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- GESAMP -**

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REVIEW OF POTENTIALLY HARMFUL SUBSTANCES

**Choosing priority organochlorines
for marine hazard assessment**



FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS

IMO/FAO/Unesco/WMO/WHO/IAEA/UN/UNEP
Joint Group of Experts on the Scientific Aspects of Marine Pollution
(GESAMP)

REVIEW OF POTENTIALLY HARMFUL SUBSTANCES

Choosing Priority Organochlorines for
Marine Hazard Assessment

NOTES

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DEFINITION OF MARINE POLLUTION BY GESAMP

"Pollution means the introduction by man, directly or indirectly, of substances or energy into the marine environment (including estuaries) resulting in such deleterious effects as harm to living resources, hazards to human health, hindrance to marine activities including fishing, impairment of quality for use of sea water and reduction of amenities".

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assessment. Rep.Stud.GESAMP, (42):10 p.

PREPARATION OF THIS STUDY

This document is based on the work of the GESAMP Working Group on Potentially Harmful Substances, sub-group on organochlorine compounds. The sub-group met from 27 to 29 July 1988 in Rome, Italy, and from 12 to 14 December 1989 in Kiel, Federal Republic of Germany. The meetings were attended by D. Calamari (Chairman), J.C. Duinker, H. Fiedler (second session), R. Lloyd (second session), H. Naeve (Technical Secretary) and J. Portmann (first session).

The Working Group was jointly sponsored by the United Nations Environment Programme (UNEP), the Food and Agriculture Organization of the United Nations (FAO) and the United Nations Educational, Scientific and Cultural Organization (Unesco). The secretariat was provided by FAO.

Lists of relevant organochlorine compounds, including those shown in Annexes I and II, were compiled by H. Fiedler and O. Hutzinger, University of Bayreuth, and provided to the Working Group through the International Register of Potentially Toxic Chemicals (IRPTC/UNEP), Geneva.

1. INTRODUCTION

Since 1985 GESAMP has published reviews of potentially harmful substances, including the amounts of individual substances which reach the marine environment, with particular attention being given to the relative importance of land-based sources, the fate of these substances and their effects on the marine environment, on living resources, human health and amenities. So far, according to the perceived priority concerns and the requirements of global and regional conventions and regulatory mechanisms, reports were prepared on cadmium, lead, tin, arsenic, mercury, selenium and organosilicon compounds. Because of the increasing importance assigned to organochlorine compounds and the tendency to deal with them as a generic group in regulatory actions, GESAMP was charged with the task of reviewing these substances and giving a scientific judgement on the hazard they pose, either as a group or as individual chemicals, to the marine environment.

It was soon recognized that organochlorine compounds are a very heterogenic group of chemicals, which makes it impossible to give a common hazard judgement on them. Therefore, as a first approach, it was agreed to use preliminary hazard assessment procedures to identify those organochlorine substances which are likely to cause more concern to the marine environment than others. This report contains a description on how to select priority substances for hazard assessment.

GESAMP, through its Working Group on Potentially Harmful Substances, intends to continue its work on organochlorines. It will endeavour to prepare specific hazard profiles for individual substances or groups of substances which appear to be of priority concern, based on available information on quantities used and likely to reach the marine environment, and assess the possible fate of such substances and the risk they are likely to pose.

2. PRIMARY GROUPING OF ORGANOCHLORINE SUBSTANCES

It is generally recognized that some chlorinated hydrocarbons have extremely harmful properties which warrant stringent controls on their use and disposal. However, such controls have been commonly applied to all chlorinated hydrocarbons, despite the fact that this group of compounds embraces a large range of substances with very different physical, chemical and biological properties. For this reason, it was decided that a generic review of the whole group would be inappropriate and that, as a first stage, a primary sub-division of the compounds into groups was required.

Group 1: Low molecular weight compounds (containing up to three carbon atoms). Most of these compounds are volatile and have similar modes of environmental distribution. Many are produced and used on a very large scale, either in their own right or as intermediates in organic chemical production processes. Control measures, if required, would in general be of a similar nature.

