aspect has been studied by Mackay *et al.* (1995) where they compare the behaviour of mercury with hexachlorocyclohexane. The relationship between temperature and the fraction of mercury adsorbed on atmospheric particulates show that at -40°C , about 50 % of atmospheric mercury would be in condensed form. This work suggests that mercury may behave similarly to compounds now classified as POP (Persistent Organic Pollutant) and may deposit in the coldest regions of earth by condensation process.

In conclusion, Hg^0 species may undergo long range transport and be deposited. The deposition process mainly understood and identified is the wet deposition process where Hg^0 is oxidised in the aqueous phase and deposited by precipitations. It cannot be excluded that Hg^0 may also behave as a semivolatile compound and be deposited by condensation process in the coldest part of the earth but the possible importance of this latter process would need confirmation.

7.2. Hg^{II} and particulate mercury.

Because of their high solubility and reactivity these species are likely to undergo rapid wet and dry deposition. (Lindberg & Stratton, 1998). Therefore, contrarily to Hg^0 species, it is possible for Hg^{II} species to undergo local deposition. In the case of particulate mercury one may expect irreversible scavenging by atmospheric water (Petersen *et al.*, 1998) and further rain deposition. This also could produce local deposition of particulate bound mercury.

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APPENDIX 3**EXPOSURE DATA – REGIONAL SCENARIO**

	Inorganic Mercury	
	Concentration	References
a. <u>Water</u>		
1. <i>River water in Europe</i>		COMMPS database (1998) Govaerts <i>et al.</i> (1999)
Total Mercury		
mean value in Europe	0.12 µg/l	
95% in UK	0.17 µg/l	
95% in D	0.25 µg/l	
Dissolved Mercury		
mean value in Europe	0.019 µg/l	
2. <i>Estuaries</i>		
Rhine	0.05 to 0.07 µg/l	WRc database (1998)
Scheldt	0.112 µg/l	Leermakers (1998)
3. <i>North Sea – Wadden Sea</i>		
Background	0.0005 to 0.003 µg/l	Slooff <i>et al.</i> (1995)
Coastal areas	0.01-0.17 µg/l	Slooff <i>et al.</i> (1995)
b. <u>Sediment</u>		
1. <i>River water in Europe</i>		
mean value	2.9 mg/kg dw	COMMPS database (1998) Govaerts <i>et al.</i> (1999)
95 percentile	0.58 mg/kg ww	COMMPS database (1998) Govaerts <i>et al.</i> (1999)
	8 mg/kg dw	
	1.6 mg/kg ww	
2. <i>Estuaries and coastal areas</i>		
Irish sea-coast	117 µg/kg dw	WRc database (1998)
	23 µg/kg ww	
Loire estuary	20 µg/kg ww	
Seine estuary	200 µg/kg ww	
Harbours sediment	2-3 mg/kg dw	Slooff <i>et al.</i> (1995)
	0.4-0.6 mg/kg ww	
3. <i>Wadden Sea</i>		
background level	0.1-0.2 mg/kg dw	Slooff <i>et al.</i> (1995)
	20-40 µg/kg ww	
typical values	0.3-0.6 mg/kg dw	
	60-120 µg/kg ww	

APPENDIX 3

Organic Mercury (in biota all mercury is supposed to be organic)		
	Ratio MeHg/Hg	References
1. <u>Sea water & sediment</u>		
Sea water and sediment	0.01-10%	Sloof <i>et al.</i> (1985)
Sea water and sediment	0.1-2%	Nieke (1998)
Sea water and sediment	0.2-2.9%	Coquery <i>et al.</i> (1997)
Sediment	< 3%	Wilekn (1999)
Elbe sediment	0.4-0.6%	UBA (1998)
	Concentration ($\mu\text{g}/\text{kg ww}$)	
2. <u>Marine fish muscle</u>		
Gulf of Finland	10-35	WRc database (1998)
Bristol channel	5	
English channel	20-100	
Irish Sea coastal	30-180	
North Sea coastal UK	30-170	
North Sea (1978-1995) mean value	115	WRc database (1998)
90 percentile	220	Govaerts <i>et al.</i> (1999)
<i>Zoarces Viviparus</i> muscle		
Watten Meere	112 \pm 5	UBA (1998)
Ostsee	43 \pm 1.5	
3. <u>Marine Mollusc</u> (whole organism)		
British channel	70-100	WRc (1998)
Irish Sea coastal	30-100	
North Sea costal UK	30-100	
<i>Mitilus edulis</i>		
Watten Meere	32.1 \pm 1.1	UBA (1998)
Ostsee	42.7 \pm 1.5	
4. <u>Marine Mammals</u> (liver)	(mg/kg ww)	
North Sea (1992) estuaries	6-49	WRc (1998)
coastal	3-15	
English channel	0.6-47	
Irish Sea	2.5-74	
Liverpool Bay	102	
5. <u>Seabirds</u>	(mg/kg)	
Feathers of sea-eagles (Mecklenburg-Vorpommern)		Nieke (1998)
1900	8	
1990	20	
1995	11	
Eggs of <i>Lerus argentatus</i> (Elbe estuary, 1995)		UBA (1998)
Hg total	0.36	
Me-Hg	0.33	

SUMMARY TABLE OF ECOTOXICITY DATA ON INORGANIC MERCURY (HgCl₂)
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1. FISH AND AMPHIBIANS

Species	Duration d (days) h (hours)	Type of study	Criterion (LC50/EC50 NOEC)	Concentration (µg Hg/l)	Validity	Comments and remarks	Reference
LC50/EC50 STUDIES							
1. Freshwater							
Cyprinus carpio	96 h	A; SS	LC50	160	2	juvenile Hg species not specified	Alam & Maughan, 1992
Etheostoma spectabile	8 d	N; SS (1/d)	EC50	18.5	4	hatchability reproduction abnormality in development cleavage stage embryo Hg species not specified	Sharp, 1992
Oncorhynchus mykiss	96 h		LC50	33	4	2-month old - Hg(NO ₃) ₂	Hale, 1977.
Oncorhynchus mykiss	96 h	N; S	LC50	193	2	juvenile	Buhl & Hamilton, 1991
Oncorhynchus mykiss	96 h	N; S	LC50	217	2	alevin	Buhl & Hamilton, 1991
Oncorhynchus kisutch	96 h	N; S	LC50	238	2	juvenile	Buhl & Hamilton, 1991
Oncorhynchus kisutch	96 h	N; S	LC50	282	2	alevin	Buhl & Hamilton, 1991
Pimephales promelas	4 d 7 d	A; F-T	LC50 LC50	168 74	1	3 month old	Snarski & Olson, 1982
Poecilia reticulata	96 h	N; S	LC50	26	2	15 mm length; 184 mg weight	Khangerot & Ray, 1987b
Summary Table (repeated header)							
Species	Duration d (days) h (hours)	Type of study	Criterion (LC50/EC50 NOEC)	Concentration (µg Hg/l)	Validity	Comments and remarks	Reference

APPENDIX 4a

SUMMARY TABLE OF ECOTOXICITY DATA ON INORGANIC MERCURY (HgCl₂)

