Science Dossier

Aquatic Environmental Risk Assessment of Hexachlorobenzene

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it's a chlorine thing.

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Summary

This report evaluates the potential risks to arctic marine predators posed by current exposure levels to hexachlorobenzene. Only the potential effects on the aquatic environment, including secondary poisoning of aquatic predators, is considered. First, an assessment of the potential risks to arctic predators as a result of contamination remaining in the environment from historic uses of hexachlorobenzene is considered. This is followed by an assessment of the risks posed to the local aquatic environment and to remote arctic predators, by only the current emissions of hexachlorobenzene,

Although hexachlorobenzene is no longer produced in Europe small quantities are inadvertently generated during the manufacture of some chemicals. Hexachlorobenzene has a low water solubility (approximately 5 μg l^{-1}), a high octanol: water partition coefficient (log K_{OW} 5.73), and a low potential for biodegradation. Hexachlorobenzene is persistent in the environment, with half-lives on the order of years in all environmental compartments. Hexachlorobenzene partitions strongly to soil and sediment phases in the environment, and its affinity for soils and sediments considerably reduces its mobility and potential for transport.

A summary of available bioaccumulation data is provided in this report. Median values of 18,000 and 52,000 were derived for the BCF and BAF respectively, based on a review of valid lab and field studies. While hexachlorobenzene has the potential to be accumulated by organisms from their surrounding environment and their food, the biomagnification of hexachlorobenzene is highly variable between different trophic linkages with BMF values varying from less than 1 to greater than 100 in extreme cases. Higher BMF values are typically found for higher organisms, such as birds and mammals, which may be expected to have higher metabolic and food intake rates than cold blooded organisms, such as invertebrates and fish. Median BMF values for lower trophic levels are in the range 1 to 4 but can be much higher for higher trophic levels, although this is not always the case. It is clear that different BMF values need to be derived for different trophic linkages in order to perform a reliable assessment, due to the differences in the behaviour and physiology of different groups of species.

Predicted No Effect Concentrations have been derived for the aquatic environment (0.08 μg l^{-1}), the marine environment (0.04 μg l^{-1}), sediment ecosystems (>84 mg kg^{-1} dry weight), food of top predators (16.7 μg kg^{-1} wet weight in food), and predator liver concentrations (17 to 28 ng g^{-1} wet weight in liver). Due to the potential of hexachlorobenzene to bioaccumulate, the critical environmental endpoint, or receptor, is the top predator. Under some circumstances hexachlorobenzene can accumulate to potentially harmful levels in top trophic levels although the environmental concentrations are not sufficiently high to cause direct toxic effects in aquatic organisms. For this reason, monitoring of hexachlorobenzene levels in the environment is best targeted towards the relevant prey species of higher predators.

Using the approach recommended under REACH, a targeted assessment of the accumulation of hexachlorobenzene for several top predators within the marine arctic ecosystem, specifically the beluga, narwhal, polar bear and glaucous gull food chains, has been undertaken. This assessment suggests that reasonable estimates of the levels of hexachlorobenzene in top predators can be made, where adequate monitoring data exist for specific BMF values to be derived for each trophic linkage. It also appears that higher BMF values tend to be identified for higher trophic levels, such as mammals and birds, which may have higher metabolic rates and consequently higher food ingestion rates. The predicted accumulation of hexachlorobenzene in these top

predators, resulting from exposure to current levels of hexachlorobenzene, indicate that a significant proportion of the populations of these species could currently be at risk from hexachlorobenzene toxicity

Risk characterizations based on the current European emissions of hexachlorobenzene indicate that no risks to arctic marine predators are expected at a typical current emission level for Euro Chlor member companies. Following the current risk assessment methodology for secondary poisoning (based on predicted food concentrations for arctic predators), a margin of safety of greater than 100,000 has been estimated for every scenario considered, while a MOS of higher than 9000 has been estimated for every scenario considered when based on predicted body burdens of arctic predators.

Based on current local emissions of hexachlorobenzene, risks are identified for freshwater fish, marine fish and marine predators, with the highest risk characterisation ratio being for freshwater fish, where there is limited potential for dilution into the receiving environment. An environmental quality standard, derived for the levels of HCB in the prey of predators, is applied under the WFD and may be measured in fish and invertebrate tissues. When the dilution into the local receiving water is not sufficiently high, potential risks due to secondary poisoning are anticipated for a local emission of 0.1 kg to water per year.

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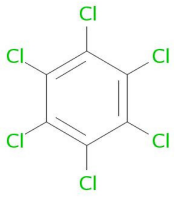
1 Identification of the substance

CAS number: 118-74-1
EC number: 204-273-9
IUPAC name: hexachlorobenzene
Molecular formula: C_6Cl_6
Molecular weight: 284.8
Structural formula:



SMILES string: ClC1=C(Cl)C(Cl)=C(Cl)C(Cl)=C1Cl

1.1 Physicochemical properties

Table 1 Physicochemical properties of hexachlorobenzene

Property	Value	Remarks
Physical state	White crystalline solid	
Melting point	231°C	
Boiling point	323-326°C	Sublimates
Density	1.5691	
Vapour pressure	2.3 mPa at 25°C	IUCLID (ECB 2000)
Water solubility	5 µg l^{-1} at 25°C	Barber et al. 2005
Log K_{OW}	5.73	Range 4.1 to 6.8
Henrys law constant	131 Pa m^{-3} mol^{-1}	Calculated
Log K_{OC}	4.72	Calculated

The physicochemical properties of hexachlorobenzene are reported in IUCLID (ECB 2000). The critical physicochemical properties for the environmental risk assessment are the vapour pressure, water solubility, and log K_{OW}. The solubility of hexachlorobenzene in distilled water is considered to be around 5 µg l^{-1} (IPCS 1997, Barber et al. 2005), although this may be influenced by other factors such as temperature and salt concentration of the water. There can also be difficulties in determining the true water solubility of highly insoluble substances due to the low limit of detection required of the analysis, and ensuring that there is no undissolved material present. Some studies have also shown that dissolved organic matter in natural waters can enhance the apparent solubility of hydrophobic organic compounds such as hexachlorobenzene by sorption to the dissolved organic matter (Freidig et al. 1998).

1.2 Regulatory information

Hexachlorobenzene is listed on Annex VI of Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures. It is classified as:

Carc. 1B (H400: May cause cancer)
STOT RE 1 (H372: Causes damage to organs through prolonged or repeated exposure)
Aquatic Acute 1 (H400: Very toxic to aquatic life)
Aquatic Chronic 1 (H410: Very toxic to aquatic life with long lasting effects)

In 2000 the European Parliament and the Council of the European Union have adopted a Directive (2000/60/EC) on the framework for community action in the field of water policy. Afterwards a Directive (2008/105/EC) on environmental quality standards (EQS) was published and hexachlorobenzene was identified as a priority hazardous substance. Furthermore this Directive reported an annual average environmental quality standard of 0.01 µg/l for surface water, while the maximum allowable concentration was 0.05 µg/l for surface water for hexachlorobenzene, although the annual average standard was later removed as it was not considered to afford an adequate level of protection. In addition, an environmental quality standard for biota of 10 µg/kg has been established for hexachlorobenzene which may be used by EU Member States. This value of 10 µg/kg is applicable for prey tissue (wet weight), in fish, and is the critical quality standard.

The Stockholm Convention on Persistent Organic Pollutants is a global treaty to protect human health and the environment from chemicals that remain intact in the environment for long periods, become widely distributed geographically, accumulate in the fatty tissue of humans and the wildlife, and have adverse effects on human health or to the environment. Hexachlorobenzene is listed on Annex A (elimination) which means that parties must take measures to eliminate the production and use of hexachlorobenzene. Furthermore it is listed on Annex C (unintentional production) which means that parties must take measures to reduce the unintentional releases with the goal of continuing minimization and where feasible, ultimate elimination.

2 Emissions

Hexachlorobenzene is currently neither produced nor used in Europe. The production of hexachlorobenzene in Europe was ended in 1993, with the discontinuation of production for the manufacture of pentachlorothiophenol (PCTP, a rubber auxiliary). Internationally the substance has since been intentionally produced in China at one site close to Ya-Er lake, Hubei province, through an Specific Exemption from the Stockholm Convention. However, this exemption expired in 2009 and there are no other exemptions recorded. A full discussion of the global emissions picture can be found in the Euro Chlor Science Dossier entitled ‘Hexachlorobenzene – Sources, environmental fate and risk characterisation.’

Although hexachlorobenzene is no longer produced in Europe small quantities are generated inadvertently, for example during some incineration processes or as an impurity in some chemical manufacturing processes. Product substitution, processing and raw materials changes and increased emission controls have resulted in continually declining emissions of hexachlorobenzene.

Euro Chlor has published hexachlorobenzene emissions levels collected from 2001 to 2010 from the chlor-alkali industry, where the substance is generated as an unintentional by-product. The total releases to air of all chlor-alkali sites in Europe have been reduced from 138 kg/y to 0.017 kg/y, and correspondingly releases to water have been reduced from 713 kg/y to 1.26 kg/y.

Current emissions of hexachlorobenzene are reported on national and international pollutant release inventories. The European Pollutant Release and Transfer Register (E-PRTR) is a Europe-wide register that provides environmental data from industrial facilities in European Union Member States and in Iceland, Liechtenstein, Norway, Serbia and Switzerland. The register contains data reported annually by some 28,000 industrial facilities covering 65 economic activities across Europe. For each facility, information is provided concerning the amounts of pollutant releases to air, water and land as well as off-site transfers of waste and of pollutants in waste water from a list of 91 key pollutants including heavy metals, pesticides, greenhouse gases and dioxins since 2007. Data on emissions of these pollutants can be found on the internet for each facility.

For the year 2009 4 facilities reported an emission of hexachlorobenzene to water and the quantities emitted were 1.10, 1.13, 3.18 and 58.5 kg, respectively. The facilities were located in Belgium, Italy and Poland. Two facilities reported an emission of hexachlorobenzene to air (22.3 and 22.0 kg) while no emissions to soil were reported.

In 2011 a total of eight facilities reported emissions of hexachlorobenzene to either air, water, or both. A total of 125 kg were emitted to air, although approximately half of this total (65.2 kg) resulted from an accidental release from a chemical production site. For the other years recorded in the E-PRTR (2007-2010), no accidental releases were reported, suggesting that the value for 2011 emissions to air may be much larger than typical annual emissions to air. Emissions to air occurred from metal processing, chemical production, and waste management. All of the reported emissions of hexachlorobenzene to water, which totalled 79.0 kg, resulted from wastewater treatment plants. The majority of the emission to water (75%) came from the Lombardy region of Italy.

3 Bioaccumulation

The bioaccumulation of hexachlorobenzene has been summarised on several occasions. Bioconcentration factor (BCF) data for hexachlorobenzene considered in the development of EQS proposals for priority substances under the Water Framework Directive (WFD) ranged from 2,000 to >200,000, with average values typically in the region of 50,000 (FHI 2005). Field data from the Federal Environment Agency (UBA) of Germany for two fish species were also considered (FHI 2005). Field derived Bioaccumulation Factor (BAF) values were used in the derivation of a proposed quality standard for secondary poisoning of top predators. The approach allows for the extrapolation from an acceptable concentration in the food of predators to an acceptable concentration in the water column, although this is subject to considerable uncertainty.

In a recent review of BCF and BAF assessments, Arnot and Gobas (2006) defined bioconcentration as the concentration of the substance in the organism divided by the concentration of freely dissolved substance in the water. Differences between the measured and freely dissolved concentrations could result in uncertainty in the calculation of the BCF. A study on the effects of humic acids on hexachlorobenzene bioaccumulation (Lores et al. 1993) concluded that the presence of humic acid did not affect the ultimate bioavailability of hexachlorobenzene, but

that significantly lower BCF values may be calculated in the presence of humic acids due to their effect of enhancing the apparent solubility of hexachlorobenzene.

Arnot and Gobas (2006) applied a data quality assessment, comparable to the Klimisch scoring system (Klimisch et al. 1997) which is used for toxicity data evaluation, to available bioconcentration and bioaccumulation data. Two hundred and forty-nine BCF and BAF values were identified for hexachlorobenzene and of these 21 were identified as valid laboratory BCF studies and 26 were identified as valid field BAF studies for hexachlorobenzene accumulation. Although the individual studies which were considered valid were not identified, this review has applied a systematic quality assessment to available data and selected those data which are considered to be of acceptable validity. Log BCF values for fish ranged from 3.57 to 4.70 with a median value of 4.26; the mean value was 4.12 (standard error 0.07). Log BAF values for fish ranged from 3.91 to 5.74 with a median value of 4.75, the mean value was 4.74 (standard error 0.09). The valid data are summarised in Table 2.

The review considered the level of confidence that could be assigned to each of the studies reviewed according to 5 criteria, and for each of these criteria assigned a confidence score ranging from 1 (high confidence) to 3 (low confidence). The criteria considered were:

1. Water analysis (high confidence for measured data)
2. Radio-labels (high if corrected for parent compound or not a radiolabel study)
3. Aqueous solubility (high if test concentration less than limit of water solubility for the test compound)
4. Exposure duration (high if >80% of steady state achieved)
5. Tissue analysis (high if both whole body concentration and lipid content reported)

Confidence scores of either 1 or 2 (high or moderate confidence) were required for all of the 5 factors considered in order for a study to be considered as reliable.

Table 2 Summarised valid fish BCF and BAF data from Arnot and Gobas (2006)

	Min	Max	Median	Mean	Number
BCF	3,720	50,100	18,200	13,200	21
BAF	8,130	550,000	52,600	55,000	26

Median and mean values calculated on the basis of log transformed data.

Variability surrounding the dissolved concentrations of hexachlorobenzene in the test system can result in considerable uncertainty. Gobas and Zhang (1992) considered that fluctuations in water concentrations during the exposure period could lead to both over- and under-estimates of the true BCF by approximately one order of magnitude. It is possible, therefore, that even studies which were reviewed by Arnot and Gobas (2006) as reliable may still be subject to a significant degree of uncertainty. Dissolved organic carbon (DOC) in test waters may also have an effect on the apparent water solubility of hexachlorobenzene, with the result of apparently lowering the BAF or BCF due to increased measured dissolved concentrations. Some of the low BCF and BAF values reported as being reliable by Arnot and Gobas (2006) may, therefore, represent underestimates of the true values. A study of the uptake of hexachlorobenzene by fish from solutions containing dissolved organic matter (DOM) (Freidig et al. 1998) showed that lower uptake rates were observed with increasing concentrations of DOM. This was considered to be due to a reduction in the bioavailability of hexachlorobenzene resulting from sorption to the DOM.

Field derived BAF values are typically higher than comparable BCF measurements due to the influence of additional routes of exposure, such as ingestion, being taken into account. Laboratory studies into food chain transfer of hexachlorobenzene have similarly found that contaminated prey can contribute significantly to the overall accumulation.

Arnot and Gobas (2006) also provided a number of recommendations on bioaccumulation assessment of chemicals within chemicals management programmes.
These are:

1. a precautionary approach is warranted as the first stage in a tiered assessment approach
2. acceptable quality BAF data should be the primary source of information
3. estimation methods will be required for most chemicals

In the specific case of hexachlorobenzene only the second of these recommendations applies, principally because there is a considerable quantity of information available on the bioaccumulation of hexachlorobenzene.

A laboratory study of the bioconcentration of chlorinated benzenes by trout (Oliver and Niimi 1983) found that observed BCF values were concentration dependent (higher exposure concentrations of hexachlorobenzene resulted in higher BCF values), although only two exposure concentrations were tested (0.3 and 8 ng l^{-1}). The fish were fed commercial fish food, which was also analysed for hexachlorobenzene and found to contain 4.2 ng g^{-1} hexachlorobenzene, although control fish fed on the same diet did not show an appreciable increase in their body burdens of hexachlorobenzene. An equilibrium concentration of hexachlorobenzene was not achieved within 119 days (the duration of the study). The authors compared their findings to the levels of chlorinated benzenes in fish from Lake Ontario and found that measured water concentrations and laboratory derived BCFs for lower chlorinated benzenes underestimated the body burden of hexachlorobenzene in lake fish by a factor of approximately 50. This study was included in the review by Arnot and Gobas (2006) and was considered to be reliable. It indicates that exposure routes other than water exposure can be important in hexachlorobenzene accumulation, although the control experiment indicates that a biomagnification factor (BMF) of less than 1 would be appropriate if food was the principal route of exposure. The possibility of accumulation of hexachlorobenzene from sediments may, therefore, play a potential role in the overall bioaccumulation of hexachlorobenzene in the environment.

A detailed study of a model food chain was undertaken by Egeler et al. (2001) in which fish (sticklebacks, *Gasterosteus aculeatus*) were exposed to hexachlorobenzene through water, sediment and food (*Tubifex tubifex*). The study considered the various sources of exposure separately (except for sediment) and also in combined exposure experiments. The fish were subjected to water-only exposures, water and sediment exposures, contaminated prey (*T. tubifex*) and water, sediment and prey in order to determine the resulting bioaccumulation factors. This study does not appear to have been considered in the review by Arnot and Gobas (2006), but was considered to be reliable when reviewed for this study. The validation criteria are available in appendix 1. The reported BAF values (on a wet weight basis) for sticklebacks were 22,000 for water only exposures, 37,000 for water and sediment exposures and 52,000 for water, sediment and food exposure. The corresponding lipid normalised BAF values were 350,000 (water only), 518,000 (water and sediment) and 784,000 (water sediment and food). This study highlights the potential for contaminated sediments to contribute to the exposure of fish to hexachlorobenzene, although such an exposure route is not usually considered explicitly within assessments of bioaccumulation. The potential additional exposure due to sediments was one of the reasons behind the proposal that the quality standard for hexachlorobenzene be assessed in biota.

3.1 Biomagnification

Biomagnification is the increase in concentration of a substance in biota with increasing position in the food chain. The BMF is defined as the relative concentration in a predatory animal compared to the concentration in its prey, and the concentrations used in its derivation should preferably be lipid normalised (ECHA 2010).

The technical guidance for risk assessment (ECHA 2008) recommends that a $PNEC_{oral,\ predator}$ is calculated from the BCF and BMF which assumes a simple two step food chain for aquatic systems. Although it is not explicitly indicated, the BCF and BMF may be replaced by a field derived BAF of acceptable quality (as recommended by Arnot and Gobas 2006) should such data be available, as is the case for hexachlorobenzene. The general relationship between the BCF, BAF and BMF is given below, although it should be noted that this relationship assumes that water and food are the only possible sources of contaminants to organisms, which may not necessarily be the case (e.g. Egeler et al. 2001).

BAF = BCF x BMF BAF / BCF = BMF

Using this general relationship between the BCF and BAF allows generic estimates of the BMF between fish and their food to be made from the summarised BCF and BAF data from reliable studies which have been reported by Arnot and Gobas (2006).

BMF (median data)	2.9
BMF (mean data)	4.2
BMF (min)	0.16
BMF (max)	148

BMF information can also be derived from monitoring of hexachlorobenzene in marine biota from Greenland (Vorkamp et al. 2004), although this study did not report the concentrations of hexachlorobenzene in either seawater or sediments. However, the concentrations of hexachlorobenzene in organisms from different trophic levels can be compared to provide a general indication of the potential for biomagnification of hexachlorobenzene within an arctic marine food chain. Hexachlorobenzene concentrations were reported from selected tissues on a lipid weight basis for a variety of marine invertebrate, fish, bird, seal and whale species. Lipid normalised concentrations of hexachlorobenzene in muscle tissue were reported for the majority of species, and in cases where other tissues were also analysed the concentrations (on a lipid normalised basis) were typically within 30% of the concentration in muscle, although greater variation between tissues was observed for some species.

The major prey species of the different predators were not reported and because of this the reliability of the derived BMF values is uncertain. Average concentrations (using both the geometric and arithmetic means) of hexachlorobenzene in muscle tissue for different types of organisms (i.e. all invertebrates (3 species), all fish (6 species), all birds (4 species), all seals (2 species, 3 groups) and all whales (3 species)) were used to estimate BMF values for several assumed food chain steps. The results of these calculations are summarised in Table 3.

Table 3 Calculated BMF values for arctic marine organisms (data from Vorkamp et al. 2004)

Prey	Predator	Geometric mean	Mean	Max	Min
invertebrates	fish	4.83	1.72	106.8	0.29
invertebrates	birds	4.55	2.38	172.7	0.08
invertebrates	seals	2.52	1.14	109.1	0.17
invertebrates	whales	39.6	15.06	1000	2.67
fish	birds	0.94	1.38	5.85	0.08
fish	seals	0.52	0.66	3.69	0.16
fish	whales	8.21	8.75	33.85	2.55

It is unlikely that many of the species considered as predators feed exclusively on either invertebrates or fish, although some whale species may feed only on invertebrates such as krill or squid (e.g. baleen whales). It is likely that some of the calculated BMF values in Table 3 do not actually relate to ecologically relevant trophic linkages, potentially resulting in extreme values which would not be observed in real systems. Therefore, BMF values have also been estimated by taking the average concentrations reported for all fish and invertebrate species as a typical prey concentration for birds, seals and whales. The results are shown in Table 4 (using data from Vorkamp et al. 2004). It is clear from this that whales accumulate greater concentrations of hexachlorobenzene than either birds or seals, although the reasons for this greater accumulation are not clear. It is possible that the longer lifespan of whales, compared to birds and seals, results in greater body burdens in older individuals although it is not possible to assess this from the available data. The data used in the calculation of BMF values are all lipid normalised, so the greater accumulation of hexachlorobenzene in whales is not due simply to differences in their overall lipid content.

Table 4 Estimated BMF values assuming a mixed fish and invertebrate diet for predators

Consumer	Geometric mean	Mean
Birds	1.59	1.61
seals	0.88	0.77
whales	13.87	10.17

Tables 3 and 4 show that BMF values for whales are highest, with values for whales preying on invertebrates apparently higher than for those preying on fish. This is because concentrations of hexachlorobenzene measured in invertebrates are, in some cases, lower than those measured in fish. Data for whales reported by Vorkamp et al. (2004) are shown in Table 5.

Table 5 Hexachlorobenzene concentrations reported in whales by Vorkamp et al. (2004)

Whale Species	Tissue Concentration (ng g^{-1} lw)	
	Muscle	**blubber**
Northern minke (*Balaneoptera acutorostrata*)	120	160
Beluga (*Delphinapterus leucas*)	350	250
Narwhal (*Monodon monoceros*)	440	490

It is appropriate, therefore, to consider in greater detail the likely diets of these whale species. Minke whale stomach contents sampled from whales caught off the cost of Norway contained only fish, 92% of which were herring (*Clupaea harengus*), with cod (*Gadus morhua*) the next most abundant prey item (Lydersen et al. 1991). Haug et al. (1995) and Pierce et al. (2004) also found that minke whale sampled in the Northeast Atlantic fed almost exclusively on fish, although they will switch to consume invertebrates such as krill (*Thysanoessa* sp. and *Meganyctiphanes norvegica*) if their preferred fish prey are unavailable (Haug et al. 2002). Northern minke whale may migrate seasonally from higher latitudes where they feed in summer to lower latitudes in the winter, but Born et al. (2002) concluded that groups of minke whales are resident for some time at their feeding grounds in the North Atlantic.

Narwhal stomach contents sampled by Laidre and Heide Jorgensen (2005) from whales caught in the eastern Canadian High Arctic and West Greenland showed that these animals feed mainly in the winter, when they consume Greenland halibut (*Reinhardtius hippoglossoides*) and squid (*Gonatus fabricii*). This may mean that narwhals have a period during which they deplete their body lipid reserves, which could result in variations in contaminant concentrations due to changes in lipid weight or body weight. If this is the case then the season of sampling may have an influence on the observed body burdens.

Beluga also feed primarily on fish, but will also eat marine worms, squids and crustaceans. Some populations of beluga migrate seasonally in search of food within Arctic waters, while others are resident in well-defined areas (Reyes 1991).

In summary, fish, and squid in the case of narwhal, are generally the preferred prey of the three whale species sampled by Vorkamp et al. (2004), but whales will switch prey if necessary to feed on invertebrates if fish (or squid) are unavailable. The food chain for these whales could therefore be one of the following:

Phytoplankton → worms/crustaceans/krill → whale (e.g. minke)

Phytoplankton → crustaceans/krill → squid/small fish (e.g. herring) → whale (e.g. narwhal/beluga)

Phytoplankton → crustaceans/krill → squid/small fish (e.g. herring) → large fish (e.g. halibut) → whale (e.g. narwhal)

The data on muscle concentrations of hexachlorobenzene in whales reported by Vorkamp et al. (2004) support the idea that the sampled minke whale (120 ng hexachlorobenzene g^{-1} lw muscle) were feeding at a position lower down the food chain than the sampled narwhal (440 ng hexachlorobenzene g^{-1} lw muscle).

In order to estimate a generic BMF value from these data an alternative approach was also taken. All fish and invertebrate species were considered to be potential prey items and all birds, seals and whales were considered to be potential predators. The average concentrations of hexachlorobenzene in muscle tissue were determined for both predators and prey (as both the arithmetic mean and as the geometric mean) and these average values were used to derive a BMF estimate. The generic BMF values calculated in this way are 2.55 on the basis of geometric means and 3.92 on the basis of arithmetic means. The use of arithmetic means provides a more conservative BMF value, whereas the use of geometric means may be more relevant to distributions of BMF values which typically appear to be log normally distributed. The generic BMF values derived in this way are comparable to the BMF values derived by comparison of the valid BCF and BAF data reported by Arnot and Gobas (2006).

The combination of BCF and BMF data from the hexachlorobenzene accumulation studies reported by Egeler et al. (2001) allows a reasonable estimation of overall BAF values determined in separate experiments. It is not, however, possible to estimate reliably the overall Biota-Sediment Accumulation Factor (BSAF; for a water, sediment, worm and fish system) from a BSAF (for a water, sediment and fish system) and a BMF. This may indicate the much smaller influence of sediment exposure on the overall accumulation of hexachlorobenzene when compared with exposure from water or food.

Lunstead-Enkel et al. (2005) studied the accumulation of several pollutants between herring (*Clupea harengus*) and guillemot (*Uria aalge*) and adopted an approach which allowed the variability in biomagnification between the two species to be defined. They analysed a variety of organochlorine compounds, including hexachlorobenzene, in individual herring muscle and guillemot egg samples collected from the Baltic Sea. The authors considered that reporting a single BMF value from average concentrations of contaminants in the two trophic levels limited the usefulness of the resulting BMF because it does not provide any information about the uncertainties surrounding the BMF value. A statistical resampling method was therefore applied to the data to derive BMF values whereby a randomly selected herring sample was compared to a randomly selected guillemot sample. This procedure was repeated 50,000 times generating 50,000 individually calculated BMF values. This then allowed the variability in the BMF between herring muscle and guillemot eggs to be considered.

Whilst the geometric mean BMF value calculated by this method did not differ from that calculated on the basis of the geometric means of both the herring and guillemot samples (i.e. a single BMF value for the whole dataset) it provided information on the variation about this average BMF value. The BMF values for hexachlorobenzene were 33.8 and 30.0 on the basis of geometric and arithmetic means respectively, and the BMF values calculated on the basis of randomly sampled ratios were 33.8 ± 1.75 and 40.1 ± 26.2 on the basis of geometric and arithmetic means respectively. This approach is considered to be a useful way of understanding the variability of BMF values within a particular trophic link.

In a study of the accumulation of hexachlorobenzene in white bass (*Morone chrysops*) in Lake Erie (Russel et al. 1995) no biomagnification was observed. The stomach contents of collected predator fish (white bass) were assessed and emerald shiner fish (*Notropis atherinoides*) were the only identified prey. There were no significant differences observed in the concentrations of hexachlorobenzene in the two fish species, although biomagnification of PCBs was observed for the same trophic linkage. A detailed study of the Detroit River food web (Russel et al. 1999) analysed concentrations of hexachlorobenzene in phytoplankton, zooplankton, benthic invertebrates and 14 fish species including planktivorous, benthic and pelagic species. The highest levels of hexachlorobenzene were recorded in zebra mussels (*Dreissena polymorpha*), followed by mayfly larvae (*Hexagenia* spp.), rock bass (*Ambloplites rupestris*) and stonecat (*Noturus flavus*). No consistent increases in hexachlorobenzene concentrations along the food chain were observed for hexachlorobenzene, although such increases were observed for chemicals with log K_{OW} values greater than 6.3, such as highly chlorinated PCBs.