Group 2: Aliphatic and aromatic compounds containing up to six carbon atoms. Most of these compounds are produced and used as intermediates in the course of production of useful end-product compounds, e.g. herbicides. A few are used in their own right, of which dichlorobenzene - used as a space deodorant and moth repellent - is one of the best examples, and enter the environment from diffuse sources; some may be encountered in the environment as degradation products.

- Group 3:** Long-chain chlorinated paraffins. These are used in their own right for a wide variety of purposes, e.g. as secondary plasticizers, adhesives and in chlorinated rubber paints.
- Group 4:** Chlorinated insecticides. This is the group of compounds about which concern has historically been expressed. It includes HCB, HCHs, DDT, Mirex, chlorinated camphenes (Toxaphene), chlordane, etc. The group could be considered alongside some of the chlorinated herbicides, e.g. 2,4-D, 2,4,5-T, since their pattern of use is similar. However, these herbicides have rather different properties and it may be more practicable to consider them as a separate group.
- Group 5:** Higher molecular weight chlorinated aromatic compounds. Examples are PCBs, polychlorinated naphthalenes and camphenes, dioxins and furans. These have a range of levels of chlorination but similar environmental behaviour and require similar analytical procedures for their determination. All the chemicals in this group exist in several isomeric or congener forms. It is suggested that for practical purposes each group, e.g. PCBs, should be sub-divided according to key characteristics, e.g. boiling point or level of chlorination, but making distinctions within each sub-group where data exist to indicate particular environmental significance.

3. ANALYSIS OF DATA

A survey of easily available literature has been carried out, and about 800 chlorinated hydrocarbons were identified as having relevance to the marine environment. It was immediately obvious that the quality and quantity of the data available on all these compounds varied widely, from those for which there were no relevant data to those, such as some pesticides, for which there was a large data base.

The selected chlorinated hydrocarbons were allocated to the 5 groups shown in Figure 1. There were 58 compounds in the group of low molecular weight (C_1 to C_3), 249 in the medium molecular weight group (C_4 to C_6) and 413 in the high molecular weight group (greater than C_6). Chemicals in these groups were listed together with data on $\log K_{ow}$ (Octanol-Water Partition Coefficient), vapour pressure, water solubility, toxicity and available information on their production and use. For the 70 pesticides identified, data on toxicity, H (Henry's Law Constant), $\log K_{ow}$, $\log K_{oc}$ (Soil Absorption Coefficient, normalized for organic carbon), persistence (normally expressed as half-life) and the major degradation pathway were listed for each chemical.

The next step in the exercise was to make a preliminary hazard assessment. It was clear that, because of the limited amount of data available for many of the compounds, the screening procedure would have to be very simple and therefore very coarse. The following criteria were used to identify those compounds (excluding pesticides and PCBs/PCDDs) which would have a greater potential for causing harm in the marine environment:

$$\log K_{ow} > 3$$

$$\text{Persistence} > 1 \text{ week}$$

$$\text{Toxicity (LC50, EC50)} < 10 \text{ mg/l}$$

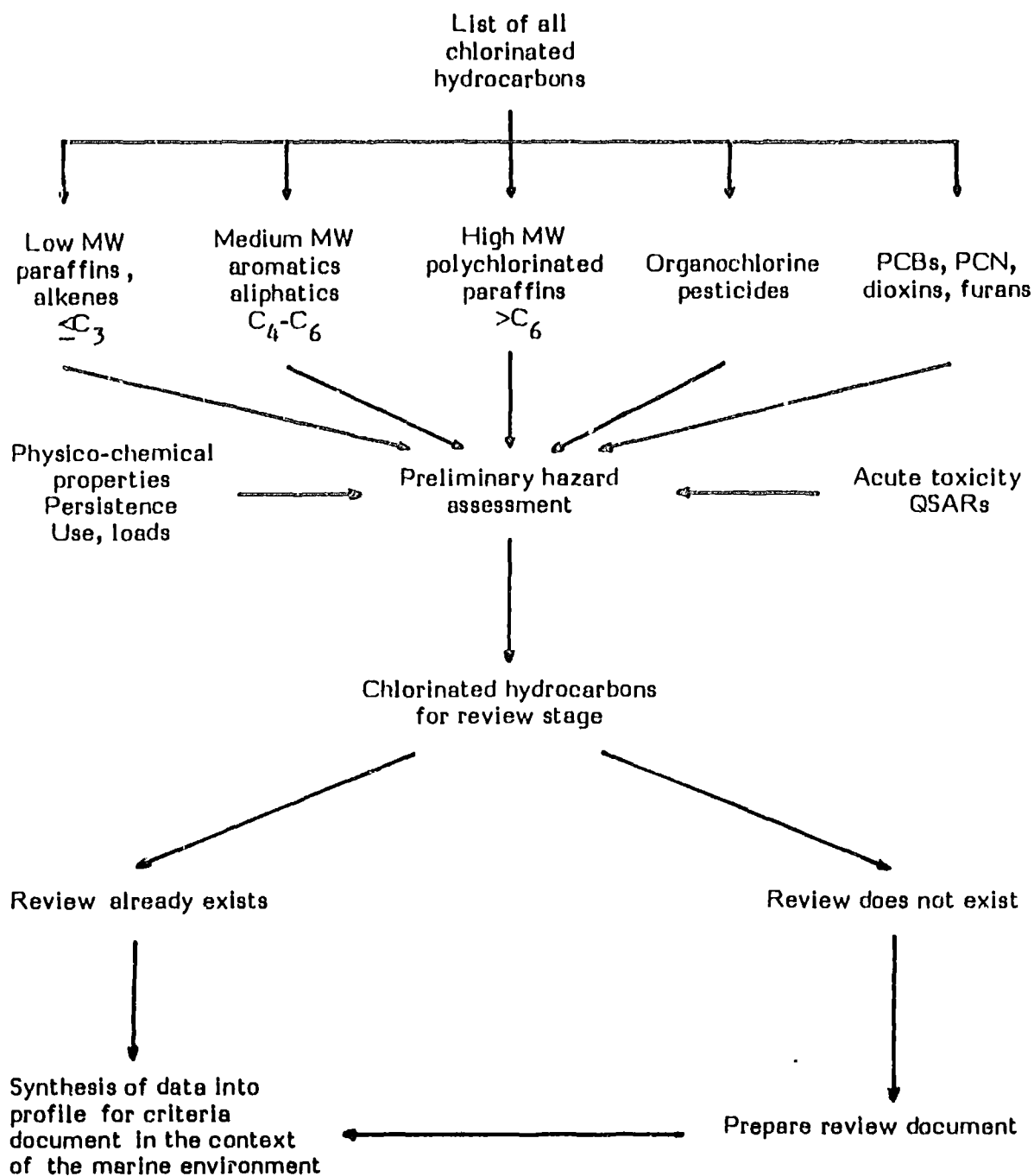


Figure 1. Recommended procedure for reviewing organochlorine compounds

Of these criteria, data for $\log K_{ow}$ were available by either direct measurements or by calculation from molecular structure. The value of > 3 was chosen because of its general international acceptance as a trigger value, corresponding to a potential bioconcentration factor of about 300 in aquatic organisms. Persistence values generally related to degradation in water, although it was recognized that persistence could be greater in other compartments such as sediments. The value of > 1 week was chosen as an indication that such substances discharged into fresh waters would appear in marine waters; also, at above this level there would be a greater potential to cause acute and chronic effects. Available data for toxicity were very varied; most of the information was for freshwater organisms and it was assumed that the sensitivity of corresponding marine life would not be too dissimilar. The value of 10 mg/l was chosen to reflect the paucity of the available data, and although it may appear to be more stringent than the internationally acceptable value of 1 mg/l as a trigger value for dangerous chemicals it reflects the uncertainty associated with the possible great sensitivity of the diverse range of marine organisms. A fourth criterion - the production and use of the chemical - was also used in some cases to influence the hazard assessment.