Species	Duration d (days) h (hours)	Type of study	Criterion (LC50/EC50 NOEC)	Concentration (µg Hg/l)	Validity	Comments and remarks	Reference
Thymallus arcticus	96 h	N; S	LC50	124	2	alevin	Buhl & Hamilton, 1991
Thymallus arcticus	96 h	N; S	LC50	218	2	juvenile	Buhl & Hamilton, 1991
<i>Amphibians</i>							
Microhyla arnata	96 h	N; S;	LC50	1120	2	1 week old tadpoles Hg species not specified	Jayaprakash Rao & Madhyastha, 1987
Microhyla arnata	96 h	N; S;	LC50	1430	2	4 week old tadpoles Hg species not specified	Jayaprakash Rao & Madhyastha, 1987
Rana hexadactyla	96 h	A; SS (1/d)	LC50	51	1	tadpoles	Khangarot <i>et al.</i> , 1985
2. Salt water							
Fundulus heteroclitus	96 h	A; SS (1/d)	LC50	67 68	1	embryos	Sharp & Neff, 1980

APPENDIX 4a**SUMMARY TABLE OF ECOTOXICITY DATA ON INORGANIC MERCURY (HgCl₂)**

Species	Duration d (days) h (hours)	Type of study	Criterion (LC50/EC50 NOEC)	Concentration (µg Hg/l)	Validity	Comments and remarks	Reference
LOEC/NOEC STUDIES							
1. FRESHWATER							
Brachydanio rerio	14 d	N; SS (1/d)	NOEC	1	2	mortality	Dave & Xiu, 1991
Pimephales promelas	41 w	A, F-T	NOEC	0.5	2	Growth and reproduction	Snarski & Olson, 1982
Pimephales promelas	30 d	A; F-T	NOEC	≤ 0.5	3	growth of progeny (F1); lack of concentration response relationship	Snarski & Olson, 1982
Pimephales promelas	60 d	A; F-T	NOEC LOEC	1.02 2.01	2	growth; 4-6 days old F ₀ ; fed on "artemia"	Snarski & Olson, 1982
Pimephales promelas	32 d	A; F-T	NOEC	0.63	1	growth and mortality; 4-6 day old; 97% of the applied Hg was measured as total, 90% of the mercury was inorganic (Hg(NO ₃) ₂)	Spehar & Fiandt, 1986
2. Salt water							
Fundulus heteroclitus	32 d	A; SS (1/d)	NOEC EC50	10 37	1	hatching success	Sharp & Neff, 1980

SUMMARY TABLE OF ECOTOXICITY DATA ON INORGANIC MERCURY (HgCl₂)
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2 CRUSTACEANS

Species	Duration d (days) h (hours)	Type of study	Criterion (LC50/EC50 NOEC)	Concentration (µg Hg/l)	Validity	Comments and remarks	Reference
LC50/EC50 STUDIES							
1. Freshwater							
Asellus aquaticus	96 h	N; S	LC50	199	2		Martin & Holdich, 1986
Ceriodaphnia reticulata	48 h	N; S;	EC50	2.9	2	<24 h old; immobility	Elnabarawy & Welter, 1986
Crangonyx pseudogracilis	96 h	N; S	LC50	1	2		Martin & Holdich, 1986
Daphnia magna	48 h 24 h	N; S	EC50 EC50	5.2 8.1	2	immobility	Khengarot & Ray, 1987b
Daphnia magna	48 h	N; S;	EC50	9.6	2	<24 h old; immobility	Elnabarawy & Welter, 1986
Daphnia magna	24 h	N; S;	EC50 NOEC	15 5	2	24 h old; immobility	Bringmann & Kühn, 1981
Daphnia pulex	48 h	N; S;	EC50	3.8	2	<24 h old; immobility	Elnabarawy & Welter, 1986
Paratelphusa hydrodromous	96 h	SS (1/d);	LC50	350	2	males	Anathalakshmikumari <i>et al.</i> , 1990
Paratelphusa hydrodromous	96 h	N; SS (1/d);	LC50	380	2	females	Anathalakshmikumari <i>et al.</i> , 1990

SUMMARY TABLE OF ECOTOXICITY DATA ON INORGANIC MERCURY (HgCl₂)
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Species	Duration d (days) h (hours)	Type of study	Criterion (LC50/EC50 NOEC)	Concentration (µg Hg/l)	Validity	Comments and remarks	Reference
LC50/EC50 STUDIES							
2. Salt water							
Acartia tonsa	96 h	N; S;	LC50	10	2	test-generation derived from parental field population; mercury species not specified	Sosnowski & Gentile, 1978
Cancer anthonyi	7 d	N; S	EC45	10	3	Hatching of embryos	MacDonald <i>et al.</i> , 1988
Penaeus indicus	96 h	A; F-T;	LC50	15.3	1		McClurgh, 1984
Penaeus merguensis	96 h	A; SS (2/d);	LC50	30	1	juvenile	Denton & Burdon-Jones, 1982
Penaeus merguensis	96 h	A; SS (2/d);	LC50	130	1	juvenile	Denton & Burdon-Jones, 1982
Penaeus merguensis	96 h	A; SS (2/d);	LC50	290	1	juvenile	Denton & Burdon-Jones, 1982
Scylla serrata	96 h	N; SS (1/d)	LC50	680	1	40-50 mm carapac length	Krishnaja <i>et al.</i> , 1987

APPENDIX 4a**SUMMARY TABLE OF ECOTOXICITY DATA ON INORGANIC MERCURY (HgCl₂)**

Species	Duration d (days) h (hours)	Type of study	Criterion (LC50/EC50 NOEC)	Concentration (µg Hg/l)	Validity	Comments and remarks	Reference
LOEC/NOEC STUDIES							
1. Freshwater							
Ceriodaphnia dubia	7 d	N; SS	NOEC	8.5	1	reproduction and mortality; 1 day old; afterwards 97% of the applied Hg was measured as total, 90% of the mercury was inorganic (Hg(NO ₃) ₂)	Spehar & Fiandt, 1986
Cyclops sp.	14 d	A; S	LOEC	18 32	1	reproduction; nauplii; natural composition; 80% as total Hg recovered after 14 days incubation	Borgmann, 1980
Daphnia magna	21 d	A; SS (1/wk)	EC16 EC50 LC50	3.4 6.7 13	1	reproduction; 12 hours old (Hg(NO ₃) ₂)	Biesinger, 1972
Daphnia magna	21 d	A; SS (3/wk)	NOEC LOEC LC50	2.2 7.0 8.3	2	mortality, intrinsic rate of natural increase and carapace length respectively; <1 day old; Hg (Hg(NO ₃) ₂) measured as acid exchangeable conc. [additional study using various aged Daphnia calculated an EC ₁₀ of 0.072 µg/l based on reproduction yield and parametric modelling of Kooijman (1983)]	Enserink <i>et al.</i> , 1991
Daphnia magna	chron.		NOLC	1.1	4	Mercury species unknown	EPA, 1986
Daphnia similis	28 d	N; SS (1/d)	NOEC	10	1	mortality; 1 day old	Soundrapandian & Venkataraman, 1990
Hyalella azteca	6-10 wk	A; SS;	NOEC	0.62	2	reproduction change of number	Borgmann <i>et al.</i> , 1993