Pastor et al. (2004) studied the accumulation of organochlorine contaminants in a rice field ecosystem. Some of the species considered, such as flies and frogs, have different feeding strategies (carnivorous or herbivorous) during their larval and adult life stages. Other factors also affect the feeding of the species considered; for example, frogs eat mainly terrestrial species during the dry season and mostly aquatic species during the wet season. The authors found that the distribution of organochlorine contaminants could be explained through equilibrium partitioning and biomagnification processes, but observed that the biological characteristics of the organisms, and ecological factors, could significantly influence the

observed levels of contaminants in different species. No clear biomagnification of hexachlorobenzene was observed within the ecosystem when assessed on either a dry weight or on a lipid normalised basis. The highest levels of hexachlorobenzene were observed in filter feeding insect larvae (chironomid larvae) and carnivorous and scavenging insects.

A study of organochlorine bioaccumulation in a high mountain lake ecosystem (Catalan et al. 2004), which included the analysis of C and N isotopic ratios in order to assess primary energy sources (i.e. pelagic or sediment) and trophic levels, did report biomagnification of hexachlorobenzene by predatory fish (brown trout, *Salmo trutta*). The diet of trout was assessed under conditions of both high and low food abundance (i.e. summer and winter conditions) to establish a representative exposure of the fish to hexachlorobenzene. A BMF value of approximately 6 was identified for hexachlorobenzene from their food. Fugacity modelling calculations indicated that hexachlorobenzene was close to a steady-state distribution between the water and food.

The biomagnification of hexachlorobenzene is clearly highly variable between different trophic linkages with BMF values varying from less than 1 to greater than 100 in extreme cases. It would appear that higher BMF values are typically found for higher organisms, such as birds and mammals, which may be expected to have higher metabolic and food intake rates than cold blooded organisms. Typical BMF values, such as the 50^{th} percentile of a distribution, for lower trophic levels are in the range 1 to 4 but can be much higher for higher trophic levels. It is clear that different BMF values need to be derived for different trophic linkages due to the differences in the behaviour and physiology of different groups of species.

3.2 Modelling bioaccumulation along food chains

A recent review of bioaccumulation models (Brooke and Crookes 2007), for setting Environmental Quality Standards to ensure protection against secondary poisoning, tested three available bioaccumulation models against field data from the literature. They found that the available models tended to underestimate field BAF values for substances with very high log K_{OW} values (>7), particularly for organisms at high trophic levels. The REACH approach (ECHA 2010) for freshwaters was found to provide a reasonable prediction of BAF values around log K_{OW} values of 5 to 6, with a slight tendency toward underestimation of BAF values. The alternative REACH approach for the marine risk assessment for top predators, which assumes an additional trophic level (through the inclusion of a second BMF value), tended slightly toward overestimation of field BAF values. Overall, the model of Voutsas et al. (2002) provided the best predictions of field BAF values. The data used for the testing of the different models were, however, all included in the development of the Voutsas model, which does not necessarily provide a valid test of the model.

However, all of the three models that were considered by Brooke and Crookes (2007) significantly overestimated field BAF values when tested against an Environment Agency dataset for the River Mersey (Environment Agency 1998). This could be due to uncertainties in the experimental data or from systematic errors in the prediction of BAF values by the models. The review did not, however, consider the uncertainties in the resulting estimations of BAF values, or $PNEC_{water}$ concentrations estimated from bioaccumulation, which result from uncertainty in the derivation of the BCF, BAF and BMF values used in the estimates.

The technical guidance for risk assessment (ECHA 2010) includes the provision to estimate BCF values from log K_{OW} values for substances where experimental data are not available or are

uncertain. However, such estimates of the BCF are very dependent upon the selected log K_{OW} value for the substance, which may also be subject to uncertainty. For example, the following are defensible estimates of the log K_{OW} value for hexachlorobenzene:

- 3.9 to 6.4 (Barber et al. 2005), with a value of 5.5 selected for risk assessment
- 5.86 (KOWWIN estimated)
- 5.73 (KOWWIN database, De Bruijn et al, 1989)

Estimation of BCF values according to a QSAR (log BCF = 0.85 x log K_{OW} -0.7), which is mentioned in the REACH guidance (ECHA 2010), are shown in Table 6. This QSAR is considered to be valid up to log K_{OW} values of 5.5, and the range of measured and predicted log K_{OW} values for hexachlorobenzene are slightly outside this range.

Table 6 QSAR estimated fish BCF values for hexachlorobenzene

Log K_{OW}	Log BCF	BCF
5.5	3.975	9441
5.7	4.145	13964
5.9	4.315	20654

These QSAR-derived BCF values are comparable to the mean and median values derived by Arnot and Gobas (2006). Hexachlorobenzene is considered to be within the domain of this QSAR as it has a log K_{OW} value of less than 6, it is a non-polar and non-ionisable chemical and is considered only to be very slowly biotransformed. The REACH guidance (ECHA 2010) considers two generic food chains in the assessment of exposure of predatory organisms to potentially bioaccumulating chemicals. These are applied to freshwater systems and marine systems, although the only difference between the two scenarios is an additional trophic link in the marine system. The summarised bioconcentration and bioaccumulation data for hexachlorobenzene reported by Arnot and Gobas (2006) is applied to the marine food chain model below, along with estimated BMF data derived from an arctic ecosystem (Vorkamp et al. 2004).

REACH approach for freshwater food chain

$$PEC_{oral,\ predator} = PEC_{water} \times BCF_{fish} \times BMF = PEC_{water} \times BAF$$

The default BMF value for hexachlorobenzene (log K_{OW} 5.7) from the REACH guidance (ECHA 2010) is 10 although numerous studies have observed much lower biomagnification of hexachlorobenzene in the field, e.g. Russell et al. (1995 and 1999) and Pastor et al. (2004). Higher BMF values have also been reported by some studies in marine food chains, although the highest BMF value identified for a freshwater system is 6 (Catalan et al. 2004).

REACH approach for marine top predator food chain

$$PEC_{oral,\ top\ predator} = PEC_{water} \times BCF_{fish} \times BMF_{predator} \times BMF_{top\ predator}$$
$$= PEC_{water} \times BAF \times BMF_{top\ predator}$$

Default BMF values for hexachlorobenzene (log K_{OW} 5.7) from the REACH guidance (ECHA 2010) are 10 for both BMF_1 and BMF_2. Whilst the default BMF from the REACH guidance is comparable to the general BMF values estimated for whales from the monitoring data for Vorkamp et al. (2004) for an arctic food web (BMF 10 to 14) it is much higher than those estimated for both seabirds and seals (BMF 0.8 to 1.6). The considerable differences between the observed

accumulation in whales and other top predators from the arctic ecosystem suggest that it may be appropriate to undertake assessments of these different groups separately. A BMF value of more than 30 was identified between herring and guillemot by Lunstead-Enkel et al. (2005).

A $PEC_{oral,\ predator}$ can be estimated by applying the mean BAF value reported by Arnot and Gobas (2006) for hexachlorobenzene uptake of 55,000 and BMF values of 1.6 (for arctic seabirds), 4.2 (as a generic reasonable worst case BMF) and 14 (for whales). All BMF values used in this example are derived from the data reported by Vorkamp et al. (2004). Recent levels of hexachlorobenzene in the arctic have been reported and summarised by Barber et al. (2005) and a concentration of 12 pg l^{-1} was considered to be typical for the Northern hemisphere. Surface seawater concentrations of hexachlorobenzene in the Southern hemisphere are estimated to be approximately one fifth of those in the Northern hemisphere.

$PEC_{oral,\ seabirds}$ = 12 pg l^{-1} x 55,000 x 1.6 — 1.056 µg kg^{-1} (wet weight)

$PEC_{oral,\ generic}$ = 12 pg l^{-1} x 55,000 x 4.2 — 2.772 µg kg^{-1} (wet weight)

$PEC_{oral,\ whales}$ = 12 pg l^{-1} x 55,000 x 14 — 9.24 µg kg^{-1} (wet weight)

This simple assessment demonstrates the variability in the predicted PEC_{oral} which results from the use of different BMF values which may be derived for different food chain linkages from within a single ecosystem.

Alternatively, the uncertainties surrounding each of the parameters required for the calculation of the $PEC_{oral,\ top\ predator}$ can be taken into account in a more probabilistic assessment, since each of the input parameters is subject to variability. This has been undertaken, using the example of whales consuming fish, by using Monte Carlo simulation implemented in Crystal Ball Software (Decisioneering, Colorado), with Latin hypercube sampling of input parameters and 10000 trials.

The BAF, taken from the summarised acceptable BAF data reported by Arnot and Gobas (2006), was used in place of the BCF and $BMF_{predator}$ and the $BMF_{top\ predator}$ values were estimated for whales from monitoring data reported by Vorkamp et al. (2004). The mean value of the PEC_{water} was assumed to be 12 pg l^{-1}, from Barber et al. (2005) and was also assumed to have a standard deviation of 10% of the mean value. The median BAF was assumed to be 56,234, with a 99^{th} percentile of 549541 (Arnot and Gobas 2006). The $BMF_{top\ predator}$ was assumed to have a 1^{st} percentile of 2.55 and a 99^{th} percentile of 33.85 (Table 3). Figure 1 shows the cumulative frequency distribution of estimated $PEC_{oral,\ top\ predator}$ values calculated, along with recent monitoring data for the levels of hexachlorobenzene in arctic fish.

The calculated $PEC_{oral,\ top\ predator}$ covers over three orders of magnitude when the uncertainties in each input parameter are taken into account, although the greatest variability is seen towards the extremes of the assessment. The distribution of calculated PECoral values for fish eating whales in the arctic compares favourably with the observed concentrations of hexachlorobenzene in arctic fish (Barber et al 2005).

Figure 1 Probabilistic assessment of $PEC_{oral,\ top\ predator}$ for whales eating fish in the Arctic (using data from Vorkamp et al. 2004) and comparison with average concentrations reported in arctic fish (Barber et al. 2005)

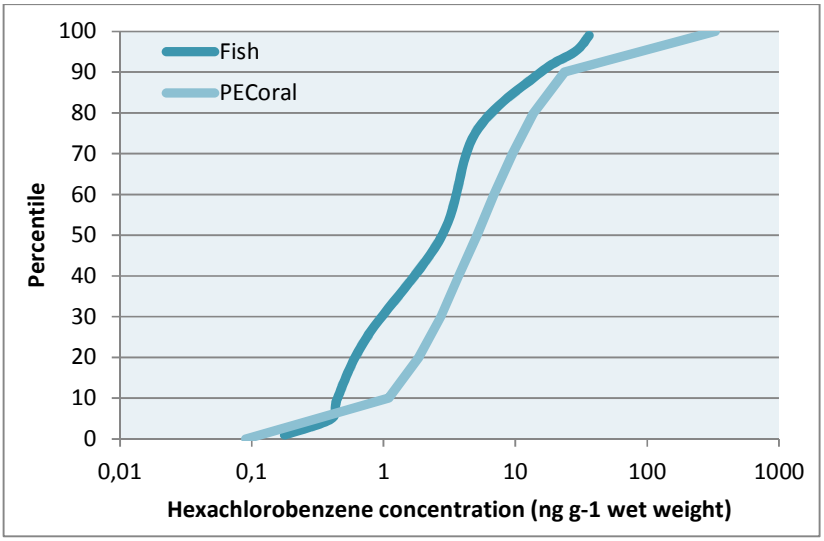
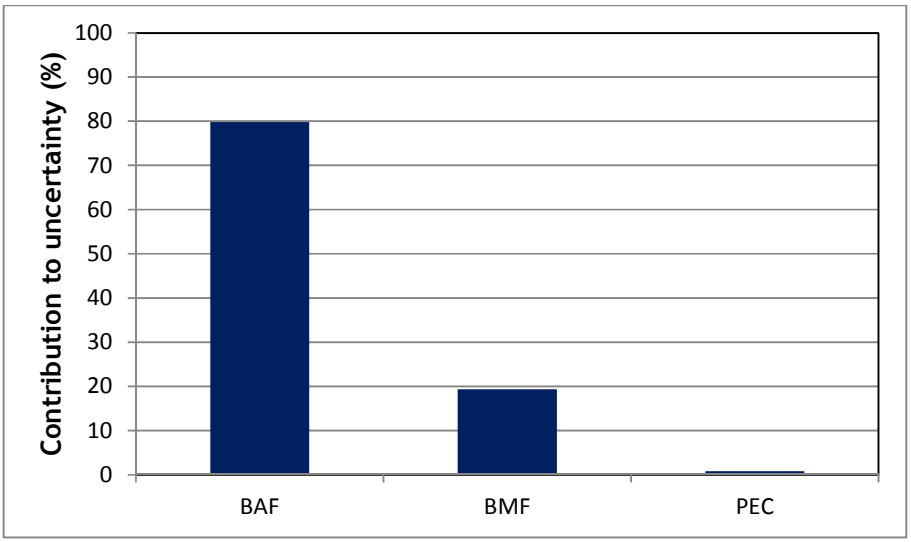


Figure 2 shows the contribution of each of the input variables to the estimated $PEC_{oral,\ top\ predator}$. It is clear from this that the majority of the uncertainty (79.8%) in the estimation of the $PEC_{oral,\ top\ predator}$ is due to uncertainties in the BAF value used in this assessment, although uncertainty in the BMF value is also significant (19.4%). In this example very little of the uncertainty is due to the concentration of hexachlorobenzene in the water, indicating that the biological processes and interactions within the food chain can result in considerable variation in the overall degree of bioaccumulation which is observed for a given chemical.

The range of predicted $PEC_{oral,\ top\ predator}$ values derived from this probablilistic assessment compare very favourably with the average observed concentrations of hexachlorobenzene in arctic fish reported by Barber et al (2005). The predicted $PEC_{oral,\ top\ predator}$ values are slightly higher than the observed average hexachlorobenzene concentrations in arctic fish, but are within a factor of 2 at the 50^{th} percentiles.

Combining probabilistic assessments of exposure with similar assessments of effects, e.g. through the use of species sensitivity distributions of effects on predatory or mammalian species, is likely to provide the most robust and useful assessment of the potential risks to ecosystems in cases where adequate information exists to do so.

Figure 2 Contribution of input parameters to uncertainty in $PEC_{oral,\ top\ predator}$ calculation



3.3 Summary of Bioaccumulation Data Used for Risk Assessment

The BCF and BAF values used for the risk assessment are derived from the summarised data of Arnot and Gobas (2006). A BCF of 18200 is used and a BMF_1 of 2.9 is derived from the difference between the BCF values and BAF values summarised by Arnot and Gobas (2006), the resulting equivalent BAF is therefore 52800. This value has been derived as the median of 26 valid field studies of hexachlorobenzene bioaccumulation.

The modelling approach for the secondary poisoning of top predators by hexachlorobenzene in their food uses empirically derived BMF values for each of the assumed food chain linkages, which are based on monitoring information for hexachlorobenzene levels in organisms from relevant environments.

Water-zooplankton (BAF, median)	18200	$BAF_{plankton}$
Zooplankton-fish (50^{th} %ile BMF)	3.65	BMF_1
Fish-fish (median BMF)	2.0	BMF2
Fish-seal (harp seal BMF)	1.35	BMF_3
Seal-polar bear (BMF, single value)	15.6	BMF_4

These BMF values have all been derived on a lipid normalised basis, as recommended in the REACH guidance (ECHA 2012). Specific BMF values have derived for each trophic linkage from data reported in Barber et al. (2005) derived from arctic food webs, as the relative difference in lipid normalised concentrations in the predator and prey samples. Median BMF values were selected for modelling from the range of BMF values calculated for each trophic linkage. Different species of seal show markedly differing hexachlorobenzene accumulation and the value applied here is an overall median value. The biomagnification of hexachlorobenzene in seals is considered in more detail in Section 7.1.

4 Effects assessment

4.1 Aquatic effects

Introduction

The aquatic effects database for hexachlorobenzene contains 39 acute data and 28 chronic data. Of these there are 19 valid acute data for 16 species from 3 trophic levels, including 6 marine species, and 19 valid chronic data for 13 species from 3 trophic levels, including 2 marine species. Data were evaluated according to quality criteria recommended by the European Commission (Commission Regulation 1488/94/EEC). The evaluation criteria are shown in Appendix 1. The available aquatic ecotoxicity data for hexachlorobenzene are summarized in Appendix 2 for both acute and chronic studies. Acute studies are short term tests considering lethal endpoints and reporting LC_{50} or EC_{50} values. Chronic studies are long term tests considering non-lethal endpoints such as growth or reproduction and reporting NOEC or EC_{10} values. Data in Appendix 2 are ranked according to trophic level (fish, invertebrates, algae), statistical endpoint (LC_{50}/EC_{50}, $NOEC/EC_{10}$), habitat (freshwater/ saltwater) and validity (scores between 1 and 4).

A number of problems have been observed with maintaining hexachlorobenzene concentrations during aquatic toxicity tests. These are principally due to volatilisation and adsorption from the test solution. Both of these processes can result in actual concentrations that are lower than nominal concentrations, highlighting the need for them to be minimised, or analysis of the exposure concentrations undertaken, in valid tests. The solubility of hexachlorobenzene in distilled water is considered to be around 5 µg l^{-1} (IPCS 1997, Barber et al. 2005), although this may be influenced by other factors such as temperature and salt concentration of the water. The apparent solubility of hexachlorobenzene may also be enhanced by the presence of dissolved organic material in the water, although this does not appear to alter the truly dissolved concentration (Lores et al. 1993). The apparent water concentration results from hexachlorobenzene which is both truly dissolved and associated with dissolved organic matter.

A summary of all data is provided in Appendix 2. In total 22 data for fish, 30 data for invertebrates and 14 data for algae are available. Respectively 7, 12 and 2 data were considered valid (without restriction) for risk assessment purposes. For the respective taxonomic groups 4, 9 and 4 of the data points are considered to be valid with restrictions, and 9, 9 and 9 data, respectively, were judged as not valid for risk assessment. The validity of 2 data points for fish and could not be assigned.

Due to the low solubility of hexachlorobenzene, a large number of studies report that an effect did not occur at the maximum concentration that could be tested. Several of these studies were considered valid (category 1) if the design and conditions of the experiment were judged to be reliable, even though the result (e.g. LC_{50} or NOEC) only represents a minimum ("greater than") value.

Acute Freshwater Toxicity

Twelve acute toxicity studies are reported for 11 freshwater fish species. Two studies (Calamari et al. 1983) were conducted with *Onchorhynchus mykiss* (rainbow trout) and *Danio rerio* (zebrafish) under static conditions, but in closed systems to prevent losses from volatilisation,

and with analysis of the test solutions. The LC_{50} values (> 30 µg l^{-1} for both species) refer to 24 h exposure (confirmed by Calamari (pers. comm. 2001) after identification of inconsistency in paper between text and table) and can be considered valid. Two other acute studies were carried out under flow-through test conditions, with analysis, and are considered valid (Call et al. 1983). The 96h LC_{50} values for *O. mykiss* and *Lepomis macrochirus* (bluegill sunfish) were >81 and >78 µg l^{-1} respectively. None of these four studies found any mortality of the fish at the maximum measured concentrations that could be tested, which exceeded the water solubility of hexachlorobenzene.

Therefore, in valid studies, no acute effects on freshwater fish are reported at concentrations up to and exceeding the water solubility of hexachlorobenzene (5 µg l^{-1}). For risk assessment purposes the 96h LC_{50} values are all considered to be greater than 5 µg l^{-1}.

Eight studies were considered invalid since they were carried out under static or semi-static conditions, without precautions to prevent losses from volatilisation and without analysis of the test solutions. Seven of these (CITI 1992, Johnson and Finley 1980, Könemann 1981) employed concentrations well above the solubility of hexachlorobenzene. The remaining static study with *Leuciscus idus* (Knie et al. 1983) reported a 48h LC_{50} of 7 µg l^{-1} based on nominal concentrations. There was no analysis of the solutions, and no other fish study found any evidence of acute toxicity, except those that tested above 10 mg l^{-1}. This is the only acute study which study suggests the potential for effects at concentrations close to the limit of water solubility of hexachlorobenzene, and is not considered to be valid due principally to uncertainty about the actual exposure concentrations.

Nine acute toxicity values are reported for six species of freshwater invertebrate (including a protozoan). Three of these were based upon nominal concentrations in static tests and are therefore considered as non-valid. The remaining values are reported as measured concentrations, and all are reported as 'greater than' values ranging from 3.3 to 58 µg l^{-1}, the maximum concentrations that were tested because of solubility limitations. Four of these were carried out under flow-through conditions (Laska et al. 1978, Nebeker et al. 1989) as part of longer-term lethal studies (durations provided in Appendix 2).

Eight acute (EC_{50}) values are reported for five freshwater algal species. Five of these values were not considered valid because they were carried out in static systems with no precautions to prevent losses of hexachlorobenzene by volatilisation and no chemical analysis. Two studies by the same authors (Calamari et al. 1983) provide data for *Pseudokirchneriella subcapitata* in closed systems with analysis, in which photosynthesis (^{14}C-fixation) was measured after a three hour exposure, and growth was measured over 96 hours. The former provided an approximate EC_{50} but should be used with care because only two concentrations were tested that showed any effect, and because of the non-standard endpoint. The growth study was considered valid, although the EC_{50} was greater than the highest concentration tested, at which there was minimal (12%) effect (see below). Thus, for risk assessment purposes, EC_{50} values for freshwater algae are greater than the limit of water solubility based on *P. subcapitata* (Calamari et al. 1983).

Acute Saltwater Toxicity

Two acute toxicity studies are reported by Parrish et al. (1975) for 2 marine fish species, *Cyprinodon variegatus* (sheepshead minnow) and *Lagodon rhomboids* (pinfish). Both were conducted in flow-through test systems with analysis of the test solutions and were considered valid. No mortalities were obtained after 96 hours at the maximum measured concentrations that could be tested, which were 13.3 µg l^{-1} for *C. variegatus* and 8.4 µg l^{-1} for *L. rhomboides*.

Therefore, no acute effects on marine fish are reported at concentrations up to and exceeding the water solubility of hexachlorobenzene (5 µg l^{-1}). For risk assessment purposes, the 96h LC_{50} values are all considered to be greater than 5 µg l^{-1} (it is assumed that the water solubility for salt water and freshwater are the same).

Seven acute toxicity studies are reported for seven marine invertebrate species. All reported LC_{50} values which were greater than the maximum concentration tested and were close to, or in excess of, the limit of water solubility. Three were conducted under static conditions with no analysis, and are considered invalid. Two studies were conducted in flow-through test systems with analysis (Parrish et al. 1975) using *Palaemonetes pugio* (grass shrimp) and *Penaeus duorarum* (pink shrimp) which were judged to be valid, and provided LC_{50} values of >17 and >25 µg l^{-1}, respectively. A semi-static study on crabs (Mortimer and Connel, 1994) with daily renewal of exposure solutions was considered valid with restrictions and reported an LC_{50} of > 10 µgl^{-1}. A semi-static study with analysis was also considered valid. This used *Crangon septemspinosa* (sand shrimp) and gave a 96 h LC_{50} of >7.2 µg l^{-1} (McLeese et al. 1980); thus for risk assessment purposes all valid LC/EC_{50} values for marine invertebrates are greater than 7.2 µg l^{-1}.

Biggs et al. (1979) report a study using two species of marine algae, *Thalassiosira pseudonana* and *Dunaliella tertiolecta*, tested together as a mixed culture. The test was static, with no analysis of the solutions, and was therefore not considered valid. However, no effects were observed on algal growth or size at the maximum concentration tested (100 µg l^{-1}). This suggests that these marine algal species are not sensitive to hexachlorobenzene at or above the limit of water solubility.

Conclusions on acute toxicity

There are 13 valid test data available covering 10 freshwater species from three trophic levels. The studies indicate that acutely toxic effects are not observed in any valid tests at levels below the limit of water solubility of hexachlorobenzene (5 µg l^{-1}). Any acute effects are likely to be due to physical effects (presence of undissolved test material) in cases where hexachlorobenzene was tested at concentrations significantly in excess of the limit of water solubility. It is not uncommon for highly hydrophobic chemicals not to show any effects in acute tests, and the focus for hexachlorobenzene toxicity is therefore on chronic effects.

Chronic Freshwater Toxicity

Fish

Seven long-term results are reported from tests with five fish species, five of which were performed in flow-through systems with analysis. The remaining two were performed in semi-static systems without analysis and are not considered to be valid for PNEC derivation. A 90-day NOEC (3.7 µg l^{-1}) for survival and growth of early life stages of *O. mykiss* is reported by US EPA (1988). Details of the study are not given in the original paper, although the test conditions given in Appendix 2 have been confirmed (Euro Chlor 2002). A validity category 2 was therefore assigned to this study. Three of the remaining studies all showed no toxic effects at the maximum concentrations that were tested. A 10 d NOEC of 25.8 µg l^{-1} was obtained for survival, haematocrit and observable symptoms in largemouth bass (*Micropterus salmoides*, Laska et al. 1978). An earlier report (Laseter et al. 1976), which appears to describe the same study, observed changes in the kidney, liver and gall-bladder histology at 25 µg l^{-1}, but with no quantitative data on the frequency or severity of these effects. A 28 d NOEC of 3.8 µg l^{-1} was

determined for survival and a qualitative assessment of growth of *Pimephales promelas* (Nebeker et al. 1989). Both the Laska et al. and Nebeker et al. studies should be used with care, because neither included a quantitative assessment of growth. However, a valid study is available that determined hatch, survival and growth of embryos and larvae of *P. promelas* in a flow-through system with analysis, which showed no effects after 28 days at 4.8 µg l^{-1}, which was the maximum (measured) concentration tested (Carlson et al. 1987, Ahmad et al. 1984). None of these studies have indicated adverse effects at, or below, the limit of solubility of hexachlorobenzene.

Two studies have investigated biomarker or endocrine responses to hexachlorobenzene exposure, although in both cases the majority of tested concentrations were in excess of the limit of water solubility of the test substance. Significant effects on brain glutathione concentrations in common carp (*Cyprinus carpio*) were observed by Song et al. (2006) at concentrations of 2 µg l^{-1} and above (higher test concentrations all exceeded the limit of water solubility for hexachlorobenzene). The ecological relevance of such effects is unclear and they are not therefore considered to be reliable for PNEC derivation. Endocrine disrupting effects have also been observed in crucian carp (*Carassius auratus gibelio*) by Zhan et al. (2000) in both male and female fish, although all of the tested concentrations were well above the limit of water solubility, making the relevance of the study questionable. Again this study is not considered to be reliable for PNEC derivation. These biomarker responses clearly indicate exposure to hexachlorobenzene, but are not necessarily indicative of ecologically relevant effects. Neither of these studies are therefore considered to be relevant to PNEC derivation.

The original source of a study with *D. rerio* (Korte et al. 1981) could not be located (category 4) but the NOEC (5 µg l^{-1}) is not the lowest reported and is consistent with other data for fish.

This discussion of available test results shows that no chronic toxicity to freshwater fish is reported at concentrations up to and including the water solubility of hexachlorobenzene. For risk assessment purposes, the NOEC for freshwater fish is equal to or greater than 4.8 µg l^{-1} (based on *P. promelas*: Carlson & Mosian 1987, Ahmad et al. 1984). When the 90 d NOEC for survival and growth of early life stages of *O. mykiss* (US EPA 1988) is taken into account, the lowest NOEC for freshwater fish is greater than 3.7 µg l^{-1}.

Invertebrates

Twelve long-term toxicity results are reported for freshwater invertebrates, including four which have also been described above when assessing acute toxicity (Laska et al. 1978, Nebeker et al. 1989) and one protozoan test (Yoshioka et al. 1985).

The Umweltbundesamt (Scheubel 1984) commissioned a study to test the feasibility and validity of various test methods to be used under the Chemicals Act, including a *Daphnia* 21 day chronic toxicity test with hexachlorobenzene. A NOEC of 0.13 µg l^{-1} (EC_{50} of 0.6 µg l^{-1}) is reported for daphnid reproduction. The author reports that no effects were found up to the maximal solubility of hexachlorobenzene in 24 hr acute tests. Analysis of the test solutions was undertaken, although details of the analytical methods were not reported. Problems in maintaining hexachlorobenzene concentrations were mentioned for some of the other tests (e.g. fish bioconcentration test), but this was not reported for the chronic *Daphnia* test. This test is considered to be reliable, although the NOEC is the lowest available and over an order of magnitude lower than another 21 d chronic *Daphnia* study (Caspers et al. 1993) conducted according to the same test guideline. Prior to the test the juveniles were treated with streptomycin, at a concentration of 10 mg l^{-1} for 24 hours, in order to protect against

mycobacteria, and it is not clear whether this may have had an influence on the outcome of the test.