It is recognized that this approach is deterministic in that a limited set of properties has been used to allocate each compound to a specific group; properties such as carcinogenicity, mutagenicity and teratogenicity have not been considered in this exercise.

Because of their obvious biocidal properties, it was clear that all the pesticides would fulfil one or more of these criteria, so that there was no need to include them in the preliminary hazard assessment exercise. Similarly, the PCBs and PCDDs formed a special group for separate treatment.

The selection procedure separated the remaining chemical into three groups:

- (1) **IN** - those chemicals which met two or more of the selection criteria (or were very similar in structure to those which met the criteria); Annex I
- (2) **OUT** - those chemicals which did not meet the selection criteria,
- (3) **NO DATA** - those chemicals which could not be assessed; Annex II

The primary list of IN compounds contained 77 chemical, of which a few were included on the basis of structural similarity. Those would need to be rechecked to ascertain whether they truly belong to the IN group. For many of the 77 chemicals there were known to exist reviews of some type on their toxic properties and it was agreed that there may be other reviews which may be applicable, for example reviews prepared for the EEC.

Decisions on the OUT compounds were made on a variety of criteria, including whether they were likely to enter the aquatic environment in significant amounts, their degradation potential, volatility, water solubility and associated potential for bioconcentration. It is clear that in some cases these were subjective judgements, but this is acceptable for the purpose of the screening process to identify the most potentially hazardous substances.

The group of chemicals which caused the most problems were those for which there were no data found within the scope of the literature search carried out. Several compounds in this group were identified as those for which relevant data were

available in other sources, and these should be consulted and the lists updated. For the others it will be necessary to calculate the basic property of K_{ow} on theoretical principles, for example on the basis of the molecular fragments constants. These data, together with other descriptors, can then be used to make an appropriate calculation of the toxicity of each chemical to aquatic organisms, based on existing quantitative structure activity relationships (QSARs). Despite its inherent inaccuracy, this approach is acceptable for the purpose of the present exercise.

4. CONCLUSIONS

It must be emphasized that within this group of compounds there is a gradation of harmful properties and that there is no clear interface or separation between the more harmful and the less harmful. As a result, there may be compounds in the IN list which are in practice less harmful than those in the OUT list. This problem of the "grey area" around the boundaries is common to all such classification schemes.

It must also be emphasized that the division was made solely on the basis of the harmful properties of each chemical. The actual damage caused to the aquatic environment is a function of the environmental loading of the particular chemical; even the most toxic chemical will be harmless in practice if the amount discharged to the environment is very small. Conversely, chemicals in the OUT group may be harmful if discharged in sufficient quantities. For this reason the lists must be regarded as provisional, pending the acquisition of further data on individual compounds. This is particularly the case for those compounds for which fundamental data are lacking and whose properties have been inferred from their chemical structure and similarity with other compounds for which more data are available.

This assessment of the potential environmental importance of individual chlorinated hydrocarbons has been made from the data available for single chemicals. A review of the theory of the toxicity of mixtures on the aquatic environment has been given by the European Inland Fisheries Advisory Commission of FAO (EIFAC); the extent to which chlorinated hydrocarbons in a complex effluent will combine in their joint toxicity will depend on whether they have a common toxic action.

No attempt has been made to assess the potential environmental impact of complex mixtures such as those found in certain pulp mill effluents. The environmental impact of these effluents has to be treated as a separate issue because remedial measures have to be based on the whole effluent rather than on the basis of the relative importance of individual compounds.