APPENDIX 4a**SUMMARY TABLE OF ECOTOXICITY DATA ON INORGANIC MERCURY (HgCl₂)**

Species	Duration d (days) h (hours)	Type of study	Criterion (LC50/EC50 NOEC)	Concentration (µg Hg/l)	Validity	Comments and remarks	Reference
			LOEC	2.42		young produced and weight; 0-1 wk; mercury species not specified	
2. Salt water							
<i>Artemia franciscana</i>	3 d	N; S	NOEC	2	2	hatching and emergence; eggs	Go <i>et al.</i> , 1990
<i>Cancer anthonyi</i>	7 d	N; S	NOEC LOEC	0.5 1.0	3	mortality and hatching of embryos	Macdonald <i>et al.</i> , 1988
<i>Callinectes sapidus</i>	10-35 d	A; SS (1/d)	NOEC	4.9	1	mortality; larvae; initial conc.; 30% loss of Hg occurred in the lowest test conc. after 24h	McKenney & Costlow, 1982
<i>Mysidopsis bahia</i>	44 d	A; F-T	NOEC LOEC	0.8 1.6	1	reproduction and mortality; life cycle; Hg species not specified	Gentile <i>et al.</i> , 1982
<i>Mysidopsis bahia</i>	35 d	A; F-T	NOEC LOEC	0.8 1.6	1	reproduction and mortality; life cycle	Lussier <i>et al.</i> , 1985
<i>Penaeus indicus</i>	28 d	A; F-T	NOEC	6	1	growth; post larval	McClurgh, 1984

SUMMARY TABLE OF ECOTOXICITY DATA ON INORGANIC MERCURY (HgCl₂)
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3. OTHER INVERTEBRATES

Species	Duration d (days) h (hours)	Type of study	Criterion (LC50/EC50 NOEC)	Concentration (µg Hg/l)	Validity	Comments and remarks	Reference
LC50/EC50 STUDIES							
1. FRESHWATER							
<i>Insecta</i>							
Chironomus tentans	48 h	N; S	EC50	29	1	immobility	Khengarot & Ray, 1989
<i>Mollusca</i>							
Viviparus bengalensis	7 d	N; SS (0.5/d)	LC50	80	1	23-26 mm shell length; summer	Muley & Mane, 1988
Viviparus bengalensis	7 d	N; SS (0.5/d)	LC50	90	1	23-26 mm shell length; HgSO ₄ ; summer	Muley & Mane, 1988
Viviparus bengalensis	7 d	N; SS (0.5/d)	LC50	140	1	23-26 mm shell length; HgSO ₄ ; winter	Muley & Mane, 1988
Viviparus bengalensis	7 d	N; SS (0.5/d)	LC50	150	1	23-26 mm shell length; winter	Muley & Mane, 1988
<i>Nematoda</i>							
Caenorhabditis elegans	96 h	N; S	LC50	440	2	3-4 days old	Williams & Dusenberry, 1990

APPENDIX 4a**SUMMARY TABLE OF ECOTOXICITY DATA ON INORGANIC MERCURY (HgCl₂)**

Species	Duration d (days) h (hours)	Type of study	Criterion (EC50/LC50 NOEC)	Concentration (µg Hg/l)	Validity	Comments and remarks	Reference
LC50/EC50 STUDIES							
2. Salt water							
<i>Polychaeta</i>							
<i>Capitella capitata</i>	96 h	N; S; C	LC50	14	2	trochophore larvae	Reish & Carr, 1978
<i>Ctenodrilus serratus</i>	96 h	N; S; C	LC50	90	2	young worms	Reish & Carr, 1978
<i>Neanthes arenaceodentata</i>	96 h	N; S; C	LC50	20	2	mature weight 60-100 mg	Reish & Carr, 1978
<i>Ophryotrocha diadema</i>	96 h	N; S; C	LC50	90	2	young worms	Reish & Carr, 1978
<i>Mollusca</i>							
<i>Crassostrea gigas</i>	48 h	N; S	EC50	6.7	1	embryos; abnormal transformation	Martin <i>et al.</i> , 1981
<i>Crassostrea gigas</i>	96 h	N; S	LC50	8.2	2	zoaea	Martin <i>et al.</i> , 1981
<i>Crassostrea virginica</i>	46 h	N; S	LC50	5.6	1	embryos	Calabrese <i>et al.</i> , 1973
<i>Crassostrea virginica</i>	12 d	N; SS (1/d)	LC50	12	1	larvae	Calabrese <i>et al.</i> , 1973
<i>Mercenaria mercenaria</i>	8-10 d	N; SS (1/d)	LC50	14.7	1	larvae	Calabrese <i>et al.</i> , 1973
<i>Mytilus edulis</i>	48 h	A; S	EC50	5.8	1	embryos; abnormal transformation	Martin <i>et al.</i> , 1981
<i>Perna perna</i>	1 h	N; S	EC50	25	3		Watling & Watling, 1982
<i>Perna viridis</i>	96 h	N; SS (1/d)	LC50	125	1	size group 15-20 mm	Krishnaja <i>et al.</i> , 1987
<i>Perna viridis</i>	96 h	N; SS (1/d)	LC50	155	1	size group 30-40 mm	Krishnaja <i>et al.</i> , 1987

APPENDIX 4a**SUMMARY TABLE OF ECOTOXICITY DATA ON INORGANIC MERCURY (HgCl₂)**

Species	Duration d (days) h (hours)	Type of study	Criterion (LC50/EC50 NOEC)	Concentration (µg Hg/l)	Validity	Comments and remarks	Reference
NOEC/LOEC STUDIES							
1. FRESHWATER							
<i>Protozoa</i>							
Tetrahymena pyriformis	4 h	N; S	NOEC	375	2	mortality; stationary phase; LOEC=1130 µg/l (23% mortality); NOEC = LOEC/3	Calabrese <i>et al.</i> , 1973
Tetrahymena pyriformis	4 h	N; S	NOEC	2250	2	mortality; stationary phase	Calabrese <i>et al.</i> , 1973
Tetrahymena pyriformis	2-6 h	N; S	NOEC	775	2	growth; 24 h log phase	Thrasher & Adams, 1972
Uronema parduczi	20 h	N; S	NOEC	34	2	growth; 2 days old; NOEC is based on toxicity threshold (TT): NOEC=TT/2	Bringmann & Kühn, 1981
Chilomonas paramecium	48 h	N; S	TT	16	2	growth; 3-4 days old; toxicity threshold (TT)	Bringmann & Kühn, 1981
Entosiphon sulcatum	72 h	N; S	TT	18	2	growth; 3-4 days old; toxicity threshold (TT)	Bringmann & Kühn, 1981
Poteroiochromonas malhamensis	3 d	N; S	NOEC	500	2	growth	Röderer, 1983
<i>Mollusca</i>							
Viviparis bengalensis	7 d	N; SS (1/d)	EC10 LC50	40 80	2	mortality; shell length 23-26 mm; summer	Muley & Mane, 1988
Viviparis bengalensis	7 d	N; SS (1/d)	EC10 LC50	110 150	2	mortality; shell length 23-26 mm; winter	Muley & Mane, 1988
Viviparis bengalensis	7 d	N, SS (1/d)	NOEC	30	2	mortality; shell length 23-26	Muley & Mane, 1988