The *Daphnia magna* study by Caspers et al. (1993) also provides a true NOEC for reproduction (14 µg l^{-1}). The next higher concentration in this study (45 µg l^{-1}) caused a significant effect (15% inhibition of reproduction), and was also the NOEC for survival. At the NOEC for reproduction the authors reported a nominal concentration of 31.6 µg l^{-1}. However, the measured concentrations for the renewed solutions were 21.6 to 29.6 µg l^{-1}, while measured concentrations for the old solutions were 6.7 to 8.2 µg l^{-1}; the NOEC is therefore expressed here as the geometric mean of these four values (14 µg l^{-1}). Although the nominal and measured concentrations exceed the water solubility of hexachlorobenzene, the result is in reasonable agreement with Calamari et al. (1983), who reported a 14 d LOEC for *D. magna* of 23 µg l^{-1} (80% inhibition of reproduction; EC_{50} 16 µg l^{-1}; NOEC not given). As the limit of water solubility of hexachlorobenzene is considered to be 5 µg l^{-1} the concentration of the NOEC for this test is also set to this value for use in PNEC derivation.

A 7 d NOEC (7 µg l^{-1}) for survival and reproduction of *Ceriodaphnia dubia* is reported by US EPA (1988). Details of the study are not given in the paper, although the test conditions provided in Appendix 2 have been confirmed (Euro Chlor 2002). Therefore validity category 2 was assigned to this study. A valid NOEC was 4.7 µg l^{-1}, for the growth, survival and reproduction of the amphipod *Hyalella azteca*, has also been reported by Nebeker et al. (1989).

Laseter et al. (1976) appear to report the same study as Laska et al. (1978) using *Procambarus clarki* (red crayfish), but describe changes in the histology of the hepatopancreas at 3.6 µg l^{-1}, albeit with little information on the exposure period, or the frequency and severity of the effect. These histopathological effects are considered to be a biomarker of exposure, rather than a biomarker of an ecologically relevant effect, and are not therefore considered to be relevant to PNEC derivation. These observations do, however, support the possibility of some effects being observed in some organisms at levels close to the limit of water solubility.

A static study with a protozoan (Geike and Parasher 1976b) employed a very high acetone level (5 ml l^{-1}) and was not considered valid. Five of the remaining studies report measured concentrations in semi-static or flow-through systems but should be used with care (validity category 2). One employed freshwater oligochaetes (*Lumbriculus variegatus*) in a sand substrate (Nebeker et al. 1989); one with *D. magna* only reported a 7 d NOEC for mortality (Nebeker et al. 1989) and another only reported a LOEC of 23 µg l^{-1} (Calamari et al. 1983). A study with *G. lacustris* provided a low invertebrate NOEC (1.8 µg l^{-1}) but was not considered fully valid because significant mortality at the next higher concentration (3.3 µg l^{-1} which was the highest concentration tested) was not attributed by the authors to the presence of hexachlorobenzene (Nebeker et al. 1989).

Several valid chronic tests on invertebrates indicate that effects may be observed at close to the limit of solubility of hexachlorobenzene, with a single test on *D. magna* indicating effects at levels significantly lower than the limit of water solubility (0.13 µg l^{-1}). Since there is another equivalent test on *D. magna* which has reported a higher NOEC for reproduction (set to the limit of water solubility, 5 µg l^{-1}) it is appropriate to use the geometric mean of the two results for PNEC derivation (0.81 µg l^{-1}). This is the lowest species NOEC in the aquatic effects database. There is, however, considerable uncertainty surrounding the chronic effects of hexachlorobenzene to *Daphnia magna* due to the fact that two apparently identical tests have resulted in NOEC values which differ by 2 orders of magnitude, and the result must therefore be treated with caution.

Algae

Four studies provide NOEC or equivalent values for algal species, although only one of these is for a test of 72 h or longer. Only the 96-h growth study with *Selenastrum capricornutum* (Calamari et al. 1983) is considered to be valid without restriction. Although a NOEC was not reported, the maximum concentration tested (30 µg l^{-1}) exceeded water solubility and was stated to have caused 12% inhibition of growth. Since EC_{10} values for algae are generally accepted to be an alternative to a NOEC, this 'EC_{12}' value is considered to be a reasonable estimate of the no effect level. Thus, the lowest valid chronic value for freshwater algae is 30 µg l^{-1} for *Selenastrum capricornutum* (Calamari et al. 1983).

An unbounded NOEC of >10 µg l^{-1} has also been reported for *Scenedesmus subspicatus* in a 96 h test (Geyer et al. 1985).

Freshwater Mesocosm Experiments

A long-term mesocosm study using the freshwater snail *Lymnaea palustris* is reported by Baturo et al. (1995). Snails were caged for 10 to 12 weeks in outdoor artificial pools (12 m^3) into which sediment, plants, invertebrates and fish had been introduced. Pools were treated with hexachlorobenzene by spraying to give nominal concentrations of 0.5, 1.25 and 5 µg l^{-1}, without replication, and compared with triplicate control pools. There was no effect on snail mortality at any concentration. Growth of juveniles from untreated mesocosms was not affected at any concentration when caged in the treated mesocosms; growth of adults was significantly lower in the lowest and highest concentrations of hexachlorobenzene, but not at the intermediate level. Fecundity and the utilisation of glycogen and polysaccharides were increased compared with controls at all concentrations. Based on the absence of analytical monitoring to define the exposure, the absence of treatment replicates, and the lack of a dose-effect relationship, this study was considered unreliable for risk assessment purposes (validity category 3).

Caspers (1993) conducted a long term (6 months) exposure of mesocosm ponds to determine the effects of hexachlorobenzene. No effects were seen in the species composition or abundance in the exposure ponds following repeated dosing (1 and 3 times per week for the duration of the study) at a nominal concentration of 10 µg l^{-1} (to achieve a target concentration of approximately 6 µg l^{-1}). The measured concentrations were much lower, usually in the range of 0.01 – 0.2 µg l^{-1}, with the maximum measured concentration being 3 µg l^{-1}. High BCF values were measured for algae, ostracada and a *Notonecta* species. Despite these high BCF values, no negative effects in abundance, motility, food uptake or reproduction were seen in these species. Due to the absence of any effects a mesocosm neither a NOEC, or a LOEC, could not be determined.

Summary of Chronic Freshwater Toxicity

Many of the valid chronic tests of hexachlorobenzene toxicity to fish, invertebrates, and algae, with the exception of a single test on *Daphnia magna*, have been tested at concentrations in excess of the limit of water solubility of hexachlorobenzene. In many cases either the NOEC or the LOEC of the test is at a concentration which is close to the limit of water solubility (5 µg l^{-1}). Whilst some of these tests do suggest that there may be some effects in some organisms at hexachlorobenzene concentrations around the limit of solubility, there is only a single test which has reported any effects due to hexachlorobenzene at concentrations below the limit of water solubility. This was a test on *Daphnia magna* (Scheubel 1984), although another test on the same

species showed effects at levels slightly above the limit of solubility (Caspers et al. 1993). A further 7 tests have reported NOEC values which are at, or below, the limit of water solubility of hexachlorobenzene (5 µg l^{-1}), with reported NOEC values between 3.3 and 5.0 µg l^{-1}. For the purpose of PNEC derivation the NOEC or EC_{10} values of all other tests which have reported an effect due to hexachlorobenzene at a concentration which is above the limit of water solubility of hexachlorobenzene are considered to be equal to the limit of water solubility (5 µg l^{-1}).

Chronic Marine Toxicity

Fish

One longer term study with marine fish is available. This was a 10-day exposure of Gulf killifish (*Fundulus grandis*) under flow-through conditions with analysis of the solutions. The maximum concentration tested of 5.7 µg l^{-1} (approximately equal to the limit of water solubility) had no significant effect on survival, haematocrit and plasma cortisol levels. Because of the relatively short duration and the non-standard endpoints, other than survival, the result should be used with care (validity category 2) (Laska et al. 1978).

No chronic toxicity to marine fish is reported at concentrations up to and including the water solubility of hexachlorobenzene (5 µg l^{-1}). For risk assessment purposes, the NOEC for marine fish is equal to or greater than 5 µg l^{-1}.

Invertebrates

Two long-term toxicity studies are reported for two marine invertebrates, a 48 hour reproduction test on marine ciliates has been reported by Persoone and Uyttersprot (1975) and a long term growth study on marine crabs (*Portunus pelagicus*) has been reported by Mortimer and Connell (1995).

Mortimer and Connell (1995) performed a nonstandard test on juvenile marine crabs which assessed the growth rate of crabs exposed to hexachlorobenzene over forty two days under semi-static conditions. Growth was assessed in terms of carapace width and was observed between the first and sixth crab instars during tests. Growth inhibition was only observed at one hexachlorobenzene test concentration (5 µg l^{-1} nominal). EC_{10} and EC_{50} concentrations could not be reported for hexachlorobenzene because effects were only observed at the highest tested concentration. The study lacked any analytical confirmation of exposure concentrations, although the authors noted that earlier studies found a 10% to 20% reduction in exposure concentrations (for chlorinated benzenes generally) over 24 hours, which was the time period between media replacements. The NOEC from this test is 4 µg l^{-1} (nominal concentration). This test is considered to be valid with restrictions due to the lack of analytical confirmation of the exposure concentrations, although it does indicate the possibility of sublethal effects on marine invertebrates at concentrations close to the limit of water solubility of hexachlorobenzene.

Persoone and Uyttersprot (1975) tested the effects of hexachlorobenzene on the growth of the ciliate *Euplotes vannus* at concentrations in excess of the limit of water solubility and found limited effects on reproduction at all tested concentrations. This test is not considered to be valid for PNEC derivation because no clear dose response was observed. Since all tests were performed at concentrations in excess of the limit of water solubility the exposure of the test organisms to dissolved hexachlorobenzene may have been similar in all cases.

Algae

Biggs et al. (1979) report a study using two species of marine algae, *Thalassiosira pseudonana* and *Dunaliella tertiolecta*, tested together as a mixed culture. The test was static, with no analysis of the solutions, and was therefore not considered valid. However, no effects were observed on algal growth or size at the maximum concentration tested (100 µg l^{-1}). This suggests that these marine algal species are not sensitive to hexachlorobenzene at or above the limit of water solubility.

PNEC Derivation

Freshwater PNEC using Assessment Factor method

The geometric mean of the two NOEC values, of 0.13 and 5 µg l^{-1} (set to the limit of solubility), for effects on the reproduction of *D. magna* (0.81 µg l^{-1}) is the most sensitive reliable NOEC for PNEC derivation. Applying an assessment factor of 10 to this species mean NOEC gives a PNEC of 0.08 µg l^{-1}. If the PNEC is derived from the lower of the two results (0.13 µg l^{-1}) with the same assesment factor then a PNEC of 0.013 µg l^{-1} is calculated.

An annual average environmental quality standard of 0.01 µg/l was derived under the Water Framework Directive for surface water. This is derived from the NOEC value of 0.13 µg l^{-1} for effects on the reproduction of *D. magna* with an assessment factor of 10 applied for PNEC derivation. This standard is not applied because it is not considered to be sufficiently protective of all ecosystem effects. Compliance with the EQS for hexachlorobenzene is assessed in biota. A maximum allowable concentration of 0.05 µg/l was also derived for hexachlorobenzene in surface water.

Freshwater PNEC using Species Sensitivity Distribution method

There are a total of 19 valid (category 1 or 2) tests, although these are not all considered to be suitable for PNEC derivation. Some of the tests are relatively short for chronic tests (*Procambarus clarki*, *Micropterus salmoides* and some tests on *Daphnia magna* and *Pseudokirchneriella subcapitata*) and are therefore not included. There are multiple data for both *Daphnia magna* and *Pimephales promelas*, and in these cases a species geometric mean has been applied. In the case of *D. magna* only reproduction endpoints were used giving a NOEC of 1.35 µg l^{-1}. The NOEC used for *P. promelas* was 4.27 µg l^{-1}. This leaves data for 8 species for use in an SSD (2 fish, 5 invertebrate and one algal species). The remaining dataset does not meet three of the eight London Workshop criteria (ECHA 2008) for representation of taxonomic groups, but does include fish, crustaceans, amphipods, oligochaetes and algae. There are no test data available for the effects of hexachlorobenzene on higher aquatic plants, or insects.

The valid ecotoxicity data generally suggest that there will either be no effects, or slight effects, at the water solubility limit of hexachlorobenzene, with the exception of a single study on *Daphnia magna*. As a result of this the distribution of NOEC (or EC_{10}) values within the ecotoxicity database is likely to reflect the differences and uncertainties in the true water solubility limit of hexachlorobenzene in each of the test systems. This ecotoxicity dataset is therefore unlikely to reflect the range of sensitivities of the test species to hexachlorobenzene. The use of an SSD to derive a PNEC for hexachlorobenzene is therefore not recommended.

Marine PNEC using Assessment Factor method

The most sensitive reliable NOEC for effects on marine organisms is the 42 d NOEC for growth of *P. pelagicus* (Mortimer and Connel 1995) of 4 µg l^{-1}. No reliable tests are available for marine specific taxa, such as echinoderms. An increased assessment factor is therefore required to calculate the marine PNEC compared to the freshwater PNEC. Applying an assessment factor of 100 to this NOEC gives a PNEC of 0.04 µg l^{-1} (40 ng l^{-1}). This is lower than the PNEC derived for freshwater ecosystems. The most sensitive effects observed in marine organisms occurred at concentrations close to the limit of water solubility of hexachlorobenzene, which indicates that marine species may not be any more sensitive than freshwater species.

Marine PNEC using Species Sensitivity Distribution method

There are insufficient valid data for marine organisms to generate an SSD on the basis of either the marine or combined freshwater and marine datasets.

Summary of PNEC derivation

PNECs for both freshwater and marine aquatic ecosystems have been derived according to both the assessment factor method and the species sensitivity distribution method, and are shown in Table 7.

Table 7 PNECs calculated for aquatic effects

Derivation	PNEC (µg l^{-1})
Freshwater (assessment factor method)	0.08
Marine (assessment factor method)	0.04

4.2 Sediment effects

As hexachlorobenzene is relatively insoluble in water and partitions strongly onto sediment, it is therefore appropriate to consider its toxicity to organisms living in the sediment.

Toxicity tests

Five studies provide data on ten tests considering the effects of treated sediments for six species of sediment-dwelling invertebrates and in three cases the data were collected under saltwater or estuarine conditions. The results of five of the reported tests are considered to be valid for PNEC derivation without restrictions, and three of the tests are considered to be valid with restrictions. The validity of the remaining two tests could not be confirmed (Fuchsman et al, 1998b).

Available data on the effects on benthic organisms of hexachlorobenzene in sediment are summarised in Appendix 3. McLeese and Metcalfe (1980) reported no mortality in sand shrimp *Crangon septemspinosa* exposed for 96 h to a maximum measured sediment concentration of 0.3 mg hexachlorobenzene kg^{-1} dry weight. Hexachlorobenzene was added to the glass vessels in a solvent, which was then evaporated. Hexachlorobenzene was allowed to partition to the sediment and overlying water during the test. The overlying water concentrations were not

reported but the paper reported an aqueous 96 h LC_{50} of >7.2 µg l^{-1}) and partitioning may not have been complete when the animals were added. The result of this test should therefore be used with care. The sediment was sand with a low organic carbon (OC) content (0.28%). The LC_{50} would be >2.1 mg kg^{-1} dry weight if normalised to an OC content of 2%.

Meller et al. (1998) conducted short-term (72 hour) sediment toxicity tests for assessment of lethal and sublethal effects of hexachlorobenzene on two species of oligochaete worms (*Tubifex tubifex* and *Limnodrilus hoffmeisteri*) at concentrations of up to 1000 mg kg^{-1}. The test system used artificial sediment of similar composition to the artificial soil employed in OECD Guideline number 207 (OECD 1984) containing 2% organic carbon, and reconstituted water according to OECD guideline number 203 (OECD, 1983), at a ratio of 1 part sediment to 4 parts water by volume. The sediments were spiked with hexachlorobenzene dissolved in n-hexane, which was used to coat the sand fraction of sediment prior to mixing, and the tests included a solvent control. There was no feeding or aeration during tests. Organisms were assessed for three sub-lethal endpoints: reworking activity, sediment avoidance and autonomy (the local constriction of circular muscles and/or the loss of body segments) in addition to mortality, although the "reworking activity" endpoint could only be assessed quantitatively. Hexachlorobenzene did not cause any sub-lethal or lethal effects in any of the experiments up to a maximum tested concentration of 1000 mg kg^{-1} dry weight. These tests resulted in unbounded NOECs of 1000 mg kg^{-1} dry weight for both species, although a lack of analytical confirmation of the exposure concentrations means that the test is considered to be reliable with restrictions for PNEC derivation.

The effects of hexachlorobenzene-spiked sediment, on the survival and growth of the amphipod *H. azteca* and the midge *Chironomus tentans* after 14 days exposure were investigated by Barber et al. (1997). The tests were carried out according to ASTM standard methods, with analysis of the sediment concentrations, and are considered valid. There were no effects on either species at the maximum (measured) sediment concentration tested, which was 84 mg kg^{-1} dry weight (normalised for 2% OC). The authors concluded that this was consistent with the absence of toxicity at the solubility limit in aqueous toxicity tests and that there was no evidence of toxicity as a result of sediment ingestion. Unbounded NOECs of >84 mg kg^{-1} (dry weight) can therefore be derived from this test for both *H. azteca* and *C. tentans*.

Fuchsman et al. (1998a) investigated the effects of hexachlorobenzene-spiked sediments on the survival and growth of *C. tentans* (freshwater), the estuarine amphipod *Leptocheirus plumulosus* (at a salinity of 10‰) and *H. azteca* (under both freshwater and estuarine conditions). The 10-day tests were according to ASTM methods. Although the sediment used for spiking was known to contain a number of contaminants, including hexachlorobenzene, these were below the level causing significant effects. No significant incremental effects of the spiked hexachlorobenzene were detected for any of the species at the maximum measured concentration of 240 mg kg^{-1} dry weight, which was equivalent to 120 mg kg^{-1} dry weight when normalised to 2 % OC.

Fuchsman (1998b) exposed *Hyalella azteca* and *Chironomus tentans* for 14 days to riverine sediments containing approximately 1.8% organic carbon, and spiked with hexachlorobenzene to levels of between 10 and 250 mg kg^{-1}. Analytical confirmation of the hexachlorobenzene concentrations revealed the actual concentrations to be approximately 50% of nominal concentrations. No effects were observed at any of the test concentrations and therefore an unbounded NOEC of approximately 125 mg kg^{-1} can be tentatively identified, which is consistent with the above findings by the same authors, although the reliability of this study could not be determined from the reported information (reliability code 4).

The absence of effects at 84 mg kg^{-1} dry weight (Barber et al. 1997) and 120 mg kg^{-1} dry weight (Fuchsman et al. 1998a and b) is in agreement with the predicted sediment quality criterion of 111.4 mg kg^{-1} dry weight (also normalised to 2 % OC) calculated by the New York Department of Environmental Conservation (1993) using the equilibrium partitioning method, although the parameters used for this estimate are not reported.

Van Leeuwen et al. (1992) used a toxicity QSAR approach, employing only $logK_{OW}$ (value used = 5.73) and molecular weight, to estimate the sediment hexachlorobenzene level at which 95% of species in the freshwater community are unlikely to be affected. The QSAR-derived level for hexachlorobenzene for benthic organisms was estimated to be 2.32 mg kg^{-1} dry weight (normalised to 2 % total OC content). The corresponding aquatic (dissolved) concentration was 0.38 µg l^{-1}.

The laboratory studies and predictions described above contrast markedly with predictions based on field data. Persaud et al. (1991) estimated a lowest-effect level for hexachlorobenzene of 0.04 mg kg^{-1} sediment (dry weight, normalised to 2% total OC content) using co-occurrence data for sediment concentrations and benthic species in the Great Lakes. The authors also estimated that benthic communities would be seriously impacted at sediment concentrations at or above 0.24 mg kg^{-1} hexachlorobenzene dry weight. For marine sediments, a similar approach, known as the Apparent Effects Threshold (AET) approach, was used to estimate the sediment concentration of hexachlorobenzene above which significant effects on benthic community composition were expected (Tetra Tech Inc. 1986). Using this approach, the effects threshold for hexachlorobenzene in marine sediment was predicted to be 7.6 µg kg^{-1} dry weight (normalised to 2% total OC content). IPCS (1997) and Barber et al. (1997) point out the limitations of these field techniques, in that that they are unable to attribute effects to any one contaminant and that impacted areas are invariably contaminated with a variety of chemicals.

Sediment PNEC derivation

The lowest reported NOECs from sediment toxicity tests are the 14 d unbounded NOECs of >84 mg kg^{-1} dry weight (normalised for 2% OC) for both *Hyalella azteca* and *Chironomus tentans* (Barber et al. 1997). Similar studies on estuarine organisms (*Leptocheirus plumulosus*) have also shown no effects at the highest tested concentrations (Fuchsman et al. 1998a) indicating that marine sediment organisms are not expected to be any more sensitive to the effects of hexachlorobenzene than freshwater sediment organisms. Additionally, a test on *Hyalella azteca* was performed under estuarine conditions by the same author and the same result was reported. No effects have therefore been observed in sub-lethal tests of 10 days or longer duration in three species, including two marine or estuarine species, representing different living and feeding conditions. The available sediment test data are, however, of relatively short duration (maximum 14 days), although none report any effects for lethal or sub-lethal endpoints. Bioaccumulation tests with sediment organisms (Egeler et al., 2001) have shown that *Tubifex tubifex* reached steady state with respect to the bioaccumulation of hexachlorobenzene from sediment within 10 days. An assessment factor of 50 is therefore considered to be appropriate for the derivation of a freshwater $PNEC_{sediment}$ according to the REACH guidance (ECHA 2008):

$PNEC_{sediment}$ = >84 mg kg^{-1} (dry weight)/50 = >1.7 mg kg^{-1} (dry weight)

The same data is also used to derive the $PNEC_{Sediment}$ for marine waters although a larger assessment factor is applied because of the greater diversity of marine ecosystems. In this case the $PNEC_{Sediment}$ is derived using an assessment factor of 100 (ECHA 2008):

$PNEC_{sediment}$ = >84 mg kg^{-1} (dry weight)/100 = >0.84 mg kg^{-1} (dry weight)

The $PNEC_{Sediment}$ can also be expressed on a wet weight basis, assimg a wet weight of freshly settled sediment of 1150 kg m^{-3}, of which 250 kg m^{-3} is solid material (ECHA 2012). This results in a freshwater $PNEC_{Sediment}$ of >0.37 mg kg^{-1} (wet weight). The $PNEC_{Sediment}$ for marine waters is 0.045 mg kg^{-1} (wwt).

A $PNEC_{sediment}$ (both freshwater and marine) can also be calculated by using the equilibrium partitioning equation (ECHA 2008), for details see Appendix 4. $PNEC_{sediment}$ values derived by equilibrium partitioning are shown in Table 8. The PNEC sediment values of Table 8 were calculated at an organic carbon content of 2% using different sources for the $PNEC_{aqua}$ and the K_{OC} value used.

The $PNEC_{sediment}$ derived by equilibrium partitioning is calculated to be >0.49 mg kg^{-1} (wet weight) from the $PNEC_{water}$ of 0.31 or 0.14 µg l^{-1}, the K_{OC} value for hexachlorobenzene and the standard environmental characteristics provided by the REACH guidance. This is equivalent to a $PNEC_{sediment}$ of 0.23 mg kg^{-1} (dry weight). The K_{OC} value calculated using the QSAR of the REACH guidance for predominantly hydrophobic substances is 36,308 and the K_{OC} value calculated by PCKOC is 3,380.

Table 8 PNEC sediment values (mg kg^{-1} (wwt)) calculated by the equilibrium partitioning method

	K_{OC} source	
PNEC	**QSAR** (from ECHA guidance)	**PCKOC**
FW AF	0.221	0.021
SW AF	0.126	0.012

The above values for the $PNEC_{sediment}$ (on a wet weight basis) derived by equilibrium partitioning are consistent with that derived from laboratory toxicity testing, for the QSAR from the ECHA guidance. The comparability of the $PNEC_{sediment}$ when calculated from both sediment effects data and by equilibrium partitioning support the assumption that the exposure of sediment dwelling organisms is principally as a result of the sediment pore water concentration.

The $PNEC_{sediment}$ is therefore >1.7 mg kg^{-1} (dry weight), or >0.37 mg kg^{-1} (wet weight).

4.3 Predator effects

The oral toxicity of hexachlorobenzene has been studied in several organisms and has been summarised previously (Van de Plassche 1994, FHI 2005). Data are available for five mammals, and one bird species, with most from studies on reproductive endpoints. The data are summarised in Table 9. The most sensitive species in the data set are mink (*Mustela vison*) and ferret (*Mustela putorius*), with NOECs of 0.5 mg kg^{-1} (wet weight) hexachlorobenzene in food for both species.

Table 9 Mammal and bird oral toxicity data for hexachlorobenzene

Species	Duration	Endpoint	NOEC (mg kg^{-1} food)	Reference
Mink (*Mustela vison*)	1 generation	Reproduction	0.5	Rush et al. 1983
Ferret (*Mustela putorius*)	1 generation	Reproduction	0.5	Van de Plassche 1994
Quail (*Coturnix c. japonica*)	90 d	Reproduction	5	Vos et al. 1968
Rat (*Rattus norvegicus*)	2 generations	Reproduction	18	Van de Plassche 1994
Dog (*Canis domesticus*)	1 yr	Growth	52	Van de Plassche 1994
Cat (*Felix domesticus*)	1 generation	Reproduction	88	Van de Plassche 1994

The NOEC values for both the mink and the ferret are derived as the LOEC/2, the NOEC for the rat is derived as the geometric mean of two values (8 and 40 mg kg^{-1} wet weight in food) and the NOEC value for the dog is derived as the NOAEL x 40 (body weight/daily food intake). In the reproduction study on mink (Rush et al. 1983) 44% effects were observed at the LOEC concentration of 1 mg kg^{-1} in food. Such a high incidence of effects at the LOEC level would typically preclude inclusion of these data. Mink are, however, clearly sensitive to the effects of hexachlorobenzene and to exclude these data would compromise the reliability of the assessment. The same data extrapolation as has been applied previously (Van de Plassche 1994, FHI 2005) has therefore been used in this assessment.

Derivation of $PNEC_{oral}$ by the assessment factor method

$PNEC_{oral} = TOX_{oral} / AF_{oral}$

The assessment factor applied (AF_{oral}) should allow for interspecies variation, acute or subchronic to chronic extrapolation, and laboratory data to field impact extrapolation in the effects assessment of predators. A factor of 30, accounting for both interspecies variation and laboratory to field extrapolation, is considered to be appropriate for this purpose.

This results in a $PNEC_{oral}$ value of 16.7 µg kg^{-1} (wet weight in food)

Whilst there is considerable uncertainty surrounding the extrapolated NOEC for mink, which is the most sensitive endpoint studied, the application of an assessment factor of 30 to derive the $PNEC_{oral}$ is considered to be sufficient to ensure an adequate level of protection for top predators.

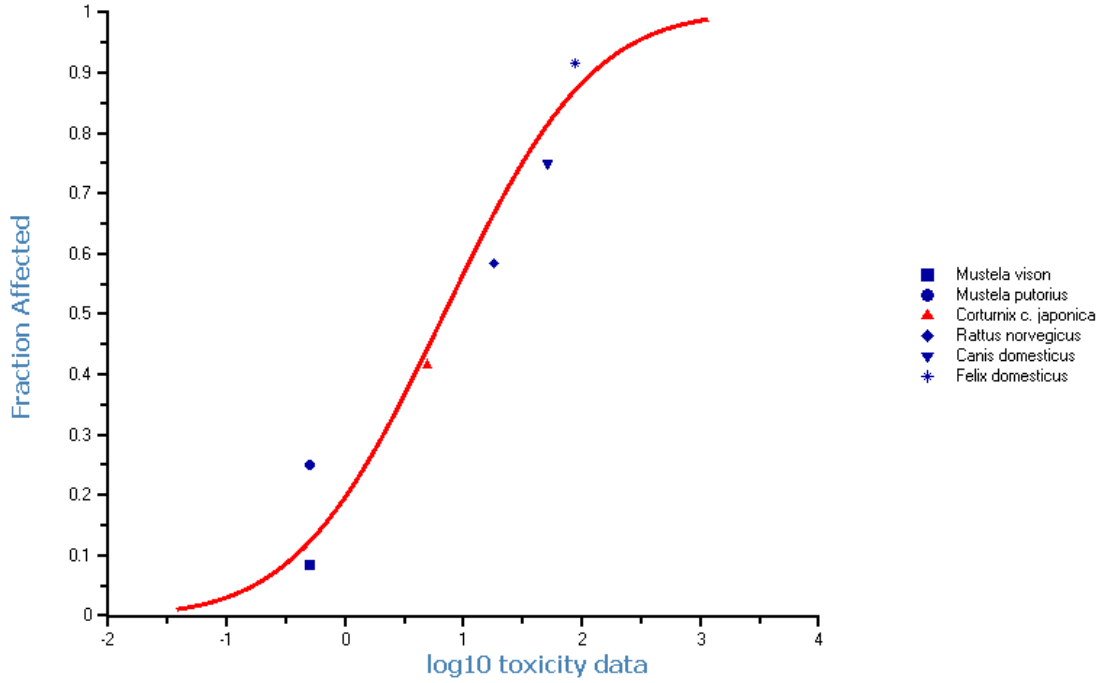
Applying an assessment factor of 10 to the extrapolated mink NOEC of 0.5 mg kg^{-1} would result in a $PNEC_{oral}$ of 50 µg kg^{-1}. Whilst the effects dataset of relevant feeding studies on birds and

mammals is relatively extensive, and mink are clearly a relevant wildlife species with potential exposure to bioaccumulating contaminants from aquatic food webs (Moore et al. 1997) the uncertainties surrounding the NOEC derivation suggest that such a low assessment factor may be inadequate to ensure protection of all predators.