The work carried out so far forms an acceptable basis for the identification of those chlorinated hydrocarbons which present the greatest potential hazard to marine organisms. There is some additional work necessary to complete the task, but this should not preclude a start being made on the preparation of one-page summaries (profiles) of essential data on selected chemicals. These profiles could be for single chemicals or for groups of chemicals with very similar molecular structures. Also, these individual profiles should not be prepared in isolation but consideration should be given to the mode of toxic action and the existence of appropriate QSARs which could cover a wider grouping of chemicals.

Notwithstanding the existence of reviews on many of the substances in the IN list, it is considered that concise profiles also on these chemicals would be valuable, especially when decisions need to be made at short notice, for example the need to

recover a cargo lost at sea. This would also satisfy the need for quick practical advice on which substances pose real risks when discharged into the marine environment.

It is clear that other "customer needs" will have to be taken into account when considering the information to be presented in the profiles. These include the need to rank the chemicals according to their ability to remain in, or migrate to, the aquatic environment and their persistence in water and sediments. This ranking would apply to the properties of the substances and it would not imply that the potentially more harmful compounds will present the greatest risk in practice.

It should be emphasized again that there is less of a perceived need for profiles in pesticides because existing reviews are widely available and probably adequate for the various needs. Also, the PCBs and PCDDs are a special case, and the recent advances in analytical techniques have opened the way to possibilities for more accurate hazard assessments in the future.

Annex I:

List of Potentially Harmful Organochlorine Substances Selected on the Basis of Data Examined

Substances of Group 1: C₁ to C₃ Compounds

1,1,2,2-Tetrachloroethane	Hexachloroethane
1,1,2,2-Tetrachloroethylene	Vinylchloride
1,1,2-Trichloroethane	Methylchloride
1,1,2-Trichloroethylene	Pentachloroethane
Chloroform	Tetrachloroethene
Dichloromethane	Tetrachloromethane
Epichlorohydrin	

Substances of Group 2: C₄ to C₆ Compounds

1,1,2,3,4,4-Hexachloro-1,3-butadiene	2-Chloro-1,3-butadiene
1,2,3,4-Tetrachlorobenzene	3,4,6-Trichlorocatechol
1,2,3,5-Tetrachlorobenzene	Chlorobenzene
1,2,3-Trichlorobenzene	Hexachlorobenzene
1,2,4,5-Tetrachlorobenzene	Hexachlorocyclohexane
1,2,4-Trichlorobenzene	Hexachlorocyclopentadiene
1,3,5-Trichlorobenzene	3-chlorophenol
1-Chloro-2-nitrobenzene	1,3-Dichlorobenzene
1-Chloro-3-nitrobenzene	2-Chlorophenol
1-Chloro-4-nitrobenzene	1,2-Dichlorobenzene
1-Chlorobutane	4-Chloroaniline
2,3,4,5-Tetrachlorophenol	4-Chlorophenol
2,3,4,6-Tetrachlorophenol	1,4-Dichlorobenzene
2,3,5,6-Tetrachlorophenol	Pentachlorobenzene
2,3-Dichlorophenol	Pentachlorophenol
2,5-Dichlorophenol	Pentachloropyridine
2,4-Dichlorophenol	Tetrachlorocatechol

Annex I: continued

Substances of Group 3: Compounds with more than C₆

DL-3-(a-Acetyl-p-chloro-benzyl)-benzylchloride

1-(o-Chlorophenyl)-1-(p-chlorophenyl)-2,2-dichloroethane (o,p'-DDD)

1,1'(Dichloroethylidene)-bis[4-Chlorobenzene] (p,p'-DDE)

1-(o-Chlorophenyl)-1-(p-chlorophenyl)-2,2,2-Trichloroethane (o,p'-DDT)