APPENDIX 4a**SUMMARY TABLE OF ECOTOXICITY DATA ON INORGANIC MERCURY (HgCl₂)**

Species	Duration d (days) h (hours)	Type of study	Criterion (LC50/EC50 NOEC)	Concentration (µg Hg/l)	Validity	Comments and remarks	Reference
			LC50	90		mm; summer; HgSO ₄	
Viviparis bengalensis	7 d	N, SS (1/d)	NOEC LC50	100 140	2	mortality; shell length 23-26 mm; winter; HgSO ₄	Muley & Mane, 1988
2. Salt water							
<i>Protozoa</i>							
Cristigera sp.	4-9 h	N; S	NOEC	2.5	2	reproduction; log phase	Gray & Ventilla, 1973
<i>Hydrozoa</i>							
Clavopsella michaeli	8 d	N; SS (1/d)	NOEC		3	growth rate and reproduction Hg(NO ₃) ₂	Piraino, 1991
<i>Worms</i>							
Ctenodrilus serratus	21 d	N; S	NOEC		3	reproduction; larvae	Reish, 1978b
Ophryotrocha diadema	28 d	N; S	NOEC		3	reproduction; larvae	Reish, 1978b
<i>Mollusca</i>							
Crassostrea virginica	46 h	N; S	NOEC	1	1	hatching; embryos	Calabrese <i>et al.</i> , 1973
Crassostrea virginica	12 d	SS (1/d)	LC5 LC50	3.3 12.0	1	estimated growth inhibition 13% at LC5; 2nd instar larvae	Calabrese <i>et al.</i> , 1977
Crepidula fornicata	112 d	A; SS (1/d)	NOEC LOEC	0.25 0.42	1	reproduction; adult	Thain, 1984
Hyanassa obsoleta	2.5 h	S	NOEC	2	2	embryonal/development	Conrad, 1988
Mercenaria mercenaria	8-10 d	SS (1/d)	LC5 LC50	4 14.7	1	mortality; 2nd instar larvae	Calabrese <i>et al.</i> , 1977

SUMMARY TABLE OF ECOTOXICITY DATA ON INORGANIC MERCURY (HgCl₂)
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4. ALGAE

Species	Duration d (days) h (hours)	Type of study	Criterion (LC50/EC50 NOEC)	Concentration (µg Hg/l)	Validity	Comments and remarks	Reference
LC50/EC50 STUDIES							
1. Freshwater							
<i>Selenastrum capricornutum</i>	96 h	N; S	EC50	9	2	Growth. Comparison with "chemostat" test, below.	Chen et al, 1997
<i>Selenastrum capricornutum</i>	24 h	N; F-T	EC50	27	2	Growth. "Chemostat" test	Chen et al, 1997
<i>Chlorella vulgaris</i>	33 d	N; S	EC50	1030	2	cell/division <i>chlor. a</i> , cell seize; log phase	Rosko & Rachlin, 1977
2. Salt water							
<i>Antithamnion plumula</i>	24 h ?	N; S	LC50	5000	4	Exposure time uncertain	Boney & Corner, 1959
<i>Ceramium flabelligerum</i>	24 h ?	N; S	LC50	3200	4	Exposure time uncertain	Boney & Corner, 1959
<i>Ceramium pedicellatum</i>	24 h ?	N; S	LC50	4200	4	Exposure time uncertain	Boney & Corner, 1959
<i>Ditylum brightwelli</i>	5 d	N; S	EC50	10	2	growth; cell counts	Canterford & Canterford, 1980
<i>Plumaria elegans</i>	24 h ?	N; S	LC50	6700	4	Exposure time uncertain	Boney & Corner, 1959
<i>Polysiphonia brodiaei</i>	24 h ?	N; S	LC50	3200	4	Exposure time uncertain	Boney, 1971
<i>Polysiphonia lanosa</i>	24 h ?	N; S	LC50	8000	4	Exposure time uncertain	Boney, 1971
<i>Polysiphonia fruticulosa</i>	24 h ?	N; S	LC50	1750	4	Exposure time uncertain	Boney & Corner, 1959
<i>Spermothamnion repens</i>	24 h ?	N; S	LC50	3000	4	Exposure time uncertain	Boney & Corner, 1959

APPENDIX 4a**SUMMARY TABLE OF ECOTOXICITY DATA ON INORGANIC MERCURY (HgCl₂)**

Species	Duration d (days) h (hours)	Type of study	Criterion (LC50/EC50 NOEC)	Concentration (µg Hg/l)	Validity	Comments and remarks	Reference
LOEC/NOEC STUDIES							
1. Freshwater							
Anabaena inaequalis	chron.		IC50	3	4	Hg species unknown	Stratton & Corke, 1979
Anacystis nidulans	14 d	N; S	NOEC	250	2	growth	Lee <i>et al.</i> , 1992
Chara vulgaris	14 d	A; S;	NOEC	20	1	growth; nominal concentration is presented, measured concentrations were 10-20% lower	Heumann, 1987
Chlorella vulgaris	33 d	N; SS(1/2wk);	NOEC	100	3	cell/division	Rosko & Rachlin, 1977
Cladophora glomerata	24 h		EC10	1	3	O ₂ -production	von Tümpling, 1972
Cladophora glomerata	3 d	N; S	NOEC	100	3	growth; Hg species not specified	Whitton, 1967
Microcystis aeruginosa	8 d	N; S;	TT	5	2	10 d population; growth; Toxicity Threshold (TT)	Bringmann & Kühn, 1978
Scenedesmus acutus	10 d	N; S;	NOEC	20	2	log phase; growth; MIDA has been applied to keep Hg ²⁺ dissolved. Probably part of the mercury has been dissolved	Huisman <i>et al.</i> , 1980
Scenedesmus quadricauda	8 d	N; S;	TT	70	2	10 days old; population growth; Toxicity Threshold (TT)	Bringmann & Kühn, 1978
2. Saltwater							

APPENDIX 4a**SUMMARY TABLE OF ECOTOXICITY DATA ON INORGANIC MERCURY (HgCl₂)**

Species	Duration d (days) h (hours)	Type of study	Criterion (LC50/EC50 NOEC)	Concentration (µg Hg/l)	Validity	Comments and remarks	Reference
<i>Carteria</i> sp.	96 h	A; S	LOEC	0.04	3	LOEC derived from graph of population size, calculated from cell counts not given. Uncertain if a control was tested.	Sick & Windom, 1974
<i>Dunaliella tertiolecta</i>	96 h	A; S	LOEC	0.04	3	LOEC derived from graph of population size, calculated from cell counts not given. Uncertain if a control was tested.	Sick & Windom, 1974
<i>Dunaliella tertiolecta</i>	18 d	N; S	NOEC	330	2	Growth	Portmann, 1972
<i>Nitzschia closterium</i>	96 h	A; S	NOEC LOEC	0.04 0.06	3	LOEC derived from graph of population size, calculated from cell counts not given. Uncertain if a control was tested.	Sick & Windom, 1974
<i>Ascophyllum nodosum</i>	10 d	N; F-T;	NOEC	9	2	growth	Strömngren, 1980
<i>Fucus serratus</i>	10 d	N; F-T;	NOEC	0.9	2	growth	Strömngren, 1980
<i>Fucus spiralis</i>	10 d	N; F-T;	NOEC	9	2	growth	Strömngren, 1980
<i>Fucus vesiculosus</i>	10 d	N; F-T;	NOEC	9	2	growth	Strömngren, 1980
<i>Pelvetia canaliculata</i>	10 d	N; F-T;	NOEC	5	2	growth	Strömngren, 1980
<i>Laminaria saccharina</i>	14 d	N; SS (2/wk)	NOEC LOEC NOEC LOEC	1 5 10 50	2	development of zoospores growth of sporophytes	Thompson & Burrows, 1984
<i>Skeletonema costatum</i>	144 h	N; S	NOEC	1	2	Growth	Rice et al, 1973