Derivation of $PNEC_{oral}$ by the species sensitivity distribution method

A species sensitivity distribution (SSD) can be derived for hexachlorobenzene toxicity to birds and mammals in feeding studies, using the data shown in Table 9. The resulting SSD, calculated using ET_X 2.0 (Van Vlaardingen et al. 2004), and shown in Figure 3, passes all goodness of fit tests for a log-normal distribution and results in an HC_5 of 0.133 mg kg^{-1} (90% confidence interval of 0.0016 to 0.95 mg kg^{-1}). No guidance is currently available on SSD use for derivation of a $PNEC_{oral}$, although the dataset includes six different species, including one bird.

Figure 3 SSD of mammalian and bird toxicity data from feeding studies for hexachlorobenzene (mg kg^{-1} wet weight in food)



The assessment factors applied in the derivation of the $PNEC_{oral}$ are 3 times higher than those applied in the aquatic effects assessment. This difference is due to the differences in food intake rates between organisms in the field and in laboratory tests. Additionally, some predator species may have particularly sensitive life-cycle stages, such as hibernation or migration, which may make them more susceptible to the effects of chemicals. The assessment factors applied to the HC_5 from the species sensitivity distribution are therefore 3 times higher than those which would be applied to an HC_5 derived for aquatic effects.

HC_5	0.133	
PNEC	(AF = 3)	44.3 µg kg^{-1} (wet weight)
PNEC	(AF = 9)	14.7 µg kg^{-1} (wet weight)
PNEC	(AF = 15)	8.9 µg kg^{-1} (wet weight)

PNEC based on Assessment Factor method (AF = 30) = 16.7 µg kg^{-1} (wet weight)

The PNECs derived by the SSD approach (using AFs of between 3 and 15) are similar to that derived by the AF approach on the most sensitive data (using an AF of 30).

Using the small sample assessment within the *E_TX* programme allows the calculation of a Hazardous Dose for 5% of mammals or birds using a preselected standard deviation. This method allows a percentile of an SSD to be derived from a very small sample of data, by assuming a standard deviation from a different dataset. This analysis considers the use of 2 external standard deviations, which were derived from pesticide toxicity data for either birds or mammals. Table 10 shows the HD_5 estimate using a standard deviation from pesticide toxicity to mammals (69 LD_{50}s) and Table 11 shows the HD_5 estimate using data for pesticide toxicity to birds (55 LD_{50}s). Whilst there is considerable uncertainty associated with this analysis, due to the fact that it is not based entirely on data for hexachlorobenzene, it does not suggest that there are likely to be any species which are more sensitive to hexachlorobenzene than mink. This therefore supports the assertion that mink are likely to represent the most sensitive species to hexachlorobenzene.

Table 10 HD_5 estimate using mammalian toxicity data

	mg kg^{-1} food (wet weight)	Extrapolation Factor
HD_5	1.75	3.91
HD_5 (lower limit)	1.00	6.82
HD_5 (upper limit)	3.06	2.24

Table 11 HD_5 estimate using bird toxicity data

	mg kg^{-1} food (wet weight)	Extrapolation Factor
HD_5	1.17	5.82
HD_5 (lower limit)	0.57	11.94
HD_5 (upper limit)	2.42	2.84

The estimated HD_5 values (1.17 and 1.75 mg kg^{-1}) are both higher than the NOECs for both mink and ferret (0.5 mg kg^{-1} wet weight in food), and indicate that these species are likely to be sensitive to hexachlorobenzene. Whilst the SSD approach is not usually applied for $PNEC_{oral}$ derivation these considerations suggest that using the extrapolated mink NOEC for PNEC derivation is likely to be protective of other potential consumers.

Conclusion on $PNEC_{oral}$ derivation

Consideration of NOEC data and $PNEC_{oral}$ values above indicates that the available data for mink and ferrets represent sensitive species for this contaminant. $PNEC_{oral}$ values using different methods and assessment factors are summarised in Table 12.

Table 12 Summary of $PNEC_{oral}$ values derived

Method	Assessment Factor	$PNEC_{oral}$ ($\mu g\ kg^{-1}$ wet weight)
Assessment Factor	30	16.7
Assessment Factor	10	50
Species Sensitivity Distribution	15	8.9
Species Sensitivity Distribution	9	14.7
Species Sensitivity Distribution	3	44.3

Given the relatively small differences between possible $PNEC_{oral}$ values when derived by the assessment factor and the species sensitivity distribution approaches it is proposed to apply an assessment factor of 30 to the extrapolated NOEC value of 0.5 mg kg^{-1} in food for mink. The same approach has also been used previously for assessments of the effects of hexachlorobenzene on predatory organisms (Van de Plassche 1994, FHI 2005), and is used as the basis for establishing the EQS for biota under the Water Framework Directive.

An alternative effects assessment for hexachlorobenzene has been applied by Moore et al. (1997) in a risk assessment of hexachlorobenzene exposure to mink in Canada. The approach taken in this risk assessment estimated impacts on the total kit biomass, at 6 weeks of age, per female as a function of the hexachlorobenzene dose. An EC_{10} for total kit biomass at 6 weeks of age of approximately 25 $\mu g\ kg^{-1}$ (body weight) d^{-1} can be derived from the calculated dose response curve. Assuming an average body weight of 1 kg and an average food ingestion rate of 0.16 kg kg^{-1} (body weight) d^{-1} for female mink (Bleavins and Aulerich 1981) allows a body weight/daily food intake conversion factor of 6.25 to be derived. This results in an estimated EC_{10} for total kit weight at 6 weeks of 156 $\mu g\ kg^{-1}$ when expressed as a concentration in food. The resulting margin of safety between the $PNEC_{oral}$ (based on the Assessment Factor approach) and the estimated EC_{10} for total kit weight at 6 weeks of age per female is a factor of 9.

A $PNEC_{oral}$ of 16.7 $\mu g\ kg^{-1}$ (wet weight) in food will be used for this risk assessment.

Environmental Quality Standards have been set on a European level for hexachlorobenzene under the Water Framework Directive. A standard of 10 $\mu g\ kg^{-1}$ has been set biota, and compliance is to be assessed against the levels in fish. This standard is comparable to the $PNEC_{oral}$ value derived above.

4.4 Summary of PNECs used in the risk assessment

PNEC values have been derived for effects on the freshwater aquatic and sediment ecosystems, marine ecosystems and predatory organisms. A tentative critical concentration for hexachlorobenzene in the livers of birds and mammals has also been derived. The values used in the risk assessment are summarised in Table 13, along with the assessment factors applied in their derivation.

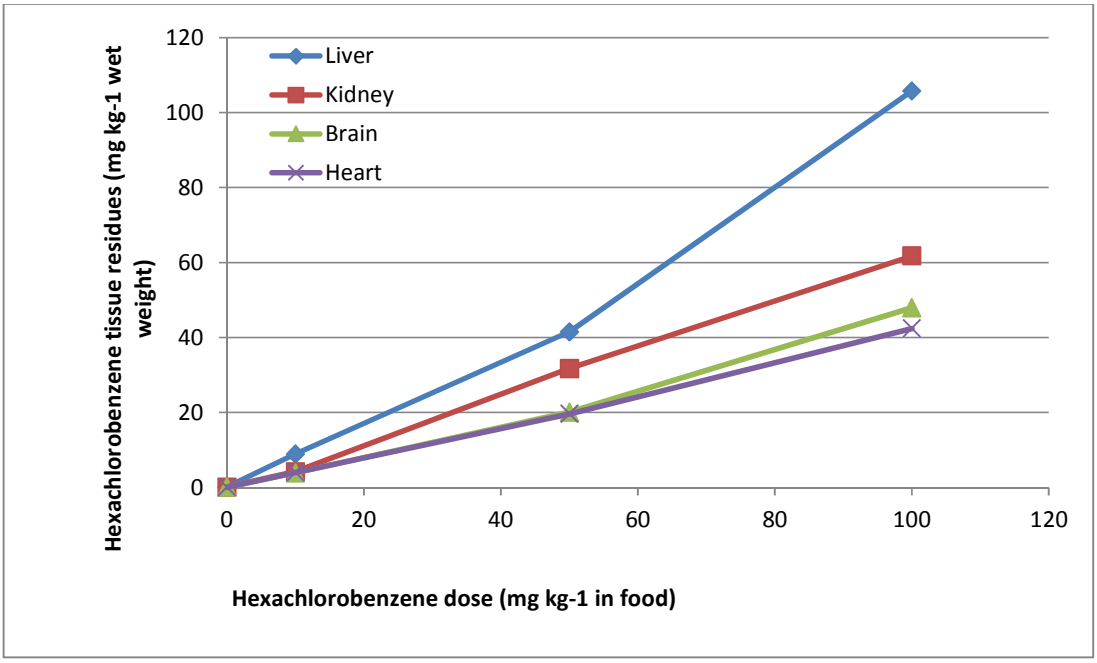
Table 13 PNEC values used in the risk assessment

Endpoint	PNEC	Units	Assessment Factor
Aquatic freshwater	0.08	µg l^{-1}	10
Aquatic marine	0.04	µg l^{-1}	50
Sediment	>21	mg kg^{-1} wwt	10
Predator food	16.7	µg kg^{-1} wwt	30

5. Critical body burdens

A study of the effects of hexachlorobenzene on some enzyme activities in male rats (Mendoza et al. 1976) also determined the concentrations of the substance in several tissues following 61 days of exposure to contaminated food (at levels of 10, 50 or 100 mg kg^{-1} food). Esterase activities in the livers of rats were observed to increase linearly with increasing dose of hexachlorobenzene in the food. Hexachlorobenzene residues in the liver (on a wet weight basis) appear to be comparable to concentrations of hexachlorobenzene in food for rats (Mendoza et al. 1976). Linear relationships between hexachlorobenzene concentrations in the food and the resulting tissue residues were observed for all tissues studied (liver, kidney, brain and heart; see Figure 4).

Figure 4 Hexachlorobenzene concentration in rat tissues as a function of concentration in food (Mendoza et al. 1976)



The NOEC for rats used in the SSD for hexachlorobenzene is 18 mg kg^{-1} in food, which is equivalent to a concentration of 18.2 mg kg^{-1} (wet weight) in rat liver, when estimated from the data of Mendoza et al. (1976) (r^2 = 0.98). Assuming that similar partitioning occurs in other mammalian species, such as mink and polar bear (*Ursus maritimus*), an acceptable concentration

of hexachlorobenzene in different animal livers can be estimated. This results in an estimated critical body burden in mink liver of 0.51 mg kg^{-1} (wet weight), which is equivalent to 510 ng g^{-1} (wet weight).

Expressing the hexachlorobenzene dose in the food of rats as a daily intake rate, rather than as a concentration in food, may allow a more appropriate extrapolation to the liver concentrations in mink. The concentration of hexachlorobenzene in rat livers (in mg kg^{-1} wet weight) can be estimated as 8.43 times the hexachlorobenzene dose, in mg kg^{-1} (body weight) d^{-1}. Converting the extrapolated $NOEC_{oral}$ for mink to a dose in mg kg^{-1} (body weight) d^{-1} allows a critical liver concentration for mink to be estimated as 674 ng g^{-1} (wet weight), assuming that the NOAEL for mink is 0.08 mg kg^{-1} (body weight) d^{-1}. This value is very close to that calculated without conversion of food concentrations to daily ingestion rates and the value of 510 ng g^{-1} (wet weight) will therefore be used as the critical liver concentration for hexachlorobenzene in mink.

A LOEC for quail is reported at a concentration of 20 mg kg^{-1} in food (Vos et al. 1968, cited in WHO 1970), which resulted in liver residue concentrations of 36 mg kg^{-1} (assumed to be on a wet weight basis). Extrapolating from this LOEC value to a NOEC value by dividing by 2 results in a NOEC of 10 mg kg^{-1} in food and a resulting critical body burden of 18 mg kg^{-1} in the liver (equivalent to 18,000 ng g^{-1} wet weight). A further study (Vos et al. 1970) identified a NOEC for hexachlorobenzene in the diet of quails of 1 mg kg^{-1} (assumed to be on a wet weight basis) using liver weight and biomarker responses as the endpoint, with an associated mean liver residue of 0.79 mg kg^{-1} in female birds. Female birds had consistently lower body residues than male birds, which was assumed to be due to the excretion of hexachlorobenzene in eggs. The mean liver residue concentration in birds from the LOEC group (5 mg kg^{-1} in food) was 6.88 mg kg^{-1}. A critical body residue of 790 ng g^{-1} wet weight in the liver can therefore be assumed for these endpoints in the quail.

A NOEC of 5 mg kg^{-1} in food was used for reproductive effects in the quail, which appears to have been taken from the same report. Reduced egg volumes and egg hatchability were noted at feed concentrations above this level. The ecological consequences of reduced liver weight and increased coproporphyrin excretion are unclear, and it is proposed to use the NOEC of 5 mg kg^{-1} (wet weight) for reproductive effects as used previously (FHI 2005, RIVM 1994), with the associated critical body burden of 6.88 mg kg^{-1} in female birds (6,880 ng g^{-1} wet weight).

A study of the perinatal toxicity of hexachlorobenzene to mink (*Mustela vison*) (Rush et al. 1983) looked at the effects on young mink which were exposed by three potential routes: in utero throughout gestation, from milk during lactation, and from contaminated food consumed directly prior to weaning. The mink were fed commercial food contaminated with hexachlorobenzene at levels of 0, 1 or 5 mg kg^{-1} and several tissues of surviving young were analysed for hexachlorobenzene at the end of the study. Hexachlorobenzene was detected in the fat of surviving young from all of the treatment groups at concentrations which increased linearly with increasing concentrations in the feed. Hexachlorobenzene was also detected in the liver of surviving young from the highest treatment group (5 mg kg^{-1} in food) at a level of 36.7 ng g^{-1}, but was reported as being undetected in the livers of young from other treatment groups. The limit of detection for the analytical method was not reported, although a concentration of 1.4 ng g^{-1} was reported in the muscle of young from the 1 mg kg^{-1} diet treatment group, suggesting that the liver residues in this treatment group may have been lower than 1.4 ng g^{-1}. The study found 44% mortality in kits from the 1 mg kg^{-1} treatment group and 77% mortality in the 5 mg kg^{-1} treatment group. Despite the relatively high level of effects observed the 1 mg kg^{-1} treatment has previously been extrapolated to a NOEC by dividing by a factor of 2 (Van de Plassche 1994, FHI 2005). The only effects noted in the surviving mink kits were p-450 and EROD induction and the reasons for the high mortality are unclear.

A liver concentration can be extrapolated from the NOEC for hexachlorobenzene in food for the mink of 0.5 mg kg^{-1}, assuming that a linear relationship exists between the concentrations of hexachlorobenzene in the diet and the levels of residues in the liver, as has been observed in rats. This results in a critical tissue level of 3.7 ng g^{-1} for hexachlorobenzene in mink liver. The assumption of a linear relationship between the hexachlorobenzene levels in food and the resulting liver residues in mink kits may, however, not be valid given that the substance was not detectable in the livers of surviving kits from the 1 mg kg^{-1} treatment group. Given that the tissue residue data relate only to the surviving kits, and not to the levels in the parent animals for which the reproductive effects were observed, this data is considered to be of questionable relevance to the derivation of an acceptable liver residue of hexachlorobenzene in wildlife.

A study of the oncogenicity of hexachlorobenzene to mice, rats and hamsters (Erturk et al. 1985) reported the levels of hexachlorobenzene in the liver, brain and fat following dietary treatment at relatively high levels of exposure for 13 weeks. A linear increase in liver and fat hexachlorobenzene concentrations was observed in response to dietary concentrations, although the lowest tested doses in food were 100 mg kg^{-1} for the mouse and 200 mg kg^{-1} for rats and hamsters. The data for rats can be used to extrapolate a critical body burden in rats, assuming the same degree of accumulation at low doses of hexachlorobenzene in food. The resulting critical body burden for hexachlorobenzene in the liver of rats is 9.0 µg g^{-1}.

The critical liver concentrations derived above are summarised in Table 14.

Table 14 Estimated critical liver residues in mammals and birds (mg kg^{-1} wet weight)

Species	Critical Liver Residue
Mink (using rat data)	0.51
Quail	6.88
Rat	9.0
Rat	18.2

5.1 Critical body burdens for predatory organisms

Four estimates of critical concentrations of hexachlorobenzene in the liver have been made for 3 species (mink, quail and rat). These data are summarised in Table 14 and the SSD is shown in Figure 5, the derived $PNEC_{liver}$ values are shown in Table 15. The resulting SSD passes all goodness of fit tests and results in an HC_5 of 0.28 mg kg^{-1} (wet weight), or 280 ng g^{-1} (wet weight) (90% confidence limits 0.0016 to 1.53 mg kg^{-1} (wet weight)).

Figure 5 Species sensitivity distribution of critical liver residues using 4 estimates for 3 species (mg kg^{-1} (wet weight)).

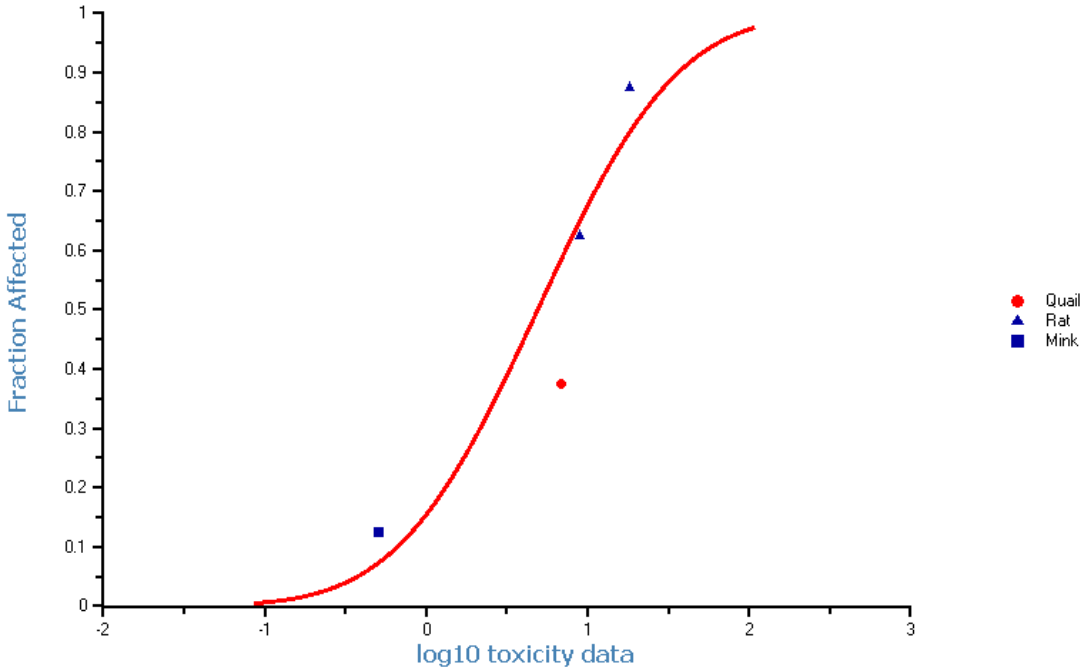


Table 15 Summary of estimated $PNEC_{Liver}$ concentrations for predatory organisms

Estimate	Critical Tissue Concentration (ng g^{-1} wwt liver)	Assessment Factor	$PNEC_{Liver}$ (ng g^{-1} wwt liver)
Estimated mink liver concentration at NOEC	510	30	17
SSD HC_5	280	10	28

Using the small sample assessment within the *E_TX* programme allows the calculation of a Hazardous Concentration for 5% of mammals or birds using a preselected standard deviation. This method allows a percentile of an SSD to be derived from a very small sample of data, by assuming a standard deviation from a different dataset. This analysis considers the use of 2 external standard deviations, which were derived from pesticide toxicity data for either birds or mammals. Table 16 shows the HC_5 estimate using a standard deviation from pesticide toxicity to mammals (69 LD_{50}s) and Table 17 shows the HC_5 estimate using data for pesticide toxicity to birds (55 LD_{50}s).

Table 16 HC_5 estimate using mammalian toxicity data

	mg kg^{-1} (wet weight)	Extrapolation Factor
HD_5	1.25	3.91
HD_5 (lower limit)	0.63	7.73
HD_5 (upper limit)	2.48	1.97

Table 17 HC_5 estimate using bird toxicity data

	mg kg^{-1} (wet weight)	Extrapolation Factor
HD_5	0.84	5.82
HD_5 (lower limit)	0.35	14.04
HD_5 (upper limit)	2.03	2.41

In this case both of the HC_5 values calculated are greater than the estimated critical concentration of hexachlorobenzene in mink liver, indicating that mink are likely to be particularly sensitive to hexachlorobenzene toxicity.

This assessment may be improved through the use of a more relevant external standard deviation. Whilst hexachlorobenzene has been used as a pesticide the data from which the external standard deviations have been derived is likely to include a wide variety of types of compounds and modes of action. By restricting the external dataset to related substances, such as halogenated narcotic substances, and by considering comparable endpoints expressed in terms of internal effect concentrations, a more reliable estimate of the critical liver concentration for predatory organisms may be obtained.

These considerations support the assertion that mink are likely to be highly sensitive to hexachlorobenzene toxicty, and that deriving a threshold for the protection of this species is likely to be protective of other predators. The critical body burden which is selcted for use in the risk assessment of top predators is derived form the lowest (extrapolated) data for mink of 510 ng g^{-1} (wwt) in liver, using an assessment factor of 30 (as applied in the derivation of the $PNEC_{oral}$). This results in a critical liver concentration of 17 ng g^{-1} (wwt) in liver.

5.2 Critical body burden for aquatic organisms

It has been proposed that a critical body burden can be derived for fish (Hoogen and Opperhuizen 1988) through the use of both the effect concentration in water and the bioconcentration factor. This approach assumes that the toxicity of the chemical occurs as a result of a critical concentration being exceeded in the fish tissues. It does not assume that there is a target organ for the substance, and so the approach is principally applicable to substances which act through apolar narcosis. Hexachlorobenzene is believed to act through apolar narcosis in aquatic organisms, although more specific modes of action may be observed in mammals. Indications from analysis of the hexachlorobenzene residues in rats and other mammals indicate that it may be accumulated to varying degrees in different body tissues, although this variability could result from the different lipid contents of the different tissues.

The critical effect concentration for aquatic organisms is the NOEC for *Daphnia magna* of 1.35 µg l^{-1}, which is the geometric mean of two chronic NOEC values for this species. The bioconcentration factor for hexachlorobenzene can be taken from the summarised data

presented by Arnot and Gobas (2006), which reported mean and median BCF values of 13200 and 18200 l kg^{-1} respectively. Where there is a requirement to compare the toxicities of a number of different substances it is necessary for the critical body burden to be expressed as a molal concentration (mol kg^{-1}).

Table 18 Estimated critical body burdens for aquatic organisms

Effect endpoint	Units	Mean BCF	Median BCF	Units
1.35	µg l^{-1}	17.8	24.6	µg g^{-1}
5	nM	66	91	µ mol kg^{-1}

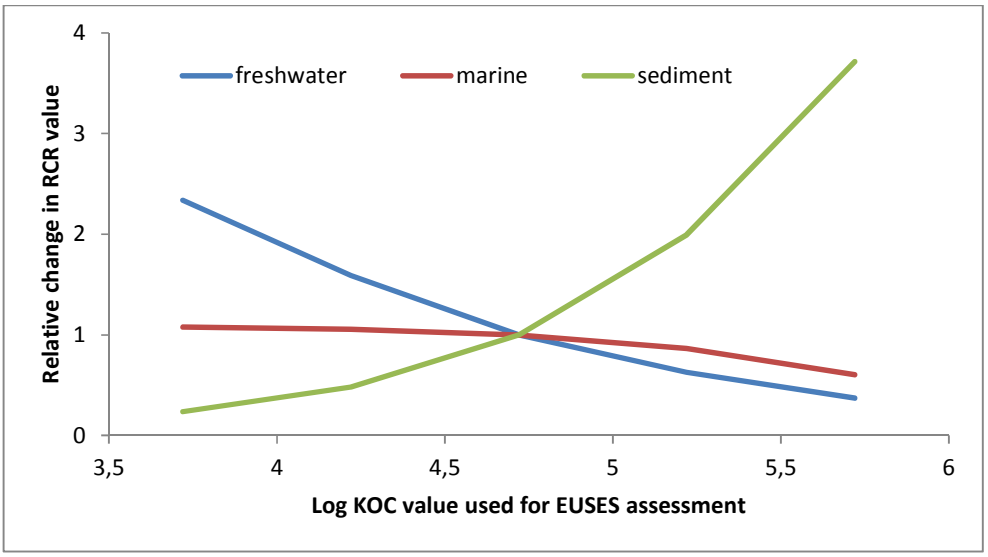
The critical body burdens calculated for aquatic organisms are shown in Table 18 in both µg g^{-1} and in µ mol kg^{-1}. These estimated values (17.8 and 24.6 µg g^{-1}) are comparable to the highest estimated critical liver concentrations derived for rats (18.2 µg g^{-1}). This suggests that a critical tissue residue which is derived to be protective of mammals and birds is also likely to be protective of aquatic organisms.

6. Environmental distribution

Hexachlorobenzene partitions strongly to soil and sediment phases in the environment, and its affinity for soils and sediments considerably reduces its mobility and potential for transport. Although hexachlorobenzene can be found throughout the globe, the majority of the emitted material remains relatively close to the area of emission. Emitted material is predominantly transported via the atmosphere following volatilisation form soils. The relatively low vapour pressure and high affinity for soils reduces the tendency for hexachlorobenzene to volatilise from soils, and explains why the majority of the emitted material remains relatively close to the area of emission in temperate regions. The tendency for hexachlorobenzene to volatilise from soil decreases with decreasing temperature.

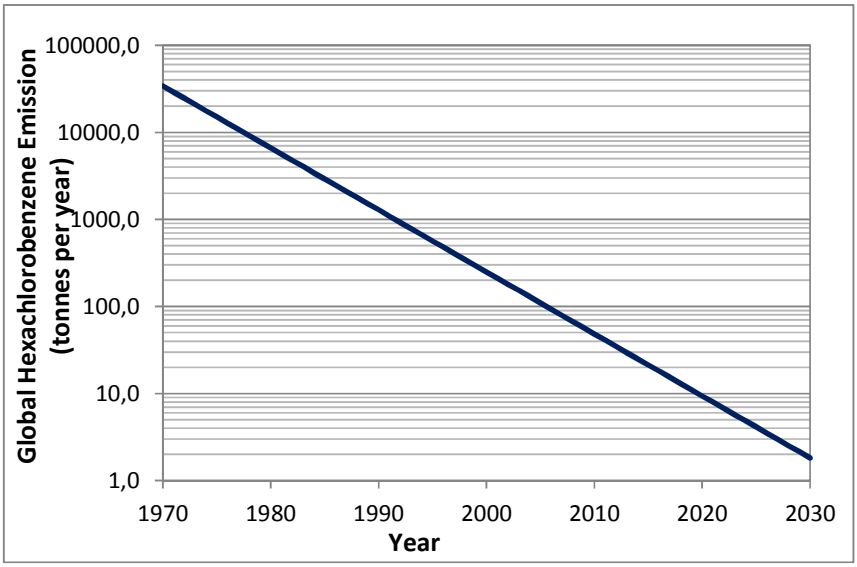
The K_{OC} value used in the risk assessment has a significant influence on the resulting risk characterisation ratios. The effect of changing the K_{OC} value used in the assessment by a factor of 3 or 10 on the predicted risks to sediments, freshwater and marine ecosystems is shown in Figure 6. The log K_{OC} values used were 3.7 (lowest), 4.2, 4.7 (default), 5.2, and 5.7 (highest). The risks to freshwater predatory fish varies in the same manner as the predicted risks to freshwater ecosystems, and the risks to the marine predators in the same manner as the risks to marine ecosystems. An increased risk to aquatic organisms is observed for a reduction in the degree of partitioning of hexachlorobenzene to sediments. The partitioning of hexachlorobenzene to sediments increases as log K_{OC} increases, and consequently higher exposures are observed for sediment organisms in scenarios where log K_{OC} is increased, with reduced availability to aquatic organisms. These changes to K_{OC} values affect only the exposure concentrations, although if the $PNEC_{Sediment}$ had been based on equilibrium partitioning it would also have affected this.