2,4,5-Trichlorophenoxy acetic acid

2,3-Dichlorotoluene

2,4,5-Trichlorotoluene

2,4-Dichlorotoluene

2,4-Dichloroacetophenone

2,5-Dichlorotoluene

2,6-Dichlorobenzonitrile

2,6-Dichlorotoluene

2-Chloro-4-nitrotoluene

3,4-Dichlorotoluene

2-Chlorotoluene

Tetrachloroguaiacol

3-Chlorotoluene

3,4,5-Trichloroguaiacol

4-Chlorotoluene

4,5,6-Trichloroguaiacol

Benzotrichloride

4-Chlorostyrene

Octachlorostyrene

$\alpha,\alpha,2,6$ -Tetrachlorotoluene

Group 4: PCBs, PCDD/PCDF

Total of 209 PCB isomers

Commercial mixtures of PCBs: Aroclors, Kaneclors, Chlophens, etc.

Total of 210 PCDD/PCDF isomers

of these 17 "toxic" isomers (= 2,3,7,8-Cl substituted PCDD/PCDF)

Annex II:

List of Organochlorine Substances for which NO or NOT SUFFICIENT DATA were Available

1,1-Dichloroethane	3,4-Dichlorocatechol
1,1-Dichloroethylene	3,4-Dichloronitrobenzene
1,2,3,4-Tetrachloronaphthalene	3,4-Dichlorophenol
1,2,3-Trichloro-4-nitrobenzene	3,4-Dichlorophenoxyacetic acid
1,2,4-Trichloro-5-nitrobenzene	3-Chloro-2-methylaniline
1,2-Dichloroethane	2,4-Dichloroguaiacol
1,2-Dichloroethylene	2,4-Dichloronitrobenzene
1,3-Dichloro-5,5-dimethylhydantoin	2,4-Dichlorophenoxyacetic acid
1,4-Dichloro-2-nitrobenzene	2,5-Dichloro-4-nitrophenol
1,4-Dichlorobutane	2,5-Dichloro-p-xylene
1,5-Dichloroanthraquinone	2,5-Dichloroaniline
1,6-Dichlorohexane	2,5-Dichlorobenzoic acid
1,8-Dichloroanthraquinone	2,5-Dichloronitrobenzene
1-(Chloromethyl)naphthalene	2,6-Dichloro-3-methylaniline
1-Chloro-3,4-dinitrobenzene	2,6-Dichloro-4-nitroaniline
1-Chloroanthraquinone	2,6-Dichloroaniline
1-Chlorohexane	2,6-Dichloroanisole
1-Chloronaphthalene	2,6-Dichlorobenzoic acid
2,3,4,5-Tetrachloroaniline	2,6-Dichlorophenol
2,3,4,5-Tetrachloronitrobenzene	2,6-Dichlorostyrene
2,3,4-Trichloroaniline	2-(2,4,5-Trichlorophenoxy)propionic acid
2,3,4-Trichlorophenol	2-Chloro-2,6'-acetoxylidide
2,3,5,6-Tetrachloroaniline	2-Chloro-4,6-diamino-1,3,5-triazine
2,3,5,6-Tetrachloronitrobenzene	2-Chloro-4-(1,1-dimethylethyl)phenol
2,3,5-Trichlorophenol	2-Chloro-4-methylaniline
2,3,6-Trichlorobenzoic acid	2-Chloro-4-nitroaniline
2,3,6-Trichlorophenol	2-Chloro-4-nitrophenol
2,3-Dichloro-1,3-butadiene	2-Chloro-5-methylaniline
2,3-Dichloroaniline	2-Chloro-5-methylphenol
2,3-Dichloroanisole	2-Chloro-5-nitroaniline
2,3-Dichloronitrobenzene	2-Chloro-6-methylaniline
2,3-Dichlorophenoxyacetic acid	2-Chloro-6-nitrotoluene
2,3-Dichloroquinoxaline	2-Chloroanthraquinone
2,4,5-Trichloroaniline	2-Chlorocyclohexanone
2,4,5-Trichlorophenol	2-Chlorocyclopentanone
2,4,6-Trichloroaniline	2-Chloropyridine
2,4,6-Trichlorophenol	2-Chloroquinoline
2,4,6-Trimethylbenzyl chloride	2-Chlorostyrene
2,4-Dichloro-3,5-dimethylphenol	3,3'-Dichlorobenzidine
2,4-Dichloro-6-nitroaniline	3,4,5-Trichloroaniline
2,4-Dichloro-6-nitrophenol	3,4,5-Trichlorophenol
2,4-Dichloroaniline	3,4,6-Trichloro-2-nitrophenol
2,4-Dichlorobenzoic acid	3,4-Dichloroaniline
3,4-Dichlorophenylisocyanate	3,4-Dichlorobenzoic acid