APPENDIX 4a

SUMMARY TABLE OF ECOTOXICITY DATA ON INORGANIC MERCURY (HgCl₂)

Species	Duration d (days) h (hours)	Type of study	Criterion (LC50/EC50 NOEC)	Concentration (µg Hg/l)	Validity	Comments and remarks	Reference
Skeletonema costatum	4 h	N; S	LOEC	1	2	Oxygen evolution; approx 13% inhibition; lowest concn. tested.	Zingmark & Miller, 1973
Amphidinium carterae	24 h	N; S	NOEC	1	2	Oxygen evolution	Zingmark & Miller, 1973
Skeletonema costatum	7 d	N; S	LOEC	5	2	Oxygen evolution; approx 40% inhibition; lowest concn. tested.	Berland et al, 1977
Isochrysis galbana	13 d	N; S	LOEC	0.77	2	Growth, approx 15% inhibition; lowest concn. tested.	Davies, 1974

SUMMARY TABLE OF ECOTOXICITY DATA ON INORGANIC MERCURY (HgCl₂)
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Abbreviations

A	concentrations were measured
N	Nominal concentrations, concentrations not measured
S	Static test system
SS	Semi Static test system
(1/wk)	renewal of test solution once a week
(1/d)	renewal of test solution once a day
F-T	Flow Through test system

APPENDIX4b**SUMMARY TABLE OF ECOTOXICITY DATA ON ORGANIC MERCURY****1 FISH**

Species	Dur.	Type of study	Crit.	Conc. (µg Hg/l)	Val.	Comments and remarks	Reference
LC50/EC50 STUDIES							
1. FRESHWATER							
Oncorhynchus kisutch	45 d	MetHgOH; A; SS (1/d)	LC50	54 65 71	1	embryos; filtered city water; temp 10°C;	Devlin & Mottet 1992
Salmo gairdneri	96 h	MetHgCl; N; SS	LC50	31	2		Matida <i>et al.</i> , 1971
Salmo gairdneri	96 h	MetHgCl	LC50	24	2	Fry	Wobeser, 1975
Salmo gairdneri	96h	MetHgCl	LC50	42	2	Fingerling	Wobeser, 1975
Trichogaster trichopterus	96 h	MetHgCl; N; S	LC50	89.5	2	weight 1.5-2.0 g;	Roales & Perlmutter, 1974
2. Saltwater							
Fundulus heteroclitus	96 h	MetHgCl; N	LC50	51	1	Salinity 20 ppt	Sharp & Neff, 1982
LOEC/NOEC STUDIES							
1. FRESHWATER							
Oncorhynchus kisutch	48 d	MetHgOH; A; SS (1/d)	NOEC LOEC	29 62	1	mortality; embryos; filtered city water; temp 10°C	Devlin & Mottet ,1992
Pimephales promelas	60 d	MetHg..	NOEC	0.07 0.13	4	(Secondary source) mortality; adult – lifecycle reproduction	Mount, 1974
Poecilia reticulata	90 d 30 d 76 d	MetHgCl; A; SS (1/3d)	NOEC NOEC LC100	1 3.2 10	1	mortality, histopathological effects (occurrence of granulomes); 28 days old; DSW; pH 8.2; Hrdn 208 mg/l as CaCO ₃ ;	Wester & Canton, 1992
Salvelinus fontinalis	144 wk	MetHgCl; A; F-T (90% 4 h)	NOEC	0.29	1	growth, mortality, reproduction and teratogenic effects; 3 generations; lakew.; pH 7.5; Hrdn 45 mg/l as CaCO ₃	McKim <i>et al.</i> , 1976

APPENDIX4b**SUMMARY TABLE OF ECOTOXICITY DATA ON ORGANIC MERCURY**

Species	Dur.	Type of study	Crit.	Conc. (µg Hg/l)	Val.	Comments and remarks	Reference
Salvelinus fontinalis	248 d	MetHgCl; A; F-T	NOEC LOEC	0.08 0.93	1	growth, yearlings exposed for 7 months, subsequently the F ₁ embryos and larvae were exposed; The NOEC is based on the effects on growth of the F ₁ larvae; tap w.; pH 7.74; Hrdn 45 mg/l as CaCO ₃	Christensen, 1975
2. Saltwater							
no data							

2 CRUSTACEANS

Species	Dur.	Type of study	Crit.	Conc. (µg Hg/l)	Val.	Comments and remarks	Reference
LC50/EC50 STUDIES							
1. FRESHWATER							
Daphnia pulex	48 h 96 h 8 d	MetHgCl; N; S	LC50	5.7 1.8 >1.0	2	neonates; test water was filtered with whatman paper; 8 d-LC25=0.5 µg/l; temp 20°C	Tian-yi & McNaught, 1992
2. Saltwater							
Artemia salina	48 h	MetHg; N; S	LC50	1400	2		Corner & Sparrow, 1977
Gammarus duebeni	96 h	MetHg; N; S.	LC50	150	2		Lockwood & Inman, 1975
LOEC/NOEC STUDIES							
1. FRESHWATER							
Daphnia pulex	30 d	MetHgCl; SS (1/3d); N	NOEC EC50 EC50	0.1 0.42 0.23	2	reproduction and growth; 3 generations; filtered lake w.; temp 20°C Nett reproduction, mean of F ₀ , F ₁ and F ₂ Nett reproduction, F ₂	Tian-yi & McNaught, 1992
2. Saltwater							
no data							

APPENDIX4b

SUMMARY TABLE OF ECOTOXICITY DATA ON ORGANIC MERCURY

3 OTHER INVERTEBRATES

Species	Dur.	Type of study	Crit.	Conc. (µg Hg/l)	Val.	Comments and remarks	Reference
LC50/EC50 STUDIES							
1. FRESHWATER							
<i>Protozoans</i>							
Tetrahymena pyriformis	2-6 h	MetHgCl; N; S	LC50	168	2	log phase; medium; art. medium; pH 7.2;	Thrasher & Adams, 1972
2. Saltwater							
<i>Molluscs</i>							
Perna perna	1 h	MetHgCl; N; S	EC50	50	2	filtering rate; seize 60-80 mm;	Watling & Watling, 1982
LOEC/NOEC STUDIES							
1. FRESHWATER							
<i>Protozoa</i>							
Tetrahymena pyriformis	2-6 h	MetHgCl; N; S	NOEC	14	2	growth; log phase; medium; pH 7.2;	Thrasher <i>et al.</i> , 1972
<i>flat-worms</i>							
Dugesia dorotocephala	14 d	MetHgCl; N; SS (1/3d)	NOEC	0.03 20 80 200	2	fissioning; 16 mm; temp 22°C; neurotoxic behavioural disorders teratogenic effects mortality	Best <i>et al.</i> , 1981
2. Saltwater							
<i>Mollusca</i>							
Mytilus edulis	32 d	MetHgOH; N; F-T	NOEC	0.3	1	growth; 3.6 cm; seaw.; amorphic TiO ₂ was applied as a carrier to increase the distribution; pH 8.0; temp 9°C; sal 26 ‰	Pelletier, 1988