Figure 6 Influence of changes to the Log K_{OC} value, from the value of 4.72 used in the assessment, on Risk Characterisation Ratios for different endpoints



Simulations using a global distribution model (Globo-POP, Wania and Mackay 1995) indicate that hexachlorobenzene becomes rapidly distributed from temperate and sub-tropical latitudes to contaminate remote regions of the globe, although the degree of contamination is relatively small compared to that experienced by the regions where the greatest emissions occur. The contamination of the remote (polar) regions is principally by atmospheric transport, although there is also some transport of hexachlorobenzene by seawater this is much less important than atmospheric transport. These modelling scenarios indicate, however, that the total concentrations of hexachlorobenzene present in each latitudinal zone reflect the levels of emission within that zone.

Figure 7 Assumed global emissions of hexachlorobenzene for global distribution modelling



The emission scenario assumed that hexachlorobenzene was only emitted from the North Boreal (5%), North Temperate (20%), North Sub-Tropic (60%), North Tropic (5%), South Tropic (5%), and South Sub-Tropic (5%) latitudinal zones. The emission scenario assumed a continuous decline in emissions starting from 1970, which is considered to coincide with the peak in global hexachlorobenzene usage. An emission of approximately 35,000 tonnes was assumed in 1970, declining to approximately 250 tonnes in 2000 and approximately 5 tonnes in 2024. The emissions of hexachlorobenzene were assumed to be released equally to air and soil. The assumed total global emissions for this simulation are shown in Figure 7.

The flux of hexachlorobenzene to the North Polar region is principally due to atmospheric transport, which accounts for between 94% and 98% of the total flux into the region during the first 10 years of the simulation, and approximately 86% for the final 10 years of the simulation. The remaining flux is due to transport in seawater. The predicted rates of removal of hexachlorobenzene from soils are dependent upon the temperature, with slower removal rates in the colder regions, and are also dependent upon the concentration of hexachlorobenzene in the compartment, with slower removal rates when concentrations have declined. Half-lives of between approximately 3 and 8 years are predicted for soils in sub-tropical regions and between approximately 5 and 8 years in boreal regions.

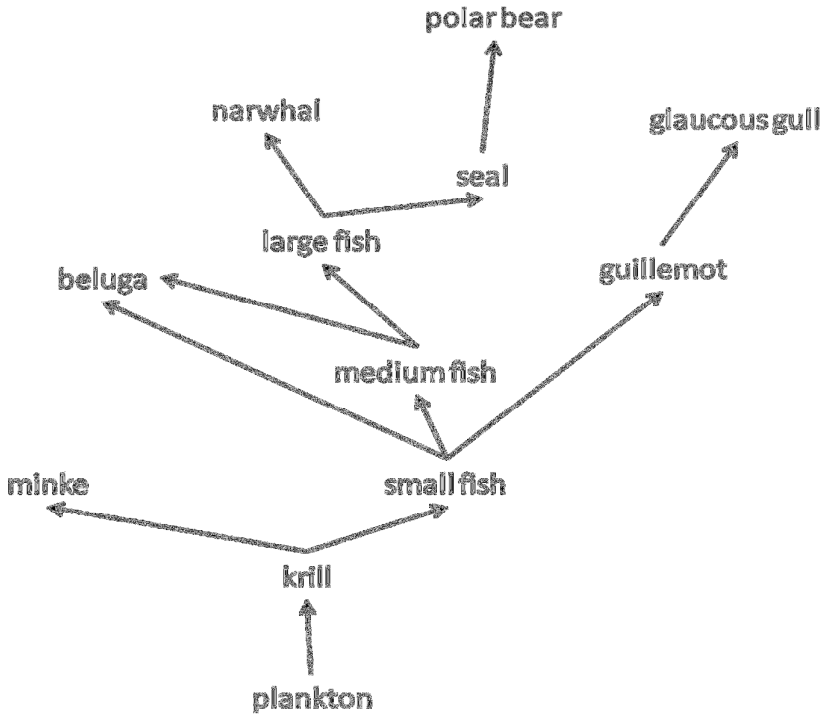
7 Risk assessment for arctic marine predators

Two approaches have been taken towards modelling the accumulation of hexachlorobenzene in marine arctic food chains and food-webs. AQUAWEB (Arnot and Gobas 2004), a model developed for the site specific assessment of bioaccumulation in freshwater food chains, and the approach recommended under REACH (ECHA 2010), which uses biomagnification factors for each food chain linkage. Several other models such as that of Gobas (1993) and AccHuman (Czub and McLachlan 2004) were not considered to be sufficiently flexible for application to the top predators of marine arctic ecosystems.

7.1 Aquaweb

AQUAWEB (1.2) can potentially employ a relatively complex food web, and it has been parameterised for PCBs in a freshwater lake. The model assumes that all organisms are freshwater aquatic species (either invertebrates or fish), and applies a single expression for the bioaccumulation to all of these organisms. This calculates the overall mass balance of the chemical in the organism, so is not suitable for calculating, or comparison with, concentrations in individual organs. Site specific data on the body weight and lipid content of each species can be used as well as specific information on the diet of each species considered. A schematic of the assumed simplified food web which was used for the modelling of the accumulation of hexachlorobenzene in arctic predators is shown in Figure 8.

Figure 8 Simplified food web assumed for AQUAWEB modelling



The environmental properties were set such that they reflected the approximate conditions in arctic seawater. A water temperature of 1°C, a DOC concentration of 1 mg l^{-1} (Cooper et al. 2005) and a POC concentration of 1 mg l^{-1} (Kinney et al. 1971). Sediments were assumed to contain 1% organic carbon (Schubert and Stein 1996). A range of hexachlorobenzene exposure scenarios were used relating to the approximate concentrations in arctic seawater from recent monitoring, plus scenarios with concentrations 3 and 10 times higher than these levels. Each organism was assumed to eat only a single prey species, with the exception of beluga which were assumed to eat equal quantities of both small and medium sized fish, i.e. the scenario was established to consider a series of food chains, rather than a food web.

Weights and lipid contents were estimated from literature information where possible, and the values used for modelling are shown below (see Table 19). Food ingestion rates are calculated internally within the model, which was developed for freshwater fish, and may not reflect well the food ingestion rates of warm blooded animals (i.e. birds and mammals). All organisms are assumed to have exposure through direct contact with water, although this may not be realistic, at least for birds and polar bears.

Seals and whales were assumed to have lipid contents of approximately 40%, although it has been suggested that the lipid content of seals may typically be close to 30% (Shahidi et al. 1996).

Table 19 Organism properties used in AQUAWEB model calculations

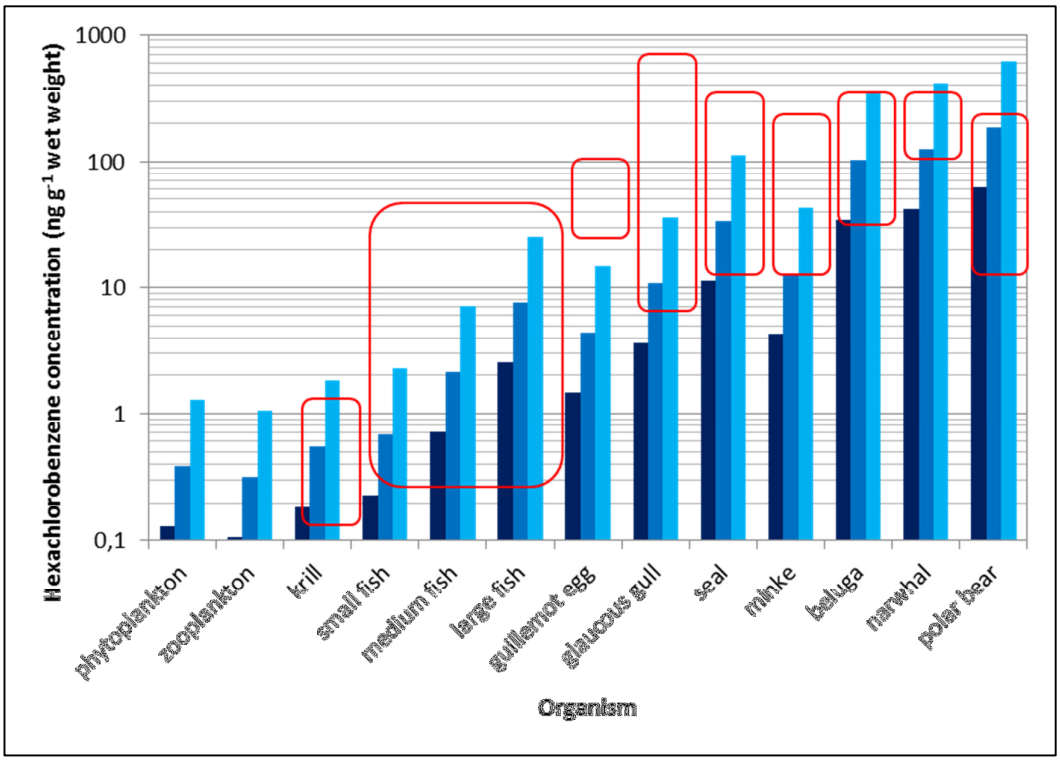
Organism	Weight	Lipid content	Food ingestion	Prey
Krill	2 g	2.2 %	2 mg d^{-1}	Zooplankton
Small fish	25 g	3 %	10 mg d^{-1}	Krill
Medium fish	250 g	5 %	7 g d^{-1}	Small fish
Large fish	2.5 kg	8 %	50 g d^{-1}	Medium fish
Guillemot	1 kg	12 %	19 g d^{-1}	Small fish
Glaucous gull	1.75 kg	5 %	38 g d^{-1}	Guillemot
Seal	50 kg	40 %	650 g d^{-1}	Large fish
Minke whale	5000 kg	40 %	32.5 kg d^{-1}	Krill
Beluga	1000 kg	40 %	8.3 kg d^{-1}	Small and medium fish
Narwhal	1200 kg	40 %	9.7 kg d^{-1}	Large fish
Polar bear	400 kg	25 %	3.8 kg d^{-1}	Seal

AQUAWEB results

The model calculations shown in Figure 9 considered three different hexachlorobenzene exposure concentrations, of which the lowest (0.01 ng l^{-1}) is considered to be the most relevant to the current levels of hexachlorobenzene in arctic seawater. An increase in the exposure concentration by an order of magnitude results in an order of magnitude increase in the predicted biota concentrations. Whilst the concentrations of hexachlorobenzene in krill and medium to large fish are broadly within the range of concentrations observed in arctic fish, the concentrations of hexachlorobenzene in higher organisms tend to be under estimated, except for polar bears which represent the highest trophic level.

The degree of under estimation is greatest for guillemot eggs, although the concentrations of hexachlorobenzene reported in guillemot muscle are much closer to the predicted concentrations (2 to 17 ng g^{-1} wet weight) which represents a similar degree of underestimation to that observed for other organisms. The organism weight assumed for the guillemot egg is considered to be typical of guillemots, although the lipid content is taken from the reported lipid content of guillemot eggs (12 % reported by Lundstedt-Enkel et al. 2005). Glaucous gulls are assumed to eat guillemot eggs, rather than adult guillemots, although this is not taken into account very well within these calculations.

Figure 9 Predicted hexachlorobenzene concentrations in arctic organisms from a simplified food web for three different exposure concentrations



Exposure concentrations 0.01 ng l^{-1}, dark blue; 0.03 ng l^{-1}, mid blue; 0.1 ng l^{-1} pale blue. Red boxes indicate the approximate ranges of concentrations observed in these organisms from recent (post 1990) monitoring (Barber et al. 2005).

The polar bear food chain is the longest one to be considered in this simplified arctic ecosystem (see Figure 8), and it may be for this reason that the predicted concentrations of hexachlorobenzene in polar bears are relatively close to the measured concentrations. AQUAWEB, when used in this way is able to provide reasonable estimates of the levels of hexachlorobenzene observed in some trophic levels (comparison against recent biota monitoring data from the arctic), although in some cases the predicted concentrations of hexachlorobenzene are around an order of magnitude lower than has been observed in biota.

AQUAWEB conclusions

Weights and lipid contents were estimated from literature information where possible, whereas food ingestion rates are calculated internally within the model and are based on freshwater fish data. These calculated ingestion rates may not reflect well the food ingestion rates of warm blooded animals (i.e. birds and mammals).

Food ingestion rates for seabirds and mammals can be estimated from relationships with body weight (US EPA 1993). The relationships described in this source relate to freshwater and terrestrial organisms and may not necessarily be relevant to the large marine mammals considered here. An assessment of energy flows through an arctic marine ecosystem (Welch et

al. 1992) has reported estimates of ingestion rates for a number of large marine mammals. A comparison of the different estimates of food intakes per day, expressed in terms of the percentage of the organism's body weight, is provided in Table 20.

Table 20 **Comparison of food ingestion rates (expressed as percentage of body weight per day) of predatory organisms used in AQUAWEB calculations and estimated from other sources**

Organism	Weight (kg)	% BW/d (AQUAWEB)	% BW/d (Welch et al. 1992)	% BW/d (US EPA 1993)
Guillemot	1	1.9		32
Glaucous gull	1.75	2.17		27
Seal	50	1.3	4.2	17
Minke whale	5000	0.65		7.5
Beluga	1000	0.83	2.5	10
Narwhal	1200	0.81	2.5	9.7
Polar bear	400	0.95	1	11.8

The food ingestion rates calculated by AQUAWEB are lower, in all cases, than the estimates of Welch et al. (1992) or estimates according to the US EPA (1993). This may account for some of the underestimation of hexachlorobenzene concentrations in higher predators, although the assumed food ingestion rate for the polar bear is very close to the estimate of Welch et al. (1992). It has been suggested that the food ingestion rates of marine mammals and terrestrial mammals are not significantly different when measured under appropriately standardised conditions, although this would require that the feeding rates were compared on the basis of energy intake (Innes et al. 1987).

All of the aquatic mammals (seals and whales) were assumed to contain 40% lipid by weight, and polar bears were assumed to contain 25% lipid by weight. Relatively little quantitative information was found for these organisms although polar bears are believed to live off fat reserves during the summer, so may have higher fat contents in spring time and lower fat contents in autumn. Variation in body lipid reserves may have a significant effect on the whole organism concentrations with very little change in the total body burden. The condition of individual organisms has been identified as a potentially important confounding factor in studies on predatory birds in the UK (e.g. Wienburg and Shaw 2004).

Due to the model being based on data for a freshwater food web, and parameterised for freshwater invertebrates and fish species, it is inappropriate to apply it to the assessment of bioaccumulation through a marine arctic food-web. Despite these difficulties the estimated concentrations in higher predators are typically within an order of magnitude of monitoring data.

7.2 REACH approach

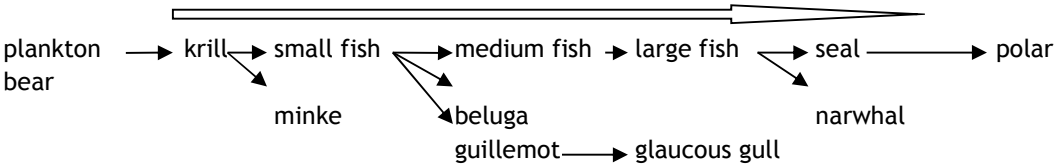
The REACH guidance approach (ECHA 2010) uses both a BCF and a BMF to calculate the concentration of a substance in predators. BMF values should be based on lipid normalised measured data, and because of differences between different predators and prey the BMF values derived may be specific to both the species and the location. The BMF approach, when applied in this way, also assumes that the predator consumes only a single prey species. This may not necessarily be a reasonable assumption in many situations. Because the BMF relates the

concentrations of the contaminant in one organism to another it takes account of any species specific differences such as differences in food intake rates or the energy content of the prey, provided that it is derived from data which adequately represent the trophic linkage under consideration.

Estimates of the concentrations of contaminants in the food of predators, on a wet weight basis, can be calculated according to the REACH guidance (ECHA 2010), using the following equation:

$BCF \times BMF_i \times BMF_j \times BMF_k$..... (where $_i$, $_j$ and $_k$ represent the trophic linkages for the food chain)

Increasing food chain position



The longest food chain in the simplified system assumed for AQUAWEB calculations is that of the polar bear, with 6 trophic linkages assumed between the plankton and the top predator.

$BCF \times BMF_1 \times BMF_2 \times BMF_3 \times BMF_4 \times BMF_5 \times BMF_6$

The marine food chain assumed in the REACH guidance uses only two BMF values to estimate the exposure to top predators, i.e. the concentration in their food.

Water ⟶ plankton ⟶ fish ⟶ predator ⟶ top predator

This is equivalent to:

Water —BCF→ plankton —BMF_1→ small fish —BMF_2→ large fish —(BMF_3)→ seal

In order to assess the exposure to (or body burden of) polar bears an additional trophic linkage must be included.

PEC_{water} ⟶ plankton ⟶ small fish ⟶ large fish ⟶ seal ~~polar~~ ⟶ bear

The concentration of hexachlorobenzene in polar bears can therefore be calculated using a modification of the REACH guidance marine food chain to include two additional trophic linkages. The first additional linkage, between large fish and seals, is necessary because the REACH guidance approach compares the levels in seal food against the $PNEC_{oral}$ for seals (or other mammals). The concentration of hexachlorobenzene in seals could be compared to the $PNEC_{oral}$ for polar bears (or other mammals). Estimation of the concentrations of hexachlorobenzene in polar bears requires a further trophic linkage to be included, i.e. that between seals and polar bears.

Taking the log K_{OW} value of hexachlorobenzene to be 5.7 a BCF value can be estimated according to the relationships provided in the REACH guidance (ECHA 2010). This log K_{OW} value results in a BCF of 13964. The default BMF value for a substance with this log K_{OW} value is 10 for the first two trophic linkages, and the same BMF value is also assumed for the additional trophic linkages. A PEC_{water} of 12 pg l^{-1} Barber et al. (2005) is assumed for the purpose of these calculations.

$PEC_{polar\ bear} = PEC_{water} \times BCF_{fish} \times BMF_1 \times BMF_2 \times BMF_3 \times BMF_4$

$PEC_{polar\ bear}$ = 1676 µg kg^{-1} (wet weight)

The REACH approach also considers different spatial scales in the assessment of secondary poisoning, by considering that top predators may obtain half of their food from "local" sources and half from "regional" sources. Given that there are no significant sources of emission in the arctic this is not considered to be relevant to the consideration of the concentrations of hexachlorobenzene in polar bears.

Replacing the REACH guidance default values with specific information for each of the trophic linkages allows the consideration of the polar bear food chain. The BCF value is taken from the summarised data of Arnot and Gobas (2006), and information on specific BMF values have been reported in Barber et al. (2005) derived from arctic food webs. These BMF values have all been derived on a lipid normalised basis, as recommended in the REACH guidance. There is a considerable quantity of data available for hexachlorobenzene and it was necessary in many cases to summarise data from a range of BMF values. Where possible the 50^{th} percentile of the range of BMF values was selected for use in modelling.

Water-zooplankton (BAF, median)	18200	$BAF_{plankton}$
Zooplankton-fish (50^{th} %ile BMF)	3.65	BMF_1
Fish-fish (median BMF)	2.0	BMF_2
Fish-seal (harp seal BMF)	1.35	BMF_3
Seal-polar bear (BMF, single value)	15.6	BMF_4

The body burdens of hexachlorobenzene in seals were observed to vary between species by Vorkamp et al. (2004), who found harp seals (*Phoca groenlandica*) to have higher hexachlorobenzene concentrations than ringed seals (*Pusa hispida*). Average concentrations of hexachlorobenzene were reported in the muscle tissue of six fish species, and by comparing these concentrations with those in harbour seals a further estimate of the fish-seal BMF may be made. The geometric mean of the six calculated fish-seal BMF values is 1.5. Geometric means of 0.24 and 0.40 can similarly be calculated for two separate ringed seal populations. This observed difference between these two species of seals is also seen in the summaries of hexachlorobenzene levels in seals reported by Barber et al. (2005), with ringed seals generally having blubber concentrations up to approximately 20 ng g^{-1} (wet weight) and harp seals having blubber concentrations between approximately 50 and 250 ng g^{-1} (wet weight).

REACH approach results

$PEC_{polar\ bear} = PEC_{water} \times BAF_{plankton} \times BMF_1 \times BMF_2 \times BMF_3 \times BMF_4$

$PEC_{polar\ bear}$ = 0.000012 µg l^{-1} x 18200 x 3.65 x 2.0 x 1.35. x 15.6

$PEC_{polar\ bear}$ = 33.6 µg kg^{-1} (wet weight)

The concentration of hexachlorobenzene in the adipose tissue of polar bears has been reported between 1984 and 1996 (Barber et al. 2005). There was no obvious time trend in the data, which is unsurprising given the small number of samples and different locations of the measurements. The concentrations ranged from 17 to 483 µg kg^{-1} (wet weight) in adipose tissue, with an average of reported average values of 115 µg kg^{-1} (wet weight). If it is assumed that adipose tissue is representative of the whole of the polar bear fat, these concentrations need to be adjusted before they can be compared directly to the calculated $PEC_{polar\ bear}$ of 33.6 µg kg^{-1} (wet weight). Polar bear liver concentrations ranged from 1 to 170 µg kg^{-1} (wet weight), with two reported

average values of 18 μg kg^{-1} (wet weight). This average value compares favourably with the predicted wet weight concentration in polar bears ($PEC_{polar\ bear}$).

Polar bears are known to live off fat reserves during the summer, when it is not possible to hunt seals on the sea ice. The polar bears fat reserves are therefore likely to vary seasonally, and variation in fat content of polar bears between approximately 10% to 50% has been observed (Farley and Robbins 1994). Lipid contents of polar bears have been reported as approximately 11% (Corsolini et al. 2002), although only liver samples were analysed and it is not clear whether the figure quoted relates to the liver samples or the whole organisms. The lipid mass of female polar bears at the beginning of hibernation has been reported as being similar to their lean body mass, i.e. the overall lipid content is approximately 50% of the total body mass (Atkinson and Ramsay 1995). A value of 25% total lipid has been used as an approximation of the lipid content for bears in intermediate condition (Sormo et al. 2006).

Assuming a typical lipid content of 25% to be generally representative of bears which are not in an extreme body condition (either very high or very low total lipid content) a typical wet weight concentration can be estimated from the data for hexachlorobenzene concentrations in adipose tissue. The resulting value of 28.7 μg kg^{-1} (wet weight) is comparable to both the average concentration in polar bear liver and also the wet weight concentration in whole polar bears ($PEC_{polar\ bear}$).

115 μg kg^{-1} (wet weight in adipose tissue) x 0.25 (lipid fraction) = 28.7 μg kg^{-1} (wet weight)

The lipid content of blubber from sperm whales (*Physeter macrocephalus*) has been reported to vary between 16% and 89% (Evans et al. 2003). Variation in the lipid content of blubber has also been observed in harbour porpoise (76-88%) and minke whales (42-96%) and bottlenose dolphins (37-68%) (Dunkin et al. 2005 and references cited therein). Assuming that adipose tissue has a lipid content of 80% the lipid normalised concentration of hexachlorobenzene in blubber would be 143.8 μg kg^{-1}, and the resulting wet weight concentration in whole polar bears 35.9 μg kg^{-1}.

Given the consistent differences observed between the body burdens of different seal species, such as harp seals and ringed seals the BMF for the seal-bear trophic linkage is particularly uncertain. BMF values for the transfer of hexachlorobenzene between seals and polar bears have also been estimated from data on the levels in arctic seals and polar bears. Considering harp seals and ringed seals separately, and comparing the blubber concentrations in seals against the adipose concentrations in bears without further corrections, results in BMF values of 0.8 for harp seals and 8.0 for ringed seals. Differences between the hexachlorobenzene levels in different species of seals have been identified previously (Hobbs et al. 2002).

Polar bears are commonly assumed to feed principally on ringed seals, although some surveys have identified harp seals as being a significant prey species, at least for polar bears in some areas (Klevaine et al. 2000). This study also found that the concentrations of organochlorine compounds were higher in harp seals than in ringed seals, with average hexachlorobenzene concentrations in harp seal blubber (144 ng g^{-1} wet weight) being around an order of magnitude higher than in ringed seals (13 ng g^{-1} wet weight). It may, therefore, be appropriate to consider different possible diet options for the polar bear.

Impact of migration on the accumulation of contaminants in higher predators, such as whales and birds, is a source of uncertainty.

The beluga (*Delphinapterus leucas*), narwhal (*Monodon monoceros*), and glaucous gull (*Larus hyperboreus*) food chains can also be assessed in a similar manner, by considering the

accumulation of hexachlorobenzene between fish and beluga, narwhal or guillemots (e.g. *Uria aalge*). Beluga, narwhal and guillemots are assumed to eat either small (planktivorous) or large (piscivorous) fish and glaucous gulls are assumed to feed equally on both fish (from the same trophic level as guillemots feed) and guillemot chicks or eggs.

Fish-beluga BMF (50th percentile)	13.3	BMF_2 or BMF_3
Fish-narwhal BMF (50th percentile)	11.5	BMF_2 or BMF_3
Fish-bird BMF (50th percentile)	8.9	BMF_2 or BMF_3
Bird-bird BMF (50th percentile)	19.0	BMF_3 or BMF_4

$PEC_{beluga} = PEC_{water} \times BAF_{plankton} \times BMF_1 \times BMF_2$ (assuming one fish level)

$PEC_{narwhal} = PEC_{water} \times BAF_{plankton} \times BMF_1 \times BMF_2$ (assuming one fish level)

$PEC_{glaucous\ gull} = PEC_{water} \times BAF_{plankton} \times BMF_1 \times (BMF_2 + BMF_3)/2$ (assuming one fish level)

PEC_{beluga} = 30.64 µg kg^{-1} (wet weight)

$PEC_{narwhal}$ = 26.49 µg kg^{-1} (wet weight)

$PEC_{glaucous\ gull}$ = 134.8 µg kg^{-1} (wet weight)

Beluga monitoring data			
Muscle	9.0-12.8	10.7	µg kg^{-1} (wet weight)
Liver	17.0-70.4	37.9	µg kg^{-1} (wet weight)
Blubber	10.3-1305	501.8	µg kg^{-1} (wet weight)

Narwhal monitoring data			
Liver	6.1-36.7	13.3	µg kg^{-1} (wet weight)
Blubber	137-1140	450	µg kg^{-1} (wet weight)

Glaucous gull monitoring data			
Muscle	32-258	148	µg kg^{-1} (wet weight)
Liver	8-1012	173	µg kg^{-1} (wet weight)
Fat	162-734	423	µg kg^{-1} (wet weight)

In the case of both the polar bear and the glaucous gull the concentrations predicted by the REACH approach, using 50th percentiles of BMF values for specific trophic linkages, has resulted in predicted levels which compare very closely to the estimated levels observed in whole organisms. One remaining area of uncertainty is that the levels of contaminants in higher organisms are reported for individual tissues, whereas the concentrations calculated by the REACH approach are for whole organisms on a wet weight basis.

The REACH approach recommends that BMF values used should be derived on a lipid normalised basis, presumably to take account of differences in the total lipid content between different trophic levels, although a recent study on a similar food chain to that considered here (Sormo et al. 2006) considered that the use of BMF values derived on a wet weight basis may be preferable to the use of BMF values derived on a lipid weight basis, due to the seasonal variation in the lipid contents of organisms.