Annex II: continued

3,5-Dichloroaniline	3-Chloro-4-methoxyaniline
3,5-Dichloroanisole	3-Chloro-4-methylaniline
3,5-Dichlorobenzoic acid	3-Chloro-4-methylaniline
3,5-Dichlorobenzonitrile	3-Chloro-5-methoxyphenol
3,5-Dichlorophenol	3-Chloropyridine
3-Chlorostyrene	Benzoylchloride
4,5-Dichloro-2-nitroaniline	Benzylchloride
4,7-Dichloroquinoline	Benzylidenechloride
4-Chloro-1-naphthol	bis-(Chloromethyl)naphthalene
4-Chloro-2-methylaniline	bis-(Chloromethyl)xylol
4-Chloro-2-methylphenol	bis-4-Chlorobutylether
4-Chloro-2-nitroaniline	Chlorocyclohexane
4-Chloro-3,5-dimethylphenol	Chlorocyclopentane
4-Chloro-3-methylphenol	Chlorofluoromethane
4-Chloro-3-nitroaniline	Chloromethylnitrobenzene
4-Chloro-3-nitroanisole	Chloronitrocyclohexane
4-Chloro-3-nitrotoluene	D-Chloramphenicol
4-Chloro-6-nitro-m-cresol	Dichlorobenzaldehyde
4-Chloro-N-methylaniline	Dichlorocyclohexane
4-Chloro-o-xylene	Dichlorodimethoxybenzene
4-Chloromethylbiphenyl	Dichloromethylbenzene
4-Chloroquinoline	Hexachlorobutane
4-Chlorosalicylic acid	Hexachloronaphthalene
4-Chlorostyrene	Hexachlorophene
5-Chloro-1,3-dimethoxybenzene	m-Chlorophenylisocyanate
5-Chloro-2-hydroxyaniline	m-Chlorothiophenol
5-Chloro-2-methoxyaniline	N-(p-Chlorobenzhydryl)piperazine
5-Chloro-2-methylaniline	o-Chlorobenzylidene malononitrile
5-Chloro-2-nitrophenol	o-Nitrobenzyl chloride
5-Chloro-2-nitrotoluene	Octachloronaphthalene
5-Chlorosalicylic acid	p-Chlorophenoxyacetic acid
6,9-Dichloro-2-methoxyacridine	p-Chlorophenylisocyanate
9-(Chloromethyl)anthracene	p-Chlorothiophenol
α ,2,6-Trichlorotoluene	Pentachloro-1,3-butadiene
α , α' ,2,3,5,6-Hexachloro-p-xylene	Pentachlorobutane
α , α' -Dichloro-m-xylene	Pentachlorobutene
α , α' -Dichloro-o-xylene	Pentachloronaphthalene
α , α' -Dichloro-p-xylene	Pentachloronitrobenzene
α , α , α' , α' , α' -Hexachloro-p-xylene	Tetrachloro-1,3-butadiene
α ,p-Dichloroanisole	Tetrachloro-o-benzoquinone
α -Chloro-m-xylene	Tetrachloro-p-benzoquinone
α -Chloro-p-xylene	Tetrachloropentane
α -Chlorostyrene	Trans-1,4-dichlorobutene-2
Trichloronaphthalene	

Reports and Studies GESAMP

The following reports and studies have been published so far. They are available from any of the organizations sponsoring GESAMP.

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