APPENDIX4b

SUMMARY TABLE OF ECOTOXICITY DATA ON ORGANIC MERCURY

4 AQUATIC PLANTS, INCLUDING ALGAE

Species	Dur.	Type of study	Crit.	Conc. (µg Hg/l)	Val.	Comments and remarks	Reference
LOEC/NOEC STUDIES							
1. FRESHWATER							
Poteriochromonas malhamensis	3 d	MetHgCl; N; S	LOEC	2	2	Growth; approximately 50% inhibition	Röderer, 1983
Euglena gracilis	?	MetHgCl	LOEC	40	3	Enzyme inhibition, extracted chloroplasts. No time period stated.	Matson <i>et al.</i> , 1972
Ankistrodesmus braunii	?	MetHgCl	LOEC	1000	3	Reduction in lipids. No time period stated.	Matson <i>et al.</i> , 1972
Coelastrum microporum	?	MetHgCl	LOEC	3	3	Growth inhibition. No time period stated	Holderness <i>et al.</i> , 1975
2. Saltwater							
Laminaria saccharina	14 d	MetHgCl; N; SS (2/wk)	LOEC NOEC LOEC	0.5 1 5	2	Development of zoospores Growth of sporophytes; Filtered seawater; temp 8°C	Thompson & Burrows, 1984
Dunaliella tertiolecta	10 min	MetHgCl	LOEC	140	3	Photosynthesis	Overnell, 1975
Phaeodactylum tricornutum	10 min	MetHgCl	LOEC	80	3	Photosynthesis	Overnell, 1975

SUMMARY TABLE OF ECOTOXICITY DATA ON ORGANIC MERCURY

Abbreviations

A	concentrations were measured
N	Nominal concentrations, concentrations not measured
S	Static test system
SS	Semi Static test system
(1/wk)	renewal of test solution once a week
(1/d)	renewal of test solution once a day
F-T	Flow Through test system

APPENDIX 5

**Summary of ecotoxicity data selected for the PNEC derivation,
with the appropriate assessment factors
for inorganic and elemental mercury**

Available valid data	Assessment factor applied to the lowest LC50/EC50 or NOEC/LOEC	Comments
At least 1 short-term LC50 from each trophic level (fish, daphnia algae)	<p style="text-align: center;">1000</p> <div style="border: 1px solid black; padding: 5px; width: fit-content; margin: 10px auto;">PNEC = 0.001 µg/l</div>	<ul style="list-style-type: none"> - <i>Poecilia reticulata</i>, 96 h LC50=26 µg/l (Khangarot & Ray, 1987b) - <i>Crangonix pseudogracilis</i>, 96 LC50=1 µg/l (Martin & Holdich, 1986) - <i>Ditylum brightwelli</i>, 5d EC50=10 µg/l (Canteford & Canterford, 1980)
Long-term NOEC from at least 3 species representing three trophic levels (fish, daphnia, algae)	<p style="text-align: center;">10</p> <div style="border: 1px solid black; padding: 5px; width: fit-content; margin: 10px auto;">PNEC = 0.025 µg/l</div>	<ul style="list-style-type: none"> - <i>Pimephales promelas</i>, 41wk NOEC growth 0.5 µg/l (Snarski & Olson, 1982) - <i>Crepidula fornicata</i>, 112d NOEC (reproduction) = 0.25 µg/l (Thain, 1984) - <i>Isochrysis galbana</i>, 13d LOEC=0.77 µg/l; NOEC=LOEC/2=0.4 µg/l (Davies, 1974)

APPENDIX 5

**Summary of ecotoxicity data selected for the PNEC derivation,
with the appropriate assessment factors
for organic mercury**

Available valid data	Assessment factor applied to the lowest LC ₅₀ /EC ₅₀ or NOEC/LOEC	Comments
At least 1 short-term LC ₅₀ from two trophic level (fish, daphnia)	<p style="text-align: center;">1000</p> <div style="border: 1px solid black; padding: 5px; width: fit-content; margin: 10px auto;">PNEC = 0.0018 µg/l</div>	<ul style="list-style-type: none"> - <i>Fundulus heteroclitus</i>, 96h LC₅₀ 51 µg/l (Sharp & Neff, 1982) - <i>Oncorhynchus kisutch</i>, 96h LC₅₀ 54 µg/l (Devlin & Mottet, 1992) - <i>Daphnia pulex</i>, 96h LC₅₀ 1.8 µg/l (Tian-yi & McNaught, 1992)
Long-term NOEC from at least 3 species representing three trophic levels (fish, daphnia, algae)	<p style="text-align: center;">10</p> <div style="border: 1px solid black; padding: 5px; width: fit-content; margin: 10px auto;">PNEC = 0.003 µg/l</div>	<ul style="list-style-type: none"> - <i>Salvelinus fontinalis</i>, 248 d NOEC growth 0.08 µg/l, Christensen, 1975) - <i>Daphnia pulex</i>, 30 d NOEC reproduction 0.1 µg/l (Tian-yi & McNaught, 1992) - <i>Dugesia dorothecephala</i>, 14 d NOEC 0.03 µg/l (Best <i>et al.</i>, 1981) - <i>Laminaria saccharina</i> 14 d LOEC reproduction 0.5 µg/l (Thompson & Burrows, 1984)

APPENDIX 6

Toxicity data for Hg inorganic, based on Appendix4a						
Taxonomic Group	Type of water	Species	Validity	NOEC's (µg/l)	NOECs with geometric means per species (µg/l)	1 value per tax group (geom. mean)
Fish	fresh	B.rerio	2	1	1	
		P. promelas	2	0.5		
		P. promelas	2	1.02		
		P. promelas	1	0.63	0.68	
	salt	F. heteroclitus	1	10	10	1.90
Crustaceans	fresh	C. dubia	1*	8.5	8.5	
		D. magna	2	2.2	2.2	
		D. similis	1	10	10	
		H. azteca	2	0.62	0.62	
	salt	A. franciscana	2*	2	2	
		C. sapidus	1	4.9	4.9	
		M. bahia	1	0.8		
		M. bahia	1	0.8	0.80	
		P. indicus	1	6	6	2.93
Protozoa	fresh	T. pyriformis	2*	375		
		T. pyriformis	2*	2250		
		T. pyriformis	2*	775	87.13	
		U. parduczi	2*	34	34	
		C. paramecium	2*	16	16	
		E. sulcatum	2	18	18	
Protozoa	salt	Cristigera sp.	2	2.5	2.5	46.89
Mollusca	fresh	V. bengalensis	2	30		
		V. bengalensis	2	100	54.60	
Mollusca	salt	C. virginica	1*	1	1	
		C. fornicata	1	0.25	0.25	
		I. obsoleta	2	2	2	2.29
Algae-blue	fresh	A. nidulans	2	250	250	
		M. aeruginosa	2	5	5	35.36
Chara		C. vulgaris	1	20	20	20.00
green		S. acutus	2	20	20	
green		S. quadricauda	2	70	70	
green	salt	D. tertiolecta	2	330	330	77.31
brown		A. nodosum	2*	9	9	
		F. serratus	2*	0.9	0.9	
		F. spiralis	2*	9	9	
		F. vesiculosus	2*	9	9	
		P. canaliculata	2*	5	5	
		L. saccharina	2*	1	1	3.85
diatoms		S. costatum	2	1	1	
		A. carterae	2	1	1	1.00
*NOEC but not truly chronic, used to obtain a broader distribution over taxonomic groups						
Results calculations:						