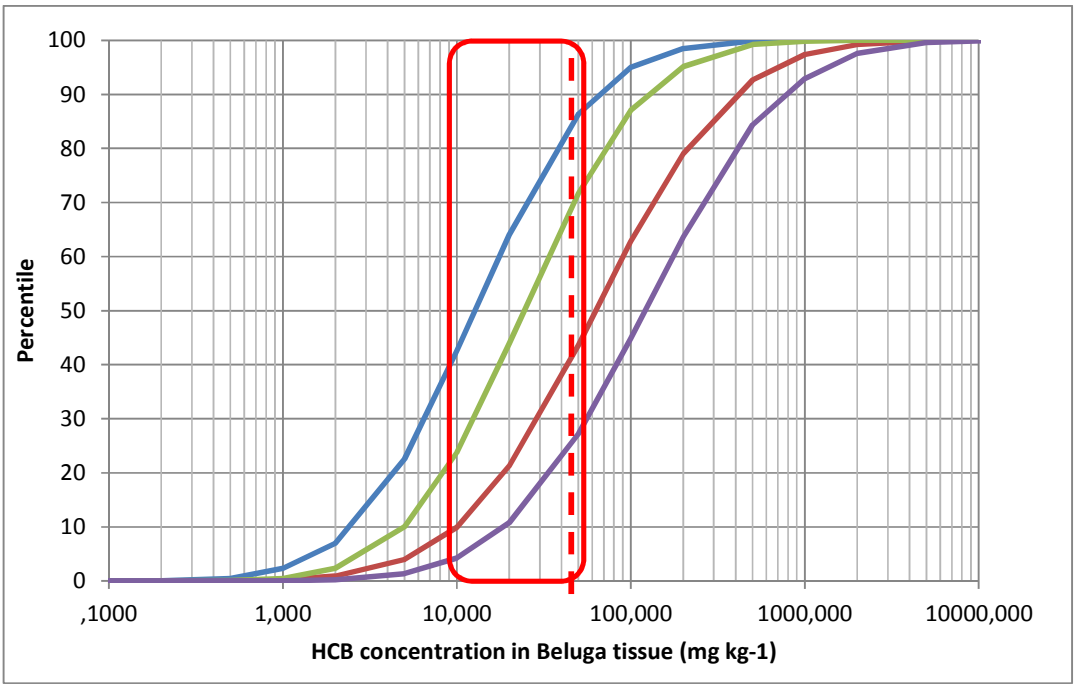
The BMF estimates used in these calculations assume that the predator is at equilibrium with respect to its prey, and that both are at equilibrium with respect to their surrounding

environment. This may not necessarily be the case. The prey type is assumed in the majority of cases, and many predators will consume a variety of prey types if necessary. For example predatory birds have been observed to change their main diet species in response to prey abundance and availability (Reif et al. 2001, Bustnes et al. 2000).

7.3 Probabilistic modelling of accumulation through arctic food chains

Probabilistic estimates of the accumulation of hexachlorobenzene in a variety of arctic predators were also undertaken, following the REACH approach. These estimates were performed assuming that BMF values are lognormally distributed and following a similar approach to that used to estimate the $PEC_{oral,\ top\ predator}$ previously (Figure 1). Results for beluga, polar bears, narwhals and glaucous gulls are shown in Figures 10 to 13 respectively.

Figure 10 Hexachlorobenzene accumulation in arctic beluga

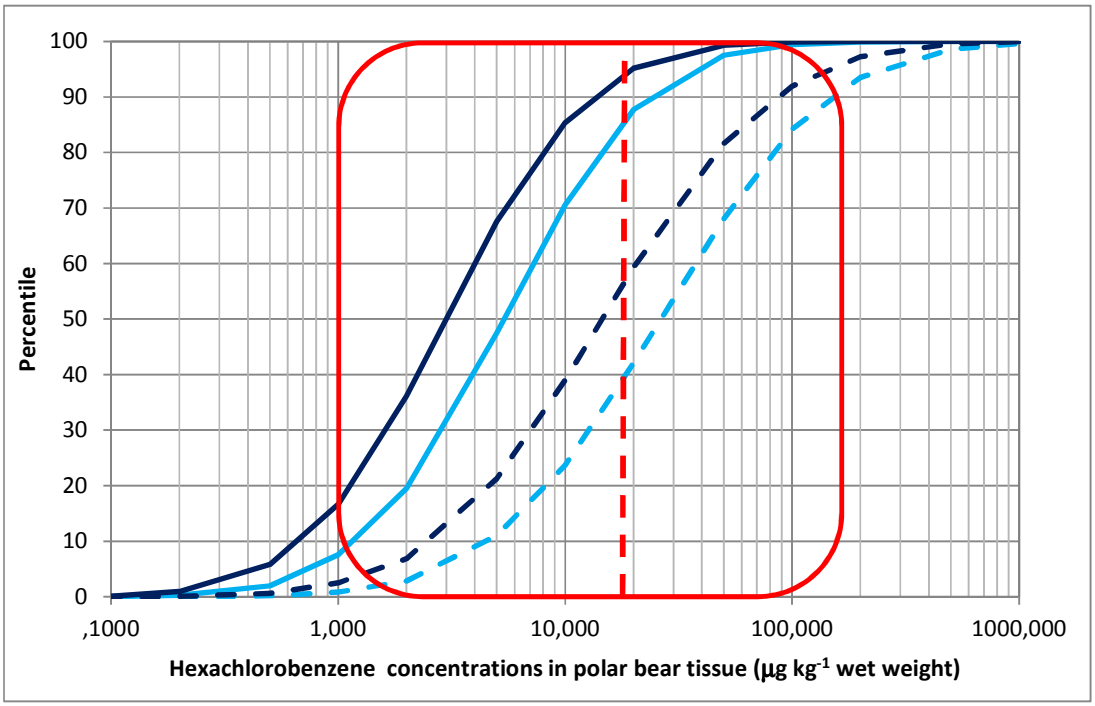


Pale blue lines indicate one fish level and dark blue lines indicate two fish levels, solid lines indicate use of a BCF for plankton and dashed lines indicate use of a BAF for plankton. The red box indicates the range of average hexachlorobenzene concentrations reported in beluga muscle, and the vertical red dashed line indicates the average concentration in beluga muscle tissue.

Four different scenarios have been considered in modelling the concentrations of hexachlorobenzene in beluga. These scenarios used either a BCF or BAF applied to the uptake of hexachlorobenzene from water to zooplankton and considered the beluga to be feeding either on planktivorous fish or piscivorous fish. There is a relatively large body of monitoring data available for beluga (Barber et al. 2005), although the majority of the data are reported as blubber concentrations. Relatively few studies have reported hexachlorobenzene concentrations in other beluga tissues, although some data are available for muscle and liver. Muscle concentrations are considered to be more relevant to whole body concentrations than blubber concentrations, which are more likely to reflect lipid normalised concentrations for the whole

organism. The range and average muscle concentrations of hexachlorobenzene compare favourably with estimates which use a BAF for the accumulation by zooplankton and in which beluga are assumed to feed on planktivorous fish. Predictions which consider beluga to be feeding on piscivorous fish overestimate the concentrations of hexachlorobenzene when compared to the available monitoring data. Predictions which use a BCF to account for the uptake of hexachlorobenzene by zooplankton appear to slightly under estimate the concentrations in beluga, although the differences are relatively small compared to estimates using a BAF.

Figure 11 Hexachlorobenzene accumulation in polar bears

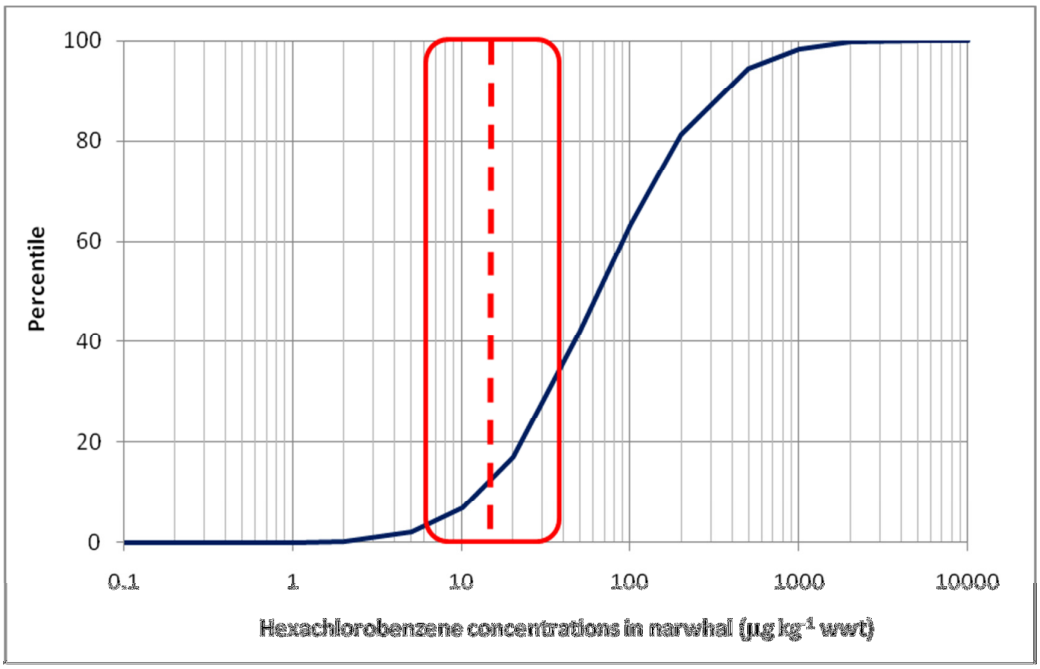


Pale blue lines indicate ringed seals and dark blue lines indicate harp seals, solid lines indicate use of a BCF for plankton and dashed lines indicate use of a BAF for plankton. The red box indicates the range of average hexachlorobenzene concentrations reported in polar bear liver, and the vertical red dashed line indicates the average concentration in polar bear liver tissue.

Four different scenarios have been considered in modelling the concentrations of hexachlorobenzene in polar bears. Again, these use either a BCF or a BAF value to account for the uptake between water and zooplankton and the polar bears were assumed to feed either on harp seals or ringed seals. The BMF values derived for the seal-polar bear trophic linkages have both been derived using the same monitoring data for polar bears. As a result of this the BMF values for the ringed seal-polar bear trophic linkage are considerably higher than those for the harp seal-polar bear trophic linkage, although it is not clear whether the uptake of hexachlorobenzene varies for different seal species when they are consumed by polar bears. Predictions which use a BCF to account for the uptake of hexachlorobenzene by zooplankton appear to underestimate the concentrations in polar bears. Predicted polar bear concentrations which assume that they consume only either ringed or harp seals both compare well with the range and average concentrations reported in polar bear liver. Liver was considered to be the most appropriate tissue for comparison against the whole body wet weight concentrations

predicted by this method (concentrations of hexachlorobenzene have also been reported in adipose tissue and blood).

Figure 12 Hexachlorobenzene accumulation in narwhals



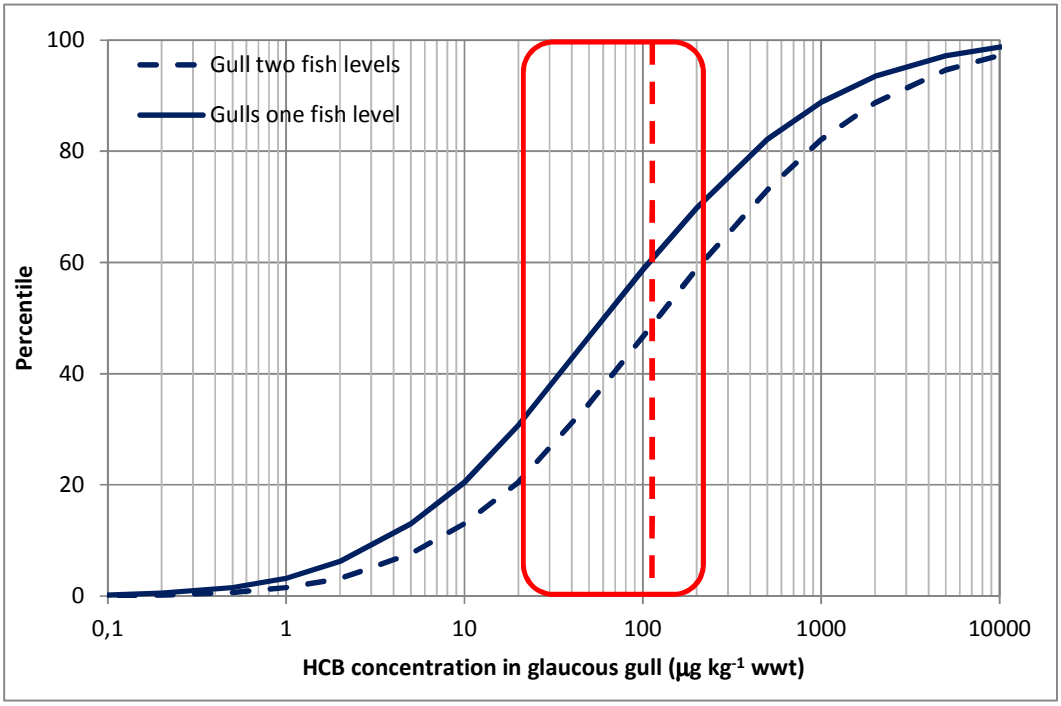
The red box indicates the range of average hexachlorobenzene concentrations reported in narwhal liver, and the vertical red dashed line indicates the average concentration in narwhal liver tissue.

Predictions of the concentrations of hexachlorobenzene in narwhals (*Monodon monoceros*) have used only a BAF value to account for the uptake between water and zooplankton, as this approach provides slightly improved estimates of the body burdens for some predators. The calculations assume that narwhals feed on small (planktivorous) fish. There are relatively few monitoring data available for the levels of hexachlorobenzene in narwhal tissue, and concentrations have only been reported in liver and blubber tissues. The measured levels of hexachlorobenzene in narwhal liver are approximately 5 times lower than those predicted for the whole narwhal (on a wet weight basis). It is possible that narwhals may be able to metabolise hexachlorobenzene more effectively than many other mammals, although differences between the real diet and that assumed for the calculations could also de responsible for the difference. The levels of hexachlorobenzene in narwhal blubber are considered to be broadly comparable to lipid normalised concentrations in whole organisms, and the average concentration is 450 µg kg^{-1} (wet weight). If this value is corrected to a wet weight concentration in the whole organism, assuming a lipid content of 40%, an approximate whole body wet weight concentration of 180 µg kg^{-1} (wet weight) is derived. Assuming blubber to be 70% lipid would give an approximate whole body wet weight concentration of 260 µg kg^{-1}. This value is comparable to the 50th percentile of the estimated narwhal concentrations, although there is considerable uncertainty involved in making such an extrapolation. It has been reported that the blubber content of beluga is typically 40% or higher (Sergeant and Brodie 1969).

Predictions of the levels of hexachlorobenzene on glaucous gulls used only BAF values to account for the uptake between water and zooplankton. The measured levels of hexachlorobenzene in

glaucous gull muscle tissue are comparable to the median levels predicted here. The calculations assumed that the glaucous gulls are obtaining 50% of their food from the young and eggs of other seabirds, and the remaining 50% from fish. Both types of birds are assumed to feed from the same fish populations. Glaucous gulls may only be able to feed on the eggs and young of other birds during the breeding season, and then only if they are close to colonies of nesting birds, so this assessment may not be relevant to all glaucous gull colonies. Seabirds are more likely to feed on small fish than large fish because they may not be able to dissect their prey, and this may result in them feeding principally on planktivorous fish (one fish level) rather than piscivorous fish (two fish levels). Although the difference between the two sets of predictions is relatively small the average levels of hexachlorobenzene in glaucous gull muscle tissue is closest to the 50th percentile of the calculations assuming two fish levels.

Figure 13 Hexachlorobenzene concentrations in glaucous gulls



The solid line indicates the use of a single fish level and the dashed line indicates the use of two fish levels. The red box indicates the range of average hexachlorobenzene concentrations reported in glaucous gull muscle, and the vertical red dashed line indicates the average concentration in glaucous gull muscle tissue.

7.4 Risk Characterisation for Polar Bears based on the $PNEC_{Oral}$

The exposure of polar bears via their food requires the concentration of hexachlorobenzene in seals to be calculated, and considers a four step food-chain using BMF values reported by Barber et al. (2005) for each trophic linkage:

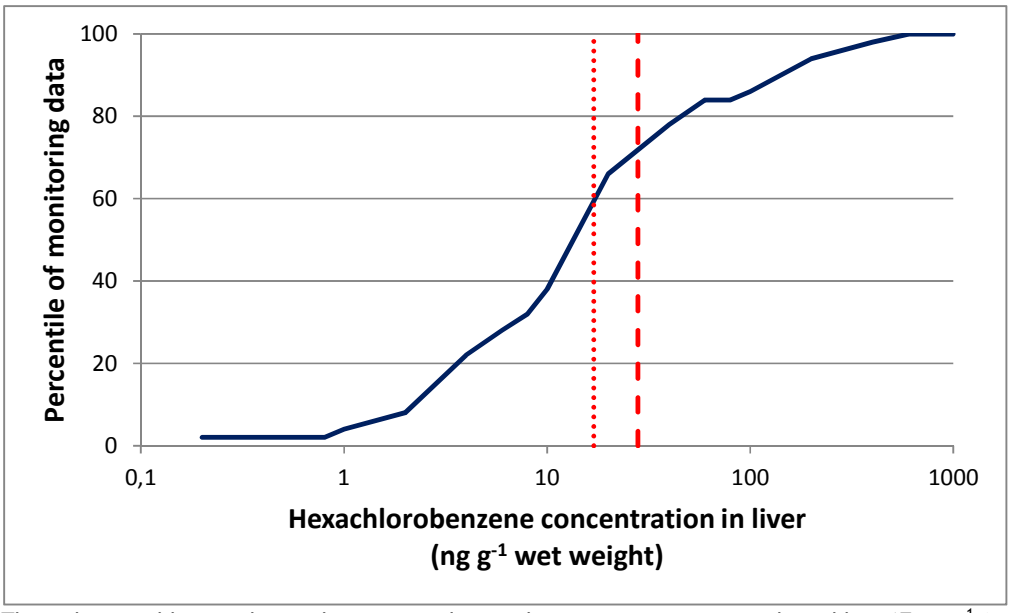
	BCF		BMF_1		BMF_2		(BMF_3)	
	18200		3.65		2.00		1.35	
Water	→	plankton	→	small fish	→	large fish	→	seal

This results in a predicted concentration of hexachlorobenzene in seals of 2.15 µg kg^{-1} (wet weight) assuming an concentration of 12 x 10^{-6} µg l^{-1} in seawater. The $PNEC_{Oral}$ is 16.7 µg kg^{-1} (wet weight), which results in a risk characterisation ratio of 0.129.

7.5 Risk characterisation based on critical body burdens

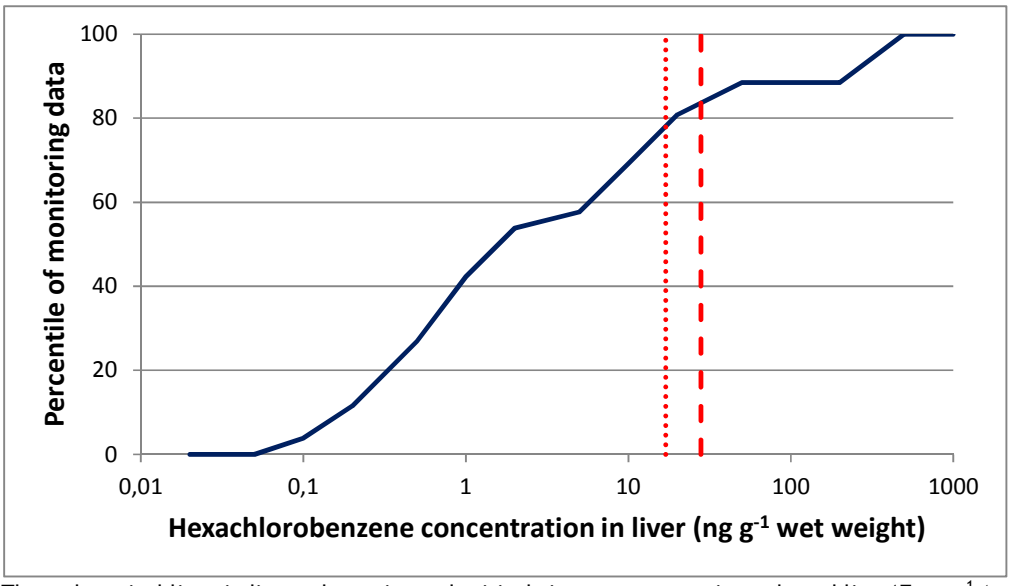
Data on hexachlorobenzene concentrations in the livers of various bird and mammal species which were summarised by Barber et al. (2005) are shown in Figures 14 (aquatic birds) and 16 (terrestrial birds and mammals), along with the critical liver concentrations derived by two methods. These indicate that the majority of birds and mammals have liver hexachlorobenzene concentrations below the estimated critical liver concentration, although some samples do have higher concentrations, particularly for the aquatic birds. It is worth noting that the highest concentrations reported in the livers of terrestrial mammals were from mink in the Canadian arctic between 1992 and 1994.

Figure 14 Cumulative frequency distribution of concentrations of hexachlorobenzene reported in aquatic bird livers (Barber et al. 2005)



The red vertical lines indicate the estimated critical tissue concentrations, dotted line 17 ng g^{-1} (wwt) liver and dashed line 28 ng g^{-1} (wwt) liver.

Figure 15 Cumulative frequency distribution of concentrations of hexachlorobenzene reported in terrestrial bird and mammal livers (Barber et al. 2005)



The red vertical lines indicate the estimated critical tissue concentrations, dotted line 17 ng g^{-1} (wwt) liver and dashed line 28 ng g^{-1} (wwt) liver.

Concentrations of hexachlorobenzene in polar bear livers, from Svalbard, Canada and Alaska, have been reported as between 1 and 170 ng g^{-1} (wet weight), with the mean of two reported average values being 18 ng g^{-1} (wet weight). The samples were taken between 1982 and 1996 and because of the small number of results reported and the spatial variation, no temporal trends were evident in the data. For the average concentration of 18 ng g^{-1} (wet weight) observed in polar bear liver and the estimated critical body burden in liver of 510 ng g^{-1} (wet weight), the margin of safety is 28. The margin of safety ranges between 3 (for 170 ng g^{-1} (wet weight)) and 510 (for 1 ng g^{-1} (wet weight)) for the highest and lowest observed values. Applying an assessment factor of 30 to the critical body burden data, as has been the case previously in the derivation of a $PNEC_{oral}$ for hexachlorobenzene (FHI 2005), results in marginal risks being predicted on the basis of the average concentrations of hexachlorobenzene reported in polar bear livers.

The predicted concentrations of hexachlorobenzene in beluga, polar bear, narwhal and glaucous gull exceed the proposed limit of 17 ng g^{-1} (wwt) for hexachlorobenzene in liver tissue in approximately 60% (beluga), 40% to 60% (polar bear), 80% (narwhal), and 70% (glaucous gull) of estimates, suggesting that a significant proportion of the populations of these species could currently be at risk from hexachlorobenzene toxicity, assuming that the threshold for hexachlorobenzene in liver tissue is reliable. The measured levels in some species also support this suggestion, e.g. polar bears.

The critical body burden is extrapolated for the most sensitive species (mink), and a further assessment factor is applied to derive the threshold. A North American study (Moore et al. 1997) suggests that the $PNEC_{oral}$ used for the risk assessment is adequately protective of mink. The available oral toxicity data for hexachlorobenzene indicate that other species are relatively unlikely to be more sensitive than mink. It is therefore not clear whether or not the levels of hexachlorobenzene found in the livers of predatory species other than mink (and closely related species such as ferrets) are likely to cause any adverse effects.

7.6 Risk Characterisation for Polar Bears based on the Critical Body Burden

In order to assess the body burden of polar bears an additional trophic linkage is included to cover the consumption of seals by polar bears.

PEC_{water} ⟶ plankton ⟶ small fish ⟶ large fish ⟶ seal ⟶ polar bear

The BMF value used for this trophic linkage is 15.6 (Barber et al. 2005), and results in a predicted concentration of hexachlorobenzene of 33.6 µg kg^{-1} (wet weight). The liver concentrations of hexachlorobenzene are considered to be a suitable surrogate for the overall concentration in polar bears, so no correction is required for the predicted body burden to compare it to the $PNEC_{Liver}$. This is slightly higher than two reported average values of 18 µg kg^{-1} (wet weight) for the concentrations of hexachlorobenzene in polar bear livers. A $PNEC_{Liver}$ has been derived in Section 5.1 of 17 µg kg^{-1} (wet weight, liver). The $PNEC_{Liver}$ is comparable to the observed average hexachlorobenzene concentration in polar bear livers by Barber et al. (2005), but is lower than the predicted body burden in polar bears following the modelling approach.

The risk characterisation ratio based on the calculated levels of hexachlorobenzene in polar bear liver is 1.97, and the risk characterisation ratio based on the measured levels of hexachlorobenzene in polar bear liver is 1.06.

7.7 Discussion

It is clear that hexachlorobenzene does bioconcentrate, and therefore also bioaccumulates. It is also clear that under some circumstances (i.e. between some trophic linkages) it will biomagnify, although the extent of such biomagnification is extremely variable. A more detailed consideration of the potential dietary exposure, in terms of the most relevant prey species and the relative contributions of different prey species may be too specific in terms of the spatial and temporal variation in predator diets. Numerous studies into the diets of particular species in different locations and at different times often provide quite different, and potentially conflicting, information. Because of this the most appropriate way forward is to consider accumulation on a reasonable worst case basis for a single predatory species which is considered to be potentially at risk.

A targeted assessment of several top predators within the marine arctic ecosystem, specifically the beluga, narwhal, polar bear and glaucous gull food chains, has been undertaken. This suggests that reasonable estimates of the levels of hexachlorobenzene in top predators can be made, where adequate monitoring data exist for specific BMF values to be derived for each trophic linkage. It also appears that higher BMF values tend to be identified for higher trophic levels, such as mammals and birds, which may have higher metabolic rates and consequently higher food ingestion rates. Consideration of a combination of both chemical and biological factors, such as log K_{OW}, trophic position and metabolic rate may allow the estimation of more accurate and relevant BMF values than the default values provided by the REACH guidance for some substances, particularly where they are not extensively metabolised by the consuming organisms.

Where calculations have been performed using both a BCF and a BAF for first trophic level, generally calculations using the BAF provide a better estimate of the accumulation in the top

predator. This suggests that the use of BAF rather than BCF for the first trophic level (accumulation by aquatic invertebrates) may be preferable for the calculation of the levels of hexachlorobenzene in arctic top predators.

The PNEC derivation for secondary poisoning is based on the most sensitive of six tested species, the mink. The oral toxicity dataset also includes data for two other carnivorous mammals, cat and dog, indicating that all carnivorous mammals cannot be assumed to be as sensitive to hexachlorobenzene as mink. The PNEC derivation approach for the $PNEC_{Oral}$ includes the use of an assessment factor, although unlike the derivation of other PNECs no consideration is made of the extent of the dataset in the selection of the assessment factor.

Where assessments are performed for a specific species, the sensitivity of species being assessed, such as polar bears, relative to the sensitivity of the most sensitive tested species, i.e. mink, is unknown. The traditional risk assessment approach aims to protect the function of the entire ecosystem. This is achieved by assuming that protecting ecosystem structure will in turn protect ecosystem function, and that protection of the most sensitive species should protect the community structure. These concepts are not relevant to the protection, or risk assessment, of a specific species for which no direct toxicity data exist unless it is assmed that all of the specific species assessed are of a similar sensitivity to the most sensitive tested species. Whilst it is not practical, or reasonable, for this issue to be resolved it is important to remember that the assumption that the species under assessment is of similar sensitivity to mink may not actually be valid for any given species assessed in the present study.

A slight risk to polar bears is indicated by the modelling, based on their estimated body burdens, and this level of risk tends to be supported by the available monitoring data. There are, however, numerous shortcommings of the monitoring data available to make the assessment. Monitoring of the levels of chemicals in polar bears is extremely limited, for practical reasons, and in many instances where monitoring is performed blood samples are taken rather than tissue samples such as blubber, adipose, or liver. Whilst some studies have shown that the levels of legacy POPs such as PCBs in some Arctic populations are declining (Bytingsvik et al. 2012) there is curently insufficient evidence to confirm that hexachlorobenzene levels are also declining.

8. Risk assessment for current emissions

Although hexachlorobenzene is no longer produced in Europe small quantities are generated inadvertently, for example during some incineration processes or as an impurity in some chemical manufacturing processes. Therefore small emissions to the environment are currently still possible and estimates of these emissions are reported in chapter 2.

In the first part of this chapter a risk assessment for marine arctic predators is described for current emissions of hexachlorobenzene. In the second part of this chapter a local risk assessment is done based on current emissions. Estimates of the distribution and environmental exposure of hexachlorobenzene have been made using EUSES (version 2.1.2). It is a mathematical model which is used for example for estimating environmental exposure of industrial chemicals under REACH (ECHA 2010).

The exposure and risk assessment discussed in this chapter does not consider historical contamination and it considers only the potential effects on the aquatic environment. This assessment does not consider risks posed to the terrestrial environment.