APPENDIX 6

Aldenberg 50%			0.47	
Toxicity data for Hg organic, based on Appendix 4b				
Taxonomic Groups	Validity	NOECs (µg/l)	NOECs with geometric means per species (µg/l)	NOECs with geometric means per taxonomic group (µg/l)
Fish	1	29	29	
	1	1	1	
	1	0.29		
	1	0.08	0.15	1.64
Crustaceans	2	0.1	0.1	0.1
Protozoa*	2	14	14	14
Dugesia	2	0.03	0.03	0.03
Molluscs	1	0.3	0.3	0.3
Algae	1	1	1	1.0
*not real chronic data but data used to have more taxonomic groups (e.g. protozoa also used by RIVM)				
Result calculation				
PNEC - Aldenberg 50%				0.01

NB: to update with new Appendix 4b

APPENDIX 7a

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APPENDIX7b

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APPENDIX 8

R S Thompson, N J Williams & G J Eales (1998)
**MERCURIC CHLORIDE: Chronic toxicity in sediment to larvae of the freshwater
midge, *Chironomus riparius*.**
Brixham Environmental Laboratory Report BL6496/B

SUMMARY

At the request of Euro Chlor, Brussels, the chronic toxicity of mercuric chloride in sediment to the freshwater midge, *Chironomus riparius*, was investigated.

Larvae of *Chironomus riparius* (<24 hours post-hatch) were exposed for 28 days to control sediment and sediment spiked with mercuric chloride at nominal concentrations of 243, 432, 756, 1350 and 2430 mg HgCl₂ kg⁻¹ dry weight (equivalent to mercury ion concentrations of 180, 320, 560, 1000 and 1800 mg Hg kg⁻¹ dry weight). All treatments were tested in triplicate.

A natural sediment (5.8% organic carbon) was employed and the test was carried out at 20 ± 1°C with partial renewal of the overlying water after 14 days. The number of animals developing successfully and emerging as adult insects was recorded.

The sediment was analysed for total mercury at the start, middle and end of the study. The mean measured concentrations ranged from 81 to 94% of the nominal concentrations. There was no indication of significant loss of mercury from the sediments over the duration of the test.

Analysis of the overlying water for total mercury at the start of the test showed a maximum of 6.2 µg l⁻¹ at the highest nominal concentration, but without a clear relationship to sediment concentration. After 14 and 28 days, all concentrations in the overlying water were below 1 µg l⁻¹.

In the control, 98% of the larvae had emerged as adults after 28 days. At the highest nominal concentration tested (1800 mg Hg kg⁻¹), only 5% emergence was obtained, and this was considered a significant effect without the need for statistical analysis.

At all lower nominal concentrations, there was no effect on the time to first emergence, time to 50% emergence or the percentage emergence after 28 days. Male:female sex ratios did not differ significantly from 50:50.

Therefore, based on concentrations of mercury ion:

No observed effect concentration (NOEC): 1000 mg Hg kg⁻¹ dry weight (Nominal)
930 mg Hg kg⁻¹ dry weight (Measured)

Based on concentrations of mercuric chloride:

No observed effect concentration (NOEC): 1350 mg HgCl₂ kg⁻¹ dry weight (Nominal)
1260 mg HgCl₂ kg⁻¹ dry weight (Measured)

APPENDIX 9**EXPOSURE DATA – REGIONAL SCENARIO**

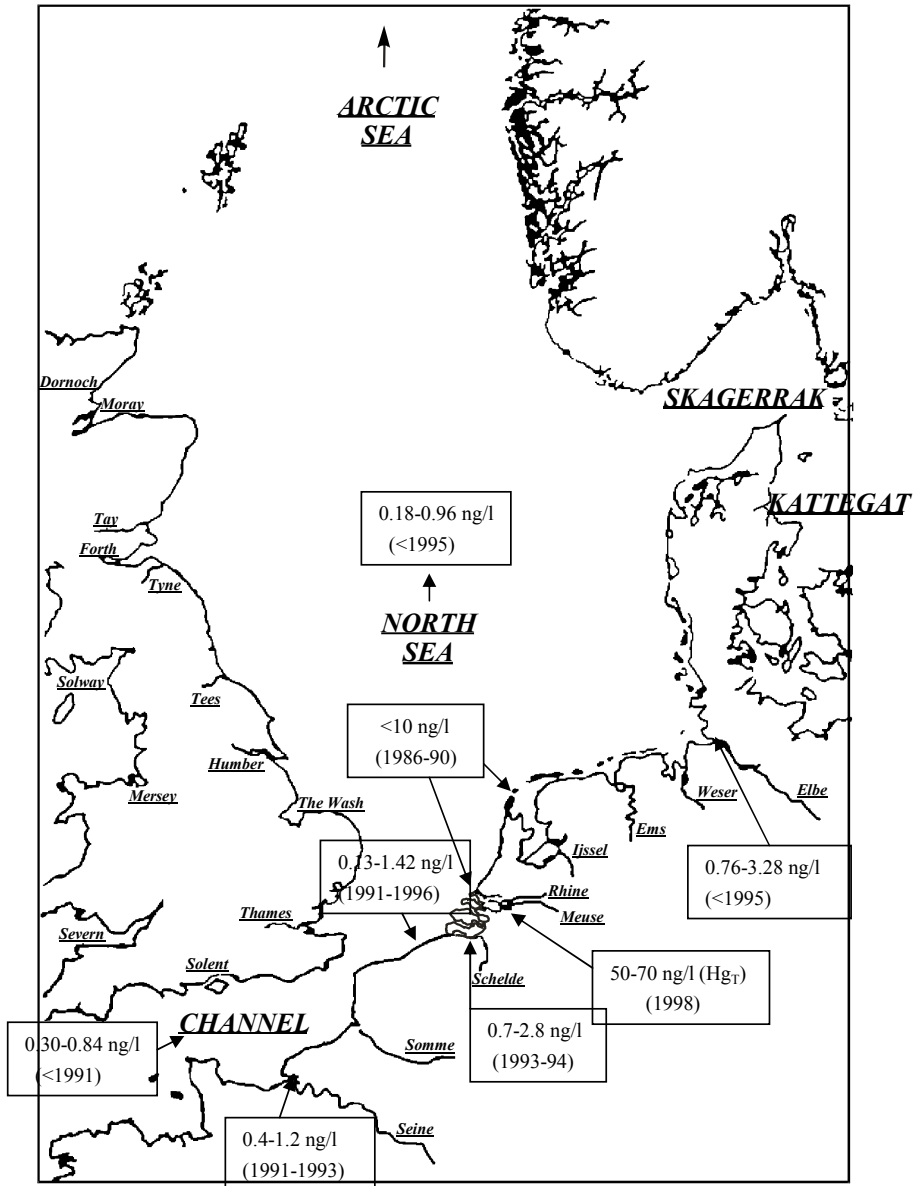
Inorganic Mercury			
	Year	Concentration	References
a. Water			
1. River water in Europe			
Total Mercury (Hg _T)			COMMPS database (1998)
mean value in Europe	1994-96	120 ng/l	Govaerts <i>et al.</i> (1999)
95% in UK		170 ng/l	
95% in D		250 ng/l	
Dissolved Mercury (Hg _D)			
mean value in Europe		19 ng/l	
2. Estuaries			
Rhine (Hg _T)	1993-94	50-70 ng/l	WRc database (1998)
Scheldt (Hg _D)	1993-94	0.7-2.8 ng/l	Leermakers (1998)
Elbe (Hg _D)	<1995	0.76-3.28 ng/l	Coquery & Cossa, 1995
Seine (Hg _D)	1990-91	0.5-11.9 ng/l	Cossa <i>et al.</i> , 1996
	1990-93	0.4-1.2 ng/l	Coquery <i>et al.</i> , 1997
Loire (Hg _D)	1990-91	0.4-2.0 ng/l	Cossa <i>et al.</i> , 1996
	1990-93	0.2-0.6 ng/l	Coquery <i>et al.</i> , 1997
3. North Sea – Wadden Sea			
Background (Hg _D)	1985	0.5-3 ng/l	Slooff <i>et al.</i> (1995)
Coastal areas (Hg _D)	1986-90	< 10 ng/l	Slooff <i>et al.</i> (1995)
(Hg _T)	1986-90	170 ng/l	Slooff <i>et al.</i> (1995)
North Sea (Hg _D)	<1995	0.18-0.96 ng/l	Coquery & Cossa, 1995
Belgian Coast (Hg _D)	1991-96	0.13-1.42 ng/l	Leermakers, 1998
English Channel (Hg _D)	<1991	0.30-0.84 ng/l	Cossa & Fileman, 1991
b. Sediment			
1. River water in Europe			
mean value	1994-96	2.9 mg/kg dw (0.58 mg/kg ww)	COMMPS database (1998) Govaerts <i>et al.</i> (1999)
95 percentile		8 mg/kg dw (1.6 mg/kg ww)	COMMPS database (1998) Govaerts <i>et al.</i> (1999)
2. Estuaries and coastal areas			
Irish sea-coast	1995	0.117 mg/kg dw (0.023 mg/kg ww)	WRc database (1998)
Loire estuary			
Seine estuary	1991-93	0.02 mg/kg ww	Coquery <i>et al.</i> (1997)
Harbours sediment (NL)	1991-93	0.2 mg/kg ww	Coquery <i>et al.</i> (1997)
	1986-90	2-3 mg/kg dw (0.4-0.6 mg/kg ww)	Slooff <i>et al.</i> (1995)
Scheldt estuary	1990	0.03-1.8 mg/kg ww	Leermakers (1998)
3. Wadden Sea			
background level	1985	0.1-0.2 mg/kg dw (0.02-0.04 mg/kg ww)	Slooff <i>et al.</i> (1995)
typical values	1987-88	0.3-0.6 mg/kg dw (0.06-0.12 mg/kg ww)	Slooff <i>et al.</i> (1995)

APPENDIX 9

Organic Mercury (in biota all mercury is supposed to be organic)		
	Ratio MeHg/Hg	References
1. <u>Sea water & sediment</u>		
Sea water and sediment	0.01-10%	Sloof <i>et al.</i> (1985)
Sea water and sediment	0.1-2%	Nieke (1998)
Sea water and sediment	0.2-2.9%	Coquery <i>et al.</i> (1997)
Sediment	< 3%	Wilken (1999)
Elbe sediment	0.4-0.6%	UBA (1998)
	Concentration (µg/kg ww)	
2. <u>Marine fish muscle</u>		
Gulf of Finland	10-35	WRc database (1998)
Bristol channel	5	
English channel	20-100	
Irish Sea coastal	30-180	
North Sea coastal UK	30-170	
North Sea (1978-1995)		
mean value	115	WRc database (1998)
90 percentile	220	Govaerts <i>et al.</i> (1999)
<i>Zoarces Viviparus</i> muscle		
Watten Meere	112 ± 5	UBA (1998)
Ostsee	43 ± 1.5	
3. <u>Marine Mollusc (whole organism)</u>		
Bristol channel	70-100	WRc (1998)
Irish Sea coastal	30-100	
North Sea coastal UK	30-100	
<i>Mytilus edulis</i>		
Watten Meere	32.1 ± 1.1	UBA (1998)
Ostsee	42.7 ± 1.5	
4. <u>Marine Mammals (liver)</u>	(mg/kg ww)	
North Sea (1992)		
estuaries	6-49	WRc (1998)
coastal	3-15	
English channel	0.6-47	
Irish Sea	2.5-74	
Liverpool Bay	102	
5. <u>Seabirds</u>	(mg/kg)	
Feathers of sea-eagles (Mecklenburg-Vorpommern)		Nieke (1998)
1900	8	
1990	20	
1995	11	
Eggs of <i>Larus argentatus</i> (Elbe estuary, 1995)		UBA (1998)
Hg total	0.36	
Me-Hg	0.33	

APPENDIX 10

North Sea Monitoring Data on Mercury (as dissolved mercury)



Hg_T = total mercury level

APPENDIX 11

PEC CALCULATION FOR THE AQUATIC COMPARTMENT

The TGD uses the following equation to calculate $PEC_{aquatic}$ from PEC_{total} (TGD equation 30, p. 302):

$$C_{localwater} = C_{localeff} / (1 + K_{psusp} * SUSP_{water} * 10^{-6}) * DILUTION$$

where:

$$K_{psusp} = \text{solids-water partition coefficient of suspended matter: } 170,000 \text{ l/kg (Slooff et al., 1995)}$$

$$SUSP_{water} = \text{concentration of suspended matter in the river: } 15 \text{ mg/l (TGD, 1996)}$$

$$C_{localeff} = \text{concentration of the chemical in the effluent (mg/l)}$$

$$C_{localwater} = \text{local concentration in surface water during emission episode (mg/l)}$$

The calculation of the concentration in suspended matter, which can be assumed similar to the concentration in sediment since the principal source for a chemical adsorbed onto sediment is via sedimentation of suspended matter, is given below.

It is calculated according to the equations given in the TGD (p.304):

$$PEC_{localsed} = \frac{K_{susp.water} * PEC_{localwater} * 1000}{RHO_{Tsusp}}$$

where:

$$RHO_{susp} = 1150 \text{ kg/m}^3 \text{ (bulk density of wet suspended matter)}$$

$$K_{susp.water} = 4.25 * 10^4 \text{ m}^3/\text{m}^3 \text{ (see below – suspended matter-water partitioning coefficient)}$$

$$PEC_{localsed} = \text{predicted environmental concentration in sediment}$$

$$PEC_{localwater} = C_{localwater} + PEC_{regionalwater}$$

$K_{suspwater}$ is calculated as follows (TGD, page 276):

$$K_{susp-water} = F_{airsusp} * K_{air-water} + F_{watersusp} + F_{solidsusp} * K_{psusp} / 1000 * RHO_{solid}$$

$$K_{psusp} = 170,000 \text{ l/kg}$$

$$K_{susp-water} = 0 + 0.9 + 0.1 * 170,000 / 1000 * 2500 = 42500.9 \text{ m}^3/\text{m}^3$$

where:

$$F_{airsusp} = 0 \text{ (fraction of air in suspended matter)}$$

$$F_{watersusp} = 0.9 \text{ (fraction of water in suspended matter)}$$

$$F_{solidsusp} = 0.1 \text{ (fraction of solids in suspended matter)}$$

$$RHO_{solid} = 2500 \text{ kg/m}^3 \text{ (density of the solid phase)}$$