8.1 Environmental Exposure and Effects

General information on the emissions of hexachlorobenzene have been reported in Section2. This risk assessment has been performed on the basis of the typical emissions from Euro Chlor member companies. Although site specific data are not available it is assumed that a representative emission per site is about 0.1 kg per year. This value has been used as a representative emission for a single site to estimate the Predicted Environmental Concentrations (PECs) for the local environment, i.e. in the vicinity of a hexachlorobenzene emitting site. Exposure scenarios involving emissions to waste water were assessed without treatment at a WWTP or STP, and for the dafult level of dilution in receiving waters (i.e. 10 fold dilution for freshwaters and 100 fold dilution for marine waters). This is considered to be representative of a reasonable worst case situation where the emission arises from historically contaminated ground in the site. A risk assessment was not only done for an emission to a local freshwater environment but also for a local marine environment. As mentioned previously, calculations were performed in EUSES.

The physicochemical and environmental fate properties and parameter values used for the EUSES calculations are presented in Table 21.

Table 21 Physicochemical and environmental fate properties of hexachlorobenzene

Physicochemical Properties[1]	Value	Units
Molecular Weight	284.8	$g.mol^{-1}$
Melting Point	2.30E+02	°C
Boiling Point	3.22E+02	°C
Vapour Pressure at 25 °C	2.50E-03	Pa
Water Solubility at 25 °C	5.00E-03	$mg\ l^{-1}$
Octanol-Water Partition Coefficient	5.70E+00	log10
Henry's Law Constant	1.42E+02	$Pa\ m^3\ mol^{-1}$
Environmental Fate Properties[2]	Value	Units
Organic carbon-water partition coefficient	5.22E+04	$l\ kg^{-1}$
Total rate constant for degradation in bulk surface water	6.00E-04	d^{-1}
Total rate constant for degradation in bulk saltwater	3.00E-04	d^{-1}
Total rate constant for degradation in bulk sediment	5.14E-04	d^{-1}
Rate constant for degradation in air	3.80E-04	d^{-1}
Total rate constant for degradation in bulk soil	3.08E-04	d^{-1}
Bioaccumulation Properties		
BCF	18200	$L\ kg^{-1}$ wwt
BMF_1	3.65	-
BMF_2	2.0	-

[1]Physicochemical properties are reported in IUCLID (ECB 2000).
[2]Environmental half-lives have been taken from Barber et al. (2005).

The regional emission is assumed to be 20% of the total continental emission, i.e. the reasonable worst case region or country is assumed to be responsible for 20% of the total European

emissions. The reasonable worst case site within a local area is assumed to be responsible for 100% of the total local emissions (i.e. FMLS = 1.0).

To determine the exposure with EUSES an emission rate of hexachlorobenzene has to be assumed. The assumed daily emissions rates are shown in Table 22 with emission occurring 350 days per year.

Table 22 Assumed daily emission rates of hexachlorobenzene (g d^{-1}) at local, regional and continental scales

Emissions	Local	Regional	Continental
Waste water	0.219	0.219	1.97
Surface water	0.055	0.055	0.49

This results in estimated annual emissions of hexachlorobenzene, for the whole of Europe, of 6.76 kg yr^{-1} to wastewater and 84 g yr^{-1} to air. These emissions to waste water are comparable to the emissions of hexachlorobenzene reported by Euro Chlor members during recent years. The emission to air is higher than that reported by Euro Chlor members during recent years, by a factor of approximately 5. It is possible that local controls have resulted in emissions from hexachlorobenzene producing processes being somewhat lower than the default emission scenarios applied within EUSES, possibly resulting in the disposal of hexachlorobenzene as waste (with the most likely route of waste disposal being incineration).

Hexachlorobenzene is persistent in the environment, with half-lives in the order of years in all environmental compartments. Any assumptions made regarding the degradation rates of hexachlorobenzene in the various different environmental compartments have very little influence on the outcome of the risk assessment. This is because environmental degradation of hexachlorobenzene is so slow. Environmental half-lives for hexachlorobenzene for use in exposure modelling have been taken from Barber et al. (2005), and the values used within EUSES are provided in Table 23.

Table 23 Half-lives of hexachlorobenzene in different environmental compartments

Compartment	Half-life	Degradation rate constant
Air	5.0 yrs	3.8×10^{-4} d^{-1}
Freshwater	6.0 yrs	6.0×10^{-4} d^{-1}
Sea water	12 yrs	3.0×10^{-4} d^{-1}
Sediment	3.7 yrs	5.1×10^{-4} d^{-1}
Soil	6.2 yrs	3.1×10^{-4} d^{-1}

The predicted no effect concentrations (PNEC) used for assessment of the potential impact of emissions of hexachlorobenzene on the aquatic environment are listed in Table 24.

Table 24 Predicted No-Effect Concentrations of hexachlorobenzene

Predicted No-Effect Concentration (PNEC)	Value	Units
PNEC for Micro-organisms in a STP	1.00E-03	mg l^{-1}
PNEC for Aquatic Organisms	8.10E-02	µg l^{-1}
PNEC for Marine Organisms	4.00E-02	µg l^{-1}
PNEC for Fresh-water Sediment-dwelling Organisms	>0.365	mg kg^{-1} wwt
PNEC for Marine Sediment Organisms	>0.183	mg kg^{-1} wwt
PNEC for Secondary Poisoning of Birds and Mammals	1.67E-02	mg kg^{-1}

8.2 Marine arctic predators

Based on the emission data mentioned above PECs for the arctic environment have been estimated with EUSES. This is essentially an extension of the concept of local, regional, and continental scales within EUSES to include global regions, and includes moderate, arctic, and tropical regions. This resulted in the following concentrations in the arctic environment:

Water 1.49×10^{-13} mg l^{-1} (0.15 fg l^{-1})
Sediment 3.11×10^{-10} mg kg^{-1} (wwt)

A seawater concentration of 0.15 fg l^{-1}, or 0.00015 pg l^{-1}, has been assumed to calculate the exposure of arctic top predators that results from the current European emissions. This concentration is that predicted for arctic water, as no predictions are made for seawater in the arctic region within EUSES. All of the estimates use a BAF value to calculate the concentration in plankton, and use the 50th percentiles of the BAF values used in the probabilistic modelling. Please find hereafter the calculated concentrations of hexachlorobenzene in the arctic top predators:

Polar bear (RWC)	0.42 ng kg^{-1}
Polar bear (Harp seal)	0.02 ng kg^{-1}
Polar bear (Ringed seal)	0.06 ng kg^{-1}
Beluga (one fish level)	0.13 ng kg^{-1}
Beluga (two fish levels)	0.27 ng kg^{-1}
Narwhal (one fish level)	0.11 ng kg^{-1}
Narwhal (two fish levels)	0.23 ng kg^{-1}
Gull (one fish level)	0.89 ng kg^{-1}
Gull (two fish levels)	1.77 ng kg^{-1}

The PNEC for hexachlorobenzene concentrations in liver tissue (17 ng g^{-1} wwt in liver) can be applied for a direct comparison against the concentrations calculated in arctic predators on the basis of the current European emissions of hexachlorobenzene. Table 25 shows the PECs, RCRs and Margin Of Safety (MOS) for each of the scenarios considered. The MOS is the difference between the PEC and the PNEC and is equivalent to the reciprocal of the RCR. This risk characterisation assumes that hexachlorobenzene concentrations in the livers of predators are equivalent to their whole body concentrations, which may not be a reasonable assumption in all cases.

Table 25 Risk characterisation for predicted body burdens of arctic predators on the basis of current emissions

	PEC (ng kg^{-1})	RCR	MOS
Polar bear (RWC)	0.42	0.000025	40476
Polar bear (harp seal)	0.02	0.000001	850000
Polar bear (ringed seal)	0.22	0.000013	77273
Beluga (one fish level)	0.13	0.000008	130769
Beluga (two fish levels)	0.27	0.000016	62963
Narwhal (one fish level)	0.11	0.000006	154545
Narwhal (two fish levels)	0.23	0.000014	73913
Gull (one fish level)	0.89	0.000052	19101
Gull (two fish levels)	1.77	0.000104	9605

In order to compare the outcome of the model calculations for current emissions against the $PNEC_{oral}$ (16.7 ng g^{-1} wwt in food) it is necessary to calculate the PEC_{oral} for each of the predators, i.e. the concentration of hexachlorobenzene in their prey. The PEC_{oral} values for each of the scenarios are shown in Table 26, along with RCR and MOS values. The PEC_{oral} values for glaucous gulls are calculated as the mean concentration in fish and small birds, reflecting that the assessment assumed that their diet consists of 50% fish and 50% small birds.

Table 26 Risk characterisation for predicted food concentrations of arctic predators on the basis of current emissions

	PEC_{oral} (ng kg^{-1})	RCR	MOS
Polar bear (RWC)	0.027	0.000002	620722
Polar bear (harp seal)	0.030	0.000002	558650
Polar bear (ringed seal)	0.008	0.000000	2094937
Beluga (one fish level)	0.010	0.000001	1675950
Beluga (two fish levels)	0.020	0.000001	837975
Narwhal (one fish level)	0.010	0.000001	1675950
Narwhal (two fish levels)	0.020	0.000001	837975
Gull (one fish level)	0.049	0.000003	338576
Gull (two fish levels)	0.099	0.000006	169288

The two PNEC values derived for hexachlorobenzene are very similar (17 ng g^{-1} wwt in liver and 16.7 ng g^{-1} wwt in food), but are assessed at different trophic levels. The assessment on the basis of the liver concentrations of predators is, therefore, more conservative because it is assessed at a higher stage of the food chain.

The results presented in Table 25 show that the Margin of Safety is higher than 9000 for all arctic marine predators, based on predicted body burdens. The results presented in Table 26 show that the Margin of Safety is higher than 100000 for all arctic marine predators, based on predicted concentrations in their prey. It can be concluded that current European emission of hexachlorobenzene do not result in a risk for arctic marine predators.

8.3 Local Risk Assessment Results

In the previous section the risks of a current emission of hexachlorobenzene on arctic predators has been assessed. However an emission of hexachlorobenzene in a specific area of Europe can also have an effect on organisms living in the vicinity of the emission site. For example an emission of hexachlorobenzene via an effluent to a river can have an effect on the pelagic organisms or sediment organisms living near the emission site. This section will address the local risk assessment of such an aquatic emission using different scenarios. Because this chapter addresses current emissions, any regional background contribution to local concentrations in air and water has not been taken into account as these were assumed to be negligible.

The results of the EUSES calculations are presented in Table 27.

Table 27 Predicted Environmental Concentrations and RCRs for hexachlorobenzene

Compartment	PEC	RCR
Local PEC in surface water (dissolved) (µg l^{-1})	1.27E-05	0.16
Local PEC in fresh-water sediment (mg kg wwt^{-1})	0.0144	<0.02
Local PEC in seawater (dissolved) (µg l^{-1})	1.27E-06	0.03
Local PEC in marine sediment (mg kg wwt^{-1})	1.44E-03	<0.004
Concentration in fish for secondary poisoning (freshwater) (mg kg wwt^{-1})	0.422	25.3
Concentration in fish for secondary poisoning (marine) (mg kg wwt^{-1})	0.042	2.53
Concentration in fish-eating marine top-predator (mg kg wwt^{-1})	0.017	1.01

The data presented in Table 27 show that the most sensitive receptor is fish eating predators in freshwaters. The greater dilution available for emissions to the marine environment results in lower risks for marine systems. The risks for the marine top predators are lower than for the marine fish eating predators which is due to the marine top predators not only eating locally contaminated prey but is foraging over a larger area and therefore also eating non-contaminated prey

The calculated PECs do not consider any background level of hexachlorobenzene contamination as a result of historic uses, and may therefore be difficult to compare with any available monitoring data. It is also important, when comparing model predictions and measured environmental concentrations, that the appropriate spatial scale (i.e. local, regional or continental) is considered. Measured data should only be compared with the predicted local concentrations where a localised source of emission can be identified.

It is clear from this assessment that secondary poisoning is the critical issue for an environmental risk assessment of hexachlorobenzene. This is consistent with the water quality standard set for hexachlorobenzene under the Water Framework Directive, in that the only standard maintained is that for the levels in biota. The bioaccumulation of hexachlorobenzene is clearly highly variable between different trophic linkages and ecosystems (see Section 3). This means that a similar environmental concentration may, or may not, result in an unacceptable level of hexachlorobenzene accumulating in the prey organisms of predators in different situations. For this reason the approach applied to the hexachlorobenzene EQS under the WFD, which is based on the actual level of hexachlorobenzene in potential prey species, is a much more reliable indicator of the potential risk than estimates based on aquatic exposure

concentrations. Many of the issues raised in Section 7.7 also apply equally to the local scale assessment of secondary poisoning. It is also clear that local emissions of hexachlorobenzene to the environment from Euro Chlor members are very low. However, an emission of 0.1 kg per year to the aquatic compartment can result in a risk when the dilution into the receiving water is not sufficiently high.

9 Conclusions

The critical physicochemical properties for the environmental risk assessment are the vapour pressure, water solubility, and log K_{OW}. Hexachlorobenzene has a moderate vapour pressure, a high log K_{OW}, and a low water solubility. These properties can be indicative of a potential cause for concern due to the potential for adverse effects to be caused over the longer term. In addition, hexachlorobenzene exhibits very little biodegradation in the environment, leading to long half-lives in environmental media. Hexachlorobenzene also partitions strongly to soils and sediments, which can reduce the availability for uptake by organisms, but also means that historic contamination can remain in the environment, particularly in soils and sediments, for extended periods of time after emissions have ceased. Hexachlorbenzene undergoes long range transport, and historic emissions from temperate regions have resulted in the contamination of remote arctic environments.

Emissions of hexachlorobenzene in Europe are tightly controlled. Although hexachlorobenzene is no longer intentionally produced, small quantities are generated inadvertently as a result of incineration and other high temperature processes, or as an impurity in some chemical manufacturing processes.

Hexachlorobenzene is accumulated by organisms from their surrounding environment and their food, and some of the measured bioconcentration, bioaccumulation, and biomagnification factors are very high. The accumulation of hexachlorobenzene by organisms is, however, subject to considerable uncertainty in any specific situation because of the considerable variability which is observed in the accumulation between different organisms and between different trophic levels.

The biomagnification of hexachlorobenzene is also highly variable between different trophic linkages with BMF values varying from less than 1 to greater than 100 in the most extreme cases. It would appear that higher BMF values are typically found for higher organisms, such as birds and mammals, which may be expected to have higher metabolic and food intake rates than cold blooded organisms. Typical BMF values, such as the 50^{th} percentile of a distribution, for lower trophic levels are in the range 1 to 4 but can be much higher for higher trophic levels. It is clear that different BMF values need to be derived for different trophic linkages due to the differences in the behaviour and physiology of different groups of species.

Predicted No Effect Concentrations have been derived for the aquatic environment (0.08 µg l^{-1}), the marine environment (0.04 µg l^{-1}), sediment ecosystems (>84 mg kg^{-1} dry weight), food of top predators (16.7 µg kg^{-1} wet weight in food), and predator liver concentrations (17 ng g^{-1} wet weight in liver). The critical environmental endpoint, or receptor, is the top predator. This is because hexachlorobenzene can accumulate to potentially harmful levels under some circumstances where the environmental concentrations are not sufficiently high to cause direct toxic effects in aquatic organisms. Monitoring of hexachlorobenzene levels in the environment is therefore best targetted towards the relevant prey species of higher predators.

A targeted assessment of several top predators within the marine arctic ecosystem, specifically the beluga, narwhal, polar bear and glaucous gull food chains, has been undertaken. This suggests that reasonable estimates of the levels of hexachlorobenzene in top predators can be made, where adequate monitoring data exist for specific BMF values to be derived for each trophic linkage. It also appears that higher BMF values tend to be identified for higher trophic levels, such as mammals and birds, which may have higher metabolic rates and consequently higher food ingestion rates. Where deterministic calculations are undertaken it is considered to be most appropriate to use the median of a range of BAF values for reliable estimates of the levels of hexachlorobenzene in top predators to be made.

A significant proportion of the populations of arctic marine predators are expected to be potentially at risk due to the predicted accumulation resulting from current levels of hexachlorobenzene exposure. Whilst measurements of the liver concentrations of birds and mammals indicate a potential risk for highly exposed populations they also suggest that the proportion potentially at risk may be slightly smaller than predicted by accumulation modelling. Risk characterisations on the basis of the current European emissions of hexachlorobenzene indicate that no risks to arctic marine predators are expected at a typical current emission level for Euro Chlor member companies. Following the current risk assessment methodology for secondary poisoning (based on predicted food concentrations for arctic predators), a margin of safety of greater than 100000 has been estimated for every scenario considered, while a MOS of higher than 9000 has been estimated for every scenario considered when based on predicted body burdens of arctic predators

Local emissions of hexachlorobenzene can potentially result in risks to predators due to accumulation in the local food chain. An environmental quality standard for hexachlorobenzene is applied under the Water Framework Directive. The quality standard is derived for the levels of hexachlorobenzene in the prey of predators, and may be measured in fish and invertebate tissues. Potential risks due to secondary poisoning are anticipated for a typical level of emission from a Euro Chlor member company is dilution in the local receiving water is not sufficiently high.

10. References

Abernethy S., Bobra A. M., Shiu W. Y., Wells P. G. and Mackay D. (1986) Acute lethal toxicity of hydrocarbons and chlorinated hydrocarbons to 2 planktonic crustaceans: The key role of organism-water partitioning; Aquatic Tox. 8 163-174.

Ahmad N., Benoit D., Brooke L., Call D., Carlson A., DeFoe D., Huot J., Moriarty A., Richter J., Shubat P., Veith G. and C. Wallbridge (1984) Aquatic toxicity tests to characterize the hazard of volatile organic chemicals in water: A toxicity data summary - Parts I and II; EPA-600/3-84-009, US Environmental Protection Agency, Duluth, MN.

Arnot, J.A, Gobas, F.A.P.C. (2004) A food web bioaccumulation model for organic chemicals in aquatic ecosystems. Environ. Toxicol. Chem. 23, 2343-2355.

Arnot, Gobas (2006) A review of bioconcentration factor (BCF) and bioaccumulation factor (BAF) assessments for organic chemicals in aquatic systems. Environ. Rev. 14, 257-297.

Atkinson and Ramsay (1995) The effects of prolonged fasting on the body composition and reproductive success of female polar bears (Ursus maritimus). Functional Ecology, 9, 559-567.

Barber, T. R., Fuchsman, P.C., Chappie, D.C., Sferra, J.C. and Sheehan, P.J. (1997) Toxicity of Hexachlorobenzene to *Hyalella azteca and Chironomus tentans* in spiked sediment bioassays. Environ. Toxicol. Chem. 16:1716-1720.

Barber, Sweetman, Jones (2005) Hexachlorobenzene – Sources, environmental fate and risk characterisation. Euro Chlor, Brussels, Belgium.

Baturo, W., Lagadic, L. and Caquet, T. (1995) Growth, fecundity and glycogen utilisation in Lymnaea palustris exposed to atrazine and hexachlorobenzene in freshwater mesocosms. Env. Toxicol. Chem. 14, 503-511.

Biggs, D.C., Rowland, R.G. and Wurster, C.F. (1979) Effects of trichroethylene, hexachlorobenzene and polychlorinated biphenyls on the growth and cell size of marine phytoplankton. Bull. Environm. Contam. Toxicol. 21, 196-201.

Bleavins M, Aulerich R (1981) Feed consumption and food passage time in mink (*Mustela vison*) and european ferrets (*Mustela putoris furo*). Lab. Anim. Sci. 31, 268-269.

Born EW, Dahlgaard H, Riget FF, Dietz R, Øien N, Haug T (2002) Regional variation of caesium-137 in minke whales *Balaenoptera acutorostrata* from West Greenland, the Northeast Atlantic and the North Sea. Polar Biology 25:907-913.

Brooke D. Crookes M. (2007) Verification of bioaccumulation models for use in environmental standards. Part A: aquatic models. Science report_SC030197/SR2. Environment Agency, UK.

Bustnes J, Erikstad K, Bakken V, Mehlum F, Skarre J. (2000) Feeding ecology and the concentration of organochlorines (OCs) in glaucous gulls. Ecotoxicology 9:179-186.

Bytingsvik J, Lie E, Aars J, Derocher AE, Wiig Ø, Jenssen BM, 2012. PCBs and OH-PCBs in polar bear mother-cub pairs: A comparative study based on plasma levels in 1998 and 2008. The Science of the Total Environment 417-418:117-128.

Call, D. J., Brooke L.T., Ahmad N. and Richter J.E. (1983) Toxicity and Metabolism Studies with EPA Priority Pollutants and Related Chemicals in Freshwater Organisms; EPA 600-3-83-095, PB 83-263-665.

Calamari, D., Galassi, S., Setti, F. and Vighi, M. (1983) Toxicity of selected chlorobenzenes to aquatic organisms. Chemosphere 12: 253-262.

Carlson, A.R. and Kosian P.A. (1987) Toxicity of chlorinated benzenes to fathead minnows (*Pimephales promelas*); Arch. Environ. Contam. Toxicol. 16 129-135.

Caspers, N., Hartmann, P., Kanne, R. and Knoop G. (1993) UWSF- Z. Umweltchem. Oekotox. 5 (5) 265-270

Caspers N. (1993) Biologische Effekte von Hexachlorbenzol (HCB) in aquatischen Modellökosystemen. Umweltchem. Ökotox. 10 (4) 205 – 213.

Catalan, Ventura, Vives & Grimalt (2004) Roles of food and water in the bioaccumulation of organochlorine compounds in high mountain lake fish. Environ. Sci. Technol. 38, 4269-4275.

CITI (1992) Biodegradation and Bioaccumulation: Data of Existing Chemicals Based on the CSCL Japan; Chemicals Inspection and Testing Institute, Japan.

Corsolini, S.; Kannan, K.; Imagawa, T.; Focardi, S.; Giesy, J.P. (2002) Polychloronaphthalenes and other dioxin like compounds in Arctic and Antarctic marine food webs. Environ. Sci. Technol. 36, 3490-3496.

Cooper, Benner, McClelland, Peterson, Holmes, Raymond, Hansell, Grebmeier and Codispoti (2005) Linkages among runoff, dissolved organic carbon, and the stable oxygen isotope composition of seawater and other water mass indicators in the Arctic Ocean, J. Geophys. Res. 110.

Czub and McLachlan (2004) A Food Chain Model to Predict the Levels of Lipophilic Organic Contaminants in Humans. Environ. Toxicol. Chem. 23, 2356-2366

De Bruijn, Busser, Seinen, Hermens (1989) Determination of octanol/water partition coefficients for hydrophobic organic chemicals with the “slow stirring” method. Environ. Toxicol. Chem. 8, 499-512.

Dunkin R, McLellan W, Blum J, Pabst A (2005) The ontogenetic changes in the thermal properties of blubber from Atlantic bottlenose dolphin Tursiops truncates. J. Exp. Biol. 208, 1469-1480.

EC (2007) Report on the proposal for a directive of the European Parliament and of the Council on environmental quality standards in the field of water policy and amending Directive 2000/60/EC. European Parliment, Brussels, Belgium. http://www.europarl.europa.eu/sides/getDoc.do?pubRef=-//EP//NONSGML+REPORT+A6-2007-0125+0+DOC+PDF+V0//EN

ECB (European Chemicals Bureau) (2000) IUCLID data set of hexachlorobenzene. Available via: http://esis.jrc.ec.europa.eu/doc/IUCLID/data_sheets/118741.pdf

ECHA (European Chemicals Agency) (2008) Guidance on information requirements and chemical safety assessment Chapter R.10: Characterisation of dose [concentration]-response for environment. Helsinki, Finland.

ECHA (European Chemicals Agency) (2010) Guidance on information requirements and chemical safety assessment Chapter R.16: Environmental exposure estimation. Helsinki, Finland.

Egeler P, Meller M, Roembke J, Spoerlein P, Streit B, Nagel R. (2001) Tubifex tubifex as a link in food chain transfer of hexachlorobenzene from contaminated sediment to fish. Hydrobiologia 463:171-184.

Environment Agency (1998) Environmental Assessment. The history of contamination in sediments from the Mersey Estuary. Environment Agency, Bristol, UK.

Erturk E. Lambrecht R. Peters H. Cripps D. Gocmen A. Morris C. Bryan G. (1985) Oncogenicity of hexachlorobenzene. In Hexachlorobenzene: Proceedings of an international symposium. Morris C. & Cabral J. (Eds.) IARC Scientific Publications No. 77. IARC, Lyon, France.

Evans K, Hindell M, Thiele D (2003) Body fat and condition in sperm whales, *Physeter macrocephalus*, from southern Australian waters. Comp. Biochem. Physiol. 134, 847-862.

Euro Chlor (2002) Hexachlorobenzene: Risk Assessment For the Marine Environment, OSPARCOM Region - North Sea. Euro Chlor, Brussels, Belgium.

Farley and Robbins (1994) Development of two methods to estimate body composition of bears. Can. J. Zool. 72, 220-226.

FHI (2005) Common Implementation Strategy for the Water Framework Directive. Environmental Quality Standards, Substance datasheets, Brussels, Belgium.

Figueroa, I. and Simmons, M.S. (1991) Structure Activity Relationships of Chlorobenzenes Using DNA Measurement as a Toxicity Parameter in Algae. Environ. Toxicol. Chem. 10:323-329

Freidig A, Garicano E, Busser F, Hermens J. (1998) Estimating impact of humic acid on bioavailability and bioaccumulation of hydrophobic chemicals in guppies using kinetic solid phase extraction. Environ. Toxicol. Chem. 17:998-1004.

Fuchsman, P.C., Barber, T.R. and Sheehan, P.J. (1998a) Sediment Toxicity Evaluation for Hexachlorobenzene; Spiked Sediment Tests with *Leptocheirus plumulosus, Hyalella azteca and Chironomus tentans*. Arch. Environ. Contam. Toxicol.35: 573-579.

Fuchsman P, Chappie D, Duda D & Barber T (1998b) Spiked sediment toxicity testing with hydrophobic organic chemicals:dioxin and hexachlorobenzene. Organohalogen Compounds, 39, 9-12.

Geike, F. and C.V. Parasher, (1976a) Effect of hexachlorobenzene on some growth parameters of Chlorella pyrenoidosa. Bull. Environ. Contam. Toxicol. 15: 670-677.

Geike, F. and C.D. Parasher (1976b) Effect of hexachlorobenzene (HCB) on growth of *Tetrahymena pyriformis*. Bull. Environ. Contam. Toxicol. 16: 347-354.

Geyer, H., Scheunert, I. and Korte, F. (1985) The effects of organic environmental chemicals on the growth of the alga Scenedesmus subspicatus: A contribution to environmental biology. Chemosphere 14(9) 1355-1369

Gobas and Zhang (1992) Measuring bioconcentration factors and rate constants of chemicals in aquatic organisms under conditions of variable water concentrations and short exposure time. Chemosphere, 25, 1961-1971.

Gobas F. (1993) A model for predicting the bioaccumulation of hydrophobic organic chemicals in aquatic food webs: application to Lake Ontario. Ecol Model 69:1- 17.

Haug T, Gjosaeter H, Lindstrom U, Nilssen KT. (1995) Diet and food availability for northeast Atlantic minke whales (*Balaenoptera acutorostrata*) during the summer of 1992. ICES Journal of Marine Science 52:77-86.

Haug T, Lindstrom U, Nilssen KT. (2002) Variations in minke whale (*Balaenoptera acutorostrata*) diet and body condition in response to ecosystem changes in the Barents Sea. Sarsia 87:409-422.

Hobbs, Lebeuf, Hammill (2002) PCBs and OCPs in male harbour, grey, harp and hooded seals from the Estuary and Gulf of St Lawrence, Canada. Sci. Tot. Env. 296, 1-18.

Hoogen and Opperhuizen (1988) Toxicokinetics of chlorobenzenes in fish. Environ. Toxicol. Chem, 7, 213-219.

Hsieh S, Hsu C, Tsal D & Chen C (2006) Quantitative structure activity relationships for toxicity of non-polar narcotic chemicals to *Pseudokirchneriella subcapitata*. ET&C. 25, 2920-2926.

Innes, Lavigne, Earle & Kovacs (1987) Feeding rates of seals and whales. Journal of Animal Ecology. 56, 115-130.

IPCS (1997) Environmental Health Criteria 195; Hexachlorobenzene. WHO, Geneva, Switzerland. Accessed on-line 17/07/08:
http://www.inchem.org/documents/ehc/ehc/ehc195.htm

Johnson, W.W. and Finley, M.T. (1980) Handbook of acute toxicity of chemicals to fish and aquatic invertebrates; US Dept. of the Interior: Fish and Wildlife Service. Resource Publication 137, Washington DC.

Kinney, Loder and Groves (1971) Particulate and Dissolved Organic Matter in the Amerasian Basin of the Arctic Ocean. Limnology and Oceanography, 16, 132-137

Klevaine, Severinsen, Skarre (2000) Biological transport and mammal to mammal transfer of organochlorines in arctic fauna. Marine Environmental Research, 49, 343-357.

Klimisch HJ, Andreae E and Tillmann U (1997). A systematic approach for evaluating the quality of experimental and ecotoxicological data. Reg.Tox. and Pharm. 25:1-5

Knie, J., Hälke, A., Juhnke, I., Schiller, W. (1983) Ergebnisse der Untersuchungen von chemischen Stoffen mit vier Biotests (results of studies on chemical substances with four biotests); Dtsch. Gewaesserkundliche Mitteilungen: 27(3): 77-79.

Könemann, H. (1981) Quantitative structure activity relationships in fish toxicity studies I: Relationship for 50 industrial pollutants; Toxicology 19 (3) 209-221.

Korte, F. et al. (1981) Ueberpruefung der Durchfuehrbarkeit von Pruefungsvorschriften und der Aussagekraft der Grundpruefung des E. Chem G. Forschungsbericht 106 04 006/01; Umweltbundesamt, Berlin.

Laidre KL and Heide Jorgensen MP. (2005) Winter feeding intensity of narwhals (*Monodon monoceros*). Marine Mammal Science 21:45-57.

Laska, A., Bartell, C., Condie, D., Brown, J., Evans, R. and Laseter J. (1978) Acute and chronic effects of hexachlorobenzene and hexachlorobutadiene in Red Swamp Crayfish (Procambarus clarki) and selected fish species; Toxicol. and Appl. Pharmacol. 43 1-12.

Lores, Patrick, Summers (1993) Humic acid effects on uptake of hexachlorobenzene by sheepshead minnows in static sediment water systems. Environ. Toxicol. Chem, 17, 998-1004.

Lundstedt-Enkel, Tysklind, Trygg, Schuller, Asplund, Eriksson, Haggberg, Odsjo, Hjelmberg, Olsson, Orberg (2005) A statistical resampling method to calculate biomagnification factors exemplified with organochlorine data from herring (Clupea harengus) muscle and guillemot (Uria aalge) egg from the Baltic sea. Environ. Sci. Technol. 39, 8395-8402.

Lydersen C, Weslawski JM, Øritsland NA. (1991) Stomach content analysis of minke whales *Balaenoptera acutorostrata* from the Lofoten and Vesterålen areas, Norway. Ecography 14:219-222.

MacGregor K, Oliver I, Duguid A, Ridgway I. (2011) Persistent Organic Pollutants in Scottish freshwater biota. Monitoring options, current levels and the way forward. Scottish Environment Protection Agency, Stirling, UK.

McLeese, D.W. and Metcalfe, C.D. (1980) Toxicities of eight organochlorine compounds in sediment and seawater to Crangon septemspinosa. Bull. Environ. Contam. Toxicol. 25: 921-928.

Meller M, Egeler P, Rombke J, Schallnass H, Nagel R & Streit B (1998) Short-term toxicity of lindane, hexachlorobenzene and copper sulphate to Tubificid sludgeworms (Oligochaeta) in artificial media. Ecotoxicology & Environmental Safety, 39, 10-20.

Moore, Breton, Lloyd (1997) The effects of hexachlorobenzene on mink in the Canadian environment: an ecological risk assessment. Environ. Toxicol. Chem. 16, 1042-1050.

Mortimer M and Connel D (1994) Critical internal and aqueous lethal concentrations of chlorobenzenes with the crab *Portunus pelagicus*. Ecotoxicology and Environmental Safety, 28, 298-312.

Mortimer M and Connel D (1995) Effect of exposure to chlorobenzenes on growth rates of the crab *Portunus pelagicus* (L). Environmental Science & Technology, 29, 1881-1886.

Nebeker, A.V., Griffis, W.L., Wise, C.M., Hopkins, E. and Barbitta, J.A. (1989) Survival, reproduction and bioconcentration in invertebrates and fish exposed to hexachlorobenzene. Environ. Toxicol. Chem. 8: 601-611.

Oliver, Niimi (1983) Bioconcentration of chlorobenzenes from water by Rainbow Trout: correlations with partition coefficients and environmental residues. Environ. Sci. Technol, 17, 287-291.

Parker, J.G. (1984) The effects of selected chemicals and water quality on the marine polychaete Ophryotrocha diadema; Water Res. 18 865-868.

Parrish, P.R., Cook, G.H. and Patrick, J.M. (1975) Hexachlorobenzene: Effects on several estuarine animals; Proc. 28th Ann. Conf. S.E. Assoc. Game Fish Commissioners, 179-186.

Pastor, Sanpera, Gonzalez-Solis, Ruiz, Albaiges (2004) Factors affecting the organochlorine pollutant load in biota of a rice field ecosystem (Ebro Delta, NE Spain). Chemosphere, 55, 567-576.

Persoone G and Uyttersprot G (1975) The influence of inorganic and organic pollutants on the rate of reproduction of a marine hypotrichous ciliate: *Euplotes Vannus* Muller. Rev. Intern. Oceanogr. Med, pp 125.

Pierce GJ, Santos MB, Reid RJ, Patterson IAP and Ross HM (2004) Diet of minke whales (*Balaenoptera acutorostrata*) in Scottish (UK) waters with notes on strandings of this species in Scotland 1992-2002. Journal of the Marine Biological Association of the United Kingdom 84:1241-1244.

Reif V, Tornberg R, Jungell S, Korpimäki E (2001) Diet variation of common buzzards in Finland supports the alternative prey hypothesis. Ecography 24:267–274.

Reyes JC (1991) The conservation of small cetaceans: a review. Report prepared for the secretariat of the Convention on the Conservation of Migratory Species of Wild Animals. UNEP/CMS Secretariat, Bonn, Germany.

RIVM (1994) Towards integrated Environmental Quality Objectives for several compounds with a potential for secondary poisoning. (679101 012) RIVM, Bilthoven, Netherlands.

Rush G. Smith J. Maita K. Bleavins M. Aulerich R. Ringer R. Hook J. (1983) Perinatal hexachlorobenzene toxicity in the mink. Environmental Research. 31, 116-124.

Russell, Lazar, Haffner (1995) Biomagnification of organochlorines in lake Eire White Bass. Environ. Toxicol. Chem. 14, 719-724.

Russell, Gobas, Haffner (1999) Role of chemical and ecological factors in trophic transfer of organic chemicals in aquatic food webs. Environ. Toxicol. Chem. 18, 1250-1257.

Scheubel (1984) Überprüfung der Durchführbarkeit von Prüfungsvorschriften und der Aussagekraft der Stufe 1 und 2 des Chemikaliengesetzes Teil III. Umweltbundesamt, Dessau, Germany.

Schubert and Stein (1996) Deposition of organic carbon in Arctic Ocean sediments: terrigenous supply vs marine productivity. Organic Geochemistry, 24, 421-436.

Sergeant and Brodie (1969) Body size in white whales, Delphinapterus leucas. Journal of the Fisheries Research Board of Canada, 26, 2561-2580.

Shahidi, Wanasundara & Wanasundara (1996) Seal blubber oil: a novel source of ¤3 fatty acids. Journal of Food Lipids, 3, 293-306.

Song S, Xu Y and Zhou B (2006) Effects of hexachlorobenzene on antioxidant status of liver and brain of common carp (*Cyprinus carpio*). Chemosphere, 65, 699-706.

Sormo, Salmer, Jenssen, Hop, Baek, Kovacs, Lydersen, Falk-Petersen (2006) Biomagnification of polybrominated diphenyl ether and hexabromocyclododecane flame retardants in the polar bear food chain in Svalbard, Norway. Environ. Toxicol. Chem. 25, 2502-2511.

Spehar, R. – Personal communication – e-mail: spehar.robert@epamail.epa.gov – February 2000

US EPA (1987) Acute toxicity handbook of chemicals to estuarine organisms; EPA/600/8-87/017 Environmental Research Laboratory, Gulf Breeze, FL.

US EPA (1988) Ambient aquatic life water quality criteria for hexachlorobenzene. Duluth, Minnesota, US Environmental Protection Agency, Office of Research and Development.

US EPA (1993) Wildlife exposure factors handbook. Vol. 1. EPA/600/R-93/187, USEPA, Washington, USA.

Van de Plassche E. (1994) Towards integrated environmental quality objectives for several compounds with a potential for secondary poisoning. RIVM report no. 679101 012, Bilthoven, Netherlands.

Van Vlaardingen PLA, Traas TP, Wintersen AM, Aldenberg T (2004) A program to calculate hazardous concentrations and fraction affected, based on normally distributed toxicity data. RIVM report 601501028/2004. RIVM, Bilthoven, Netherlands.

Vorkamp, Riget, Glasius, Pecseli Ledeuf and Muir (2004) Chlorobenzenes, chlorinated pesticides, coplanar chlorobiphenyls and other organochlorine compounds in Greenland biota. Sci. Tot. Env. 331, 157-175.

Vos de, J.G., Breeman, H.A. and Benschop, H. (1968) The occurrence of the fungicide hexachlorobenzene in wild birds and its toxicological importance. A preliminary communication. Mededelingen Rijksfakulteit Landbouwwetenschappen Gent. 33:1263-9

Voutsas, Magoulas and Tassios (2002) Prediction of the bioaccumulation of persistent organic pollutants in aquatic food webs. Chemosphere, 48, 645-651.

Welch, Bergmann, Siferd, Martin, Curtis, Crawford, Conover and Hop (1992) Energy flow through the marine arctic ecosystem of the Lancaster Sound region, arctic Canada. Arctic, 45, 343-357.

WHO (1970) 1969 Evaluations of some pesticide residues in food; Hexachlorobenzene, WHO, Rome, Italy. WHO/FOOD ADD./70.38. Accessed on-line 17/07/08. http://www.inchem.org/documents/jmpr/jmpmono/v069pr20.htm

Wienburg and Shaw (2004) Factors influencing Liver PCB concentrations in sparrowhawks (Accipter nisus), Kestrels (Falco tinnunculus) and herons (Ardea cinerea) in Britain. Environmental Pollution, 132, 41-50.

Wania F and Mackay D (1995) A global distribution model for persistent organic chemicals. Sci. Tot. Env. 160/161, 211-232.

Yoshioka, Y., Ose, Y. and Sato, T. (1985) Testing for the toxicity of chemicals with *Tetrahymena pyriformis*; The Science of the Total Environment 43 149-157.

Zhan W, Xu Y, Li A, Zhang J, Schramm K and Kettrup A (2000) Endocrine disruption by hexachlorobenzene in Crucian Carp (*Carassius auratus gibelio*) Bull. Environ. Contam. Toxicol., 65, 560-566.

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 summarised 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 LC_{50}, EC_{50} 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

Summary table of aquatic ecotoxicity data for hexachlorobenzene

Species	Duration (h, hours; d, days)	Type of Study	Criterion (LC_{50}/EC_{50} NOEC/LOEC)	Concentration (µg l^{-1})	Validity	Comments	Reference
Acute fish studies							
1. Freshwater							
Lepomis macrochirus	96h	A, FT	LC_{50}	>78	1	No mortality, Above water solubility	Call et al., 1983
Oncorhynchus mykiss	96h	A, FT	LC_{50}	>81	1	No mortality or other symptoms, Above water solubility	Call et al., 1983; Ahmad et al., 1984
Oncorhynchus mykiss	48h	A, S, C	LC_{50}	>30	1	No mortality, Above water solubility	Calamari et al., 1983
Brachydanio rerio	48h	A, S, C	LC_{50}	>30	1	No mortality, Above water solubility	Calamari et al., 1983
Leuciscus idus	48h	N, S	LC_{50}	7	3		Knie et al., 1983
Poecilia reticulate	14d	N, SS	LC_{50}	>28.5	3	No mortality, Above water solubility	Konemann, 1981
Oryzias latipes	48h	N, S	LC_{50}	>5,000	3	Above water solubility	CITI, 1992
Oncorhynchus kisutch	96h	N, S	LC_{50}	>50,000	3	Above water solubility	Johnson & Finley, 1980
Ictalurus punctatus	96h	N, S	LC_{50}	14,000	3	Above water solubility	Johnson & Finley, 1980
Lepomis macrochirus	96h	N, S	LC_{50}	12,000	3	Above water solubility	Johnson & Finley, 1980
Micropterus salmoides	96h	N, S	LC_{50}	12,000	3	Above water solubility	Johnson & Finley, 1980
Pimephales promelas	96h	N, S	LC_{50}	22,000	3	Above water solubility	Johnson & Finley, 1980

Species	Duration (h, hours; d, days)	Type of Study	Criterion (LC_{50}/EC_{50} NOEC/LOEC)	Concentration (µg l^{-1})	Validity	Comments	Reference
2. Saltwater							
Lagodon rhomboids	96h	A, FT	LC_{50}	>8.4	1	No mortality	Parrish et al., 1975
Cyprinodon variegatus	96h	A, FT	LC_{50}	>13.3	1	No mortality	Parrish et al., 1975
Chronic fish studies							
1. Freshwater							
Pimephales promelas	32d	A, FT	NOEC	4.8	1	Hatch, survival & growth. Maximum concentration tested	Carlson & Kosain, 1987; Ahmad et al., 1984
Pimephales promelas	28d	A, FT	NOEC	3.8	2	Survival. Growth normal but not analysed statistically. Maximum concentration tested.	Nebeker et al., 1989
Micropterus salmoides	10d	A, FT	NOEC	25.8	2	Survival, hematocrit and observable symptoms. Maximum concentration tested. Above water solubility	Laska et al., 1978
Oncorhynchus mykiss	90d	A, FT	NOEC	3.7	2	Growth and survival. Maximum concentration tested.	US EPA (1987) Spehar (2000)
Cyprinus carpio	20d	N, SS	LOEC	2	3	Ecological relevance of endpoints unclear	Song et al., 2006
Brachydanio rerio	14d	A, FT	NOEC	5	4	Original data not located	Korte et al., 1981
Carassius auratus gibelio	14d	N, SS	LOEC	50	4	Above water solubility and ecological relevance not clear	Zhan et al., 2000
2. Saltwater							

Species	Duration (h, hours; d, days)	Type of Study	Criterion (LC_{50}/EC_{50} NOEC/LOEC)	Concentration (µg l^{-1})	Validity	Comments	Reference
Fundulus grandis	10d	A, FT	NOEC	5.7	2	Survival, hematocrit and plasma cortisol levels. Maximum concentration tested. Salinity 4 -5 ‰.	Laska et al., 1978
Acute invertebrate studies							
1. Freshwater							
Gammarus lacustris	96h	A, FT	LC_{50}	>3.3	1	28d LC_{50} also >3.3 µg l^{-1}, but significant mortality. No significant mortality at 1.8 µg /l.	Nebeker et al., 1989
Hyalella azteca	96h	A, FT	LC_{50}	>4.7	1	30d LC_{50} also >4.7 µg l^{-1}. No significant mortality at 4.7 µg l^{-1}.	Nebeker et al., 1989
Daphnia magna	48h	A, FT	LC_{50}	>5	1	Solubility limit. Also no mortality after 7 days.	Nebeker et al., 1989
Procambarus clarki	96h	A, FT	LC_{50}	>27	1	10d LC_{50} also >27 µg l^{-1}. No significant mortality at 27 µg l^{-1}. Above water solubility	Laska et al., 1978
Daphnia magna	24h	N, S, C	EC_{50}	>30	1	Above water solubility	Calamari et al., 1986
Tanytarsus dissimilis	48h	A, S	LC_{50}	>58	1	(Midge larve), Above water solubility	Call et al., 1983
Daphnia magna	48h	N, S, C	LC_{50}	>4.7	3	Non-standard age, temperature and distilled water as diluent.	Abernethy et al., 1986
Daphnia magna	24h	N, S	EC_{50}	>100	3	Above water solubility	Knie et al., 1983
Tetrahymena pyriformis (Protozoan)	24h	N, S	EC_{50}	>50,000	3	Extrapolated (estimated) value, greatly above	Yoshioka et al., 1985

Species	Duration (h, hours; d, days)	Type of Study	Criterion (LC_{50}/EC_{50} NOEC/LOEC)	Concentration (µg l^{-1})	Validity	Comments	Reference
						solubility.	
2. Saltwater							
Crangon septemspinosa	96h	A, SS	LC_{50}	>7.2	1	No mortality, 48h renewal	McLeese & Metcalfe, 1980
Palaemonetes pugio	96h	A, FT	LC_{50}	>17	1	Above water solubility	Parrish et al., 1975
Penaeus duorarum	96h	A, FT	LC_{50}	>25	1	33% mortality at this concentration. Above water solubility	Parrish et al., 1975
Portunus pelagicus	7d	N, SS, C	LC_{50}	>10	2	Insufficient mortality to calculate LC_{50}. Above water solubility	Mortimer & Connel 1994
Artemia spp	24h	N, S, C	LC_{50}	>3.3	3		Abernethy et al., 1986
Ophryotrocha diadema	48h	N, S	LC_{50}	>10,000	3	Above water solubility	Parker, 1984
Crassostrea virginica	48h	N, S	EC_{50}	>1,000	3	Embryo-larval development. Above water solubility	US EPA, 1987
Chronic invertebrate studies							
1. Freshwater							
Hyalella azteca	30d	A, FT	NOEC	4.7	1	Growth reproduction and survival. Maximum concentration tested	Nebeker et al., 1989
Daphnia magna	21d	A, SS	NOEC	14	1	NOEC for reproduction which was inhibited 15% at 45 µg l^{-1}	Caspers et al., 1993
Daphnia magna	21d	A, SS	NOEC	45	1	NOEC for mortality (zero effect). Maximum concentration tested.	Caspers et al., 1993

Species	Duration (h, hours; d, days)	Type of Study	Criterion (LC_{50}/EC_{50} NOEC/LOEC)	Concentration (µg l^{-1})	Validity	Comments	Reference
Daphnia magna	21d	A, SS	NOEC	0.13	2	Calculated NOEC reference could not be obtained, data abstracted from IUCLID. Test parameter: reproduction.	Scheubel, 1984
Gammarus lacustris	28d	A, FT	NOEC	3.3	2	Parameter: survival. Significant mortality 3.3 µg l^{-1}, but not attributed to hexachlorobenzene.	Nebeker et al., 1989
Lumbriculus variegatus	49d	A, FT	NOEC	4.7	2	Survival, growth and asexual reproduction. Worms held in quartz sand.	Nebeker et al., 1989
Daphnia magna	7d	A, FT	NOEC	5	2	NOEC for mortality.	Nebeker et al., 1989
Daphnia magna	14d	A, SS	LOEC	23	2	80% inhibition of reproduction at 23 µg l^{-1}. NOEC not reported. Above water solubility	Calamari et al., 1983
Procambarus clarki	10d	A, FT	NOEC	27	2	NOEC for mortality. Above water solubility	Laska et al., 1978
Ceriodaphnia dubia	7d	A, SS	NOEC	7	2	Survival and reproduction. Maximum concentration tested	US EPA 1988 Spehar (2000)
Lymnaea palustris	70 to 84h	N, S	NOEC	5	3	Mesocom study. No replication of treatments. No effect on survival. Growth and	Baturo et al., 1995

Species	Duration (h, hours; d, days)	Type of Study	Criterion (LC_{50}/EC_{50} NOEC/LOEC)	Concentration (µg l^{-1})	Validity	Comments	Reference
						fecundity generally enhanced.	
Tetrahymena pyriformis **(Protozoan)**	10d	N, S	NOEC	<1	3	Acetone at 5 ml/l. Effects on dry matter, total-N, etc. No statistical analysis.	Geike & Parasher 1976a
2. Saltwater							
Portunus pelagicus	42d	N, SS, C	NOEC	4	2	Growth, concentrations within 20% of nominal. Effects only at highest tested concentration	Mortimer & Connel 1995
Euplotes Vannus **(Cilliate)**	48h	N, S	LOEC	10	3	All test concentrations above water solubility and similar level of inhibition seen at all concentrations	Persoone & Uyttersprot 1975
Acute aquatic plant studies							
Acute studies							
1. Freshwater							
Selenastrum capricornutum	96h	A, S, C	EC_{50}	>30	1	Growth. 12% inhibition at this concn. Above water solubility	Calamari et al., 1983
Selenastrum capricornutum	3h	A, S, C	EC_{50}	30	2	Photosynthesis inhibition. Approx. value based on 2 concentrations. Above water solubility	Calamari et al., 1983
Pseudokirchneriella subcapitata	48h	N, S, C	EC_{50}	370	2	Dissolved oxygen production (EC_{50} for growth 0.65 mg l^{-1}).	Hsieh et al, 2006

Species	Duration (h, hours; d, days)	Type of Study	Criterion (LC_{50}/EC_{50} NOEC/LOEC)	Concentration (µg l^{-1})	Validity	Comments	Reference
						Above water solubility	
Cyclotella meneghiniana	48h	N, S	EC_{50}	2	3	DNA reduction	Figueroa & Simmons, 1991
Chlorella pyrenoidosa	76h	N, S	EC_{50}	>10,000	3	<50% effect on chlorophyll, dry matter, carbohydrates and total-N. Acetone as solvent at 0.33%, with aeration. Solvent control showed effects. Above water solubility	Parasher & Geike, 1978
Chlorella pyrenoidosa	46h	N, S	EC_{50}	>10,000	3	<50% effect on chlorophyll, dry matter, carbohydrates and total-N. Acetone at 0.33% with aeration. Tested at 30°C. Above water solubility	Geike & Parasher, 1976b
Scenedesmus subspicatus	96h	N, S	EC_{50}	>10	3	Above water solubility	Geyer et al., 1985
Haematococcus pluvialis	4h	N, S	EC_{50}	>40	3	Oxygen production. Above water solubility	Knie et al., 1983
2. Saltwater							
Thalassiosira pseudonana and *Dunaliella tertiolecta* (mixed)	72h	N, S	EC_{50}	>100	3	Growth and cell size. Above water solubility	Biggs et al., 1979
Chronic aquatic plant studies							
1. Freshwater							
Selenastrum capricornutum	96h	A, S, C	EC_{12}	30	1	12% inhibition of growth. Approx equivalent of NOEC. Above water	Calamari et al., 1983

Species	Duration (h, hours; d, days)	Type of Study	Criterion (LC_{50}/EC_{50} NOEC/LOEC)	Concentration (µg l^{-1})	Validity	Comments	Reference
						solubility	
Selenastrum capricornutum	3h	A, S, C	NOEC	18	2	Photosynthesis inhibition. Above water solubility	Calamari et al., 1983
Pseudokirchneriella subcapitata	48h	N, S, C	EC_{10}	100	2	Dissolved oxygen production and growth, Above water solubility	Hsieh et al., 2006
Scenedesmus subspicatus	96h	N, S	EC_{10}	>10	3	Above water solubility	Geyer et al., 1985
Haematococcus pluvialis	4h	N, S	EC_{10}	>40	3	Oxygen production, Above water solubility	Knie et al., 1983
2. Saltwater							
Thalassiosira pseudonana and ***Dunaliella tertiolecta*** (mixed)	72h	N, S	NOEC	>100	3	Growth and cell size. Maximum concentration tested. Above water solubility	Biggs et al., 1979

Abbreviations used

Duration	*Test concentrations*	*Test system*
d - days	A - Analysis of test concentrations	S - Static
h - hours	N – Nominal test concentrations	SS – Semi-static
	C – Closed system or controlled evaporation	FT – Flow through

Appendix 3

Hexachlorobenzene sediment ecotoxicity summary

Species	Treatment	Validity	Reference
Chironomus tentans	No significant mortality or reduction in growth following a 14-day exposure to sediments spiked at a measured concentration of 84 mg kg^{-1} (2% OC).	1	Barber et al (1997)
Hyella azteca	No significant mortality or reduction in growth following a 14-day exposure to sediments spiked at a measured concentration of 84 mg kg^{-1} (2% OC).	1	Barber et al (1997)
Leptocheirus plumulosus (saltwater/estuarine)	No significant mortality or reduction in growth following a 10-day exposure to sediments spiked at a concentration of 120 mg kg^{-1} (2% OC).	1	Fuchsman et al (1998a)
Hyella azteca (estuarine)	No significant mortality or reduction in growth following a 10-day exposure to sediments spiked at a concentration of 120 mg kg^{-1} (2% OC) in freshwater and at a salinity of 10‰ .	1	Fuchsman et al (1998a)
Chironomus tentans	No significant mortality or reduction in growth following a 10-day exposure to sediments spiked at a concentration of 120 mg kg^{-1} (2% OC).	1	Fuchsman et al (1998a)
Tubifex tubifex	72h test. No observed effects due to HCB, unbounded NOECs derived of 1000 mg kg^{-1}. No analytical confirmation of exposure concs, but otherwise reliable.	2	Meller et al., 1998
Limnodrilus hoffmeisteri	72h test. No observed effects due to HCB, unbounded NOECs derived of 1000 mg kg^{-1}. No analytical confirmation of exposure concs, but otherwise reliable.	2	Meller et al., 1998
Crangon septemspinosa (saltwater/estuarine)	No evidence of mortality in *Crangon septemspinosa* treated for 96 hours at a concentration of 2.1 mg kg^{-1} (normalized to 2% OC).	2	McLeese & Metcalfe, (1980)
Hyalella azteca	Very little information on the test provided, and no effects noted at highest tested concentrations, NOEC ~ 125 mg kg^{-1}	4	Fuchsman et al (1998b)
Chironomus tentans	Very little information on the test provided, and no effects noted at highest tested concentrations, NOEC ~ 125 mg kg^{-1}	4	Fuchsman et al (1998b)

Appendix 4

PNEC calculation by equilibrium partitioning theory

A $PNEC_{sediment}$ (both freshwater and marine) can also be calculated by using the equilibrium partitioning equation (ECHA 2008):

$PNEC_{sediment} = (K_{susp\text{-}water} / RHO_{susp}) . PNEC_{water} . 1000$

Where $PNEC_{water}$ is the Predicted No Effect Concentration in either freshwater or saltwater (see Section 7.1.7 in which the $PNEC_{freshwater}$ and $PNEC_{saltwater}$ are estimated to be the same value of >0.00037 mg l^{-1}), RHO_{susp} is the bulk density of suspended matter, $K_{susp\text{-}water}$ is the partition coefficient between suspended matter and water and $PNEC_{sediment}$ is the PNEC in sediment.

$K_{susp\text{-}water} = F_{water} + F_{solid} . (Kp / 1000) . RHO_{solid}$

Where F_{water} is the fraction of water in suspended matter (0.9 m^3m^{-3}), F_{solid} is the fraction of solids in suspended matter (0.1 m^3m^{-3}), Kp is the solid water partition coefficient in suspended matter (see below). RHO_{solid} is the density of the solid phase (2500 kg m^{-3}). $K_{susp\text{-}water}$ is the dimensionless suspended matter saltwater partition coefficient. The dimensionless suspended matter partition coefficient can therefore be calculated as 1815.5, according to the information below.

$Kp_{susp\text{-}water} = F_{OC} . K_{OC}$

Where F_{OC} is the weight fraction of organic carbon in suspended matter (0.02 kg_{OC} kg_{Solid}^{-1}), K_{OC} is the organic carbon normalised partition coefficient (36308, from Section 4), and $Kp_{susp\text{-}water}$ is the partition coefficient between water and suspended matter. This provides a partition coefficient between water and suspended matter of 726.2 l kg^{-1}.

$RHO_{susp} = Fsolid_{susp} . RHOsolid + Fwater_{suspended\ matter} . RHO_{water}$

Where $Fsolid_{susp}$ is the volume fraction of solids in marine suspended matter (0.1 m^3m^{-3}), RHOsolid is the density of the solid phase (2500 kgm^{-3}), $Fwater_{sediment}$ is the volume fraction of water in suspended matter (0.9 m^3m^{-3}) and RHO_{water} is the density of water (1000 kg m^{-3} for saltwater. This provides a density for suspended matter of 1150 kg m^{-3}.

The $PNEC_{sediment}$ can be calculated as >5.8 mg kg^{-1} (wet weight) from the $PNEC_{water}$ of >0.00037 mg l^{-1} and the standard environmental characteristics provided by the REACH guidance. This is equivalent to a $PNEC_{sediment}$ of 2.7 mg kg^{-1} (dry weight).

The above value for the $PNEC_{sediment}$ derived by equilibrium partitioning is consistent with that derived above from laboratory toxicity testing. This indicates that despite the high octanol:water partition coefficient of hexachlorobenzene it would not be necessary to increase the derived risk characterisation ratios by a factor of 10 in order to take account of potential additional exposure as a result of sediment ingestion. Furthermore, the comparability of the $PNEC_{sediment}$ when calculated from both sediment effects data and by equilibrium partitioning support the assumption that the exposure of sediment dwelling organisms is principally as a result of the sediment pore water concentration.

The Science Dossiers produced by Euro Chlor's Working Groups aim to improve the understanding of key topics related to the chlorine industry in order to support science-based decision-making.

Science Dossiers are often dealing with chlorinated substances, both natural and man-made, explaining their formation, fate, occurrence or breakdown in the environment.

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