

Micropollutants

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Preliminary proposals for classification of marine environmental quality respecting micropollutants in water, sediments and selected organisms

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### Abstract:

A compilation of water quality criteria and information about "background levels" of micropollutants (selected metals, organochlorines, polycyclic aromatic hydrocarbons) have been used as basis for proposals of marine environmental quality classification. As knowledge of effects - except at levels wich must be regarded as strong contamination - is inadequate, the classification is based mainly on occurrence. The selected indicator organisms comprise benthic algae (metal indicators only), mussels, snails and fish.

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For the Administration

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# PRELIMINARY PROPOSALS FOR CLASSIFICATION OF MARINE ENVIRONMENTAL QUALITY RESPECTING MICROPOLLUTANTS IN WATER, SEDIMENTS AND SELECTED ORGANISMS

Oslo,

May 30, 1992.

Project leader:

Jon Knutzen

Co-worker:

Jens Skei

# **Preface**

The present report is a summary of a more comprehensive document (Knutzen and Skei, 1990) with collation of water quality criteria from several sources together with information on "background levels" of micropollutants in water, sediments and organisms, as a basis for preliminary proposals for classification of marine environmental quality. The original report was sponsored by the Norwegian State Pollution Control Authority, and inteded to serve mainly three purposes: Guidelines for water management, standardization of terms relating to the evaluation of pollutional state, and rapid communication of summary information to the public.

The basic concept for the proposals is assumed "high background levels at merely diffuse loading", i.e. commonly found concentrations of micropollutants which cannot be traced to definite point sources. Obviously, the concept is not very precise and thus disputable in itself, considering among other factors regional differences due to variable exposure from diffuse sources. Further, in many cases the data base is quite sparse.

With the present limited knowledge of occurrence, and even more so as regards effects, any classification system should be viewed critically, and be subject to revision with intervals of few years. It is also emphasized that the system presented is not adopted officially.

In the above mentioned initial work, Jens Skei has been responsible for the parts relating to occurrence and classification of micropollutants in water and sediments.

Oslo, May 30, 1992.

Jon Knutzen Project leader

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# 1. INTRODUCTION

The greatest micropollutant problems in the fjords and coastal waters of Norway are caused by various types of industrial effluents: production of magnesium, nickel and zinc; aluminium and ferromanganese works; refining of ores from mining. The substances of main concern have been persistent organochlorine compounds (eg. from magnesium and nickel production), potentially carcinogenic tars (discharge from smelters) and mercury, lead, cadmium, copper and zinc (from production of zinc, chlorine-alkali plants and ore dressing plants).

Ecological damage has in Norway only been observed locally (a few km<sup>2</sup> in the vicinity of effluent outfalls) whereas physiological stress reactions and increased micropollutant concentrations in organisms are more widespread. Increased contaminant levels have brought about warnings against consumption of fish and shellfish, as well as restrictions on fishing and aquaculture, in fjord and coastal areas of about of 1000 km<sup>2</sup>.

The following report first gives a summary of water quality criteria, and then presents preliminary proposals for the classification of water quality according to the occurrence of selected micropollutants in water, sediments and organisms. The presentation is an abridged version of a previous basis report (Knutzen and Skei, 1990). In specific cases it will often be necessary to take into account assumptions and reservations which are mentioned in the more comprehensive basis report and the literature referred therein.

### 2. DEFINITIONS

The term "water quality criteria" for micropollutants is understood as referring to the upper limits of the content of substances in water which are not detrimental to aquatic communities or their exploitation (here as human food and nutrition for higher levels in food chains originating in water).

The term "micropollutants" refers here to substances with one or more of the following properties:

- very high acute toxicity (ng μg/l level)
- pronounced persistence in organisms and/or sediments
- marked tendency for bioaccumulation, possibly in some cases also biomagnification (increasing concentration up through the food chain), and thus possibility of chronic toxicity and damage to embryos.

Examples of chronic damage of particular interest are cancer, changes in genetic material, disturbance to hormone balances, reduced reproductivity and reduced resistance to disease.

In Knutzen and Skei (1990) a further practical limitation was made on the basis of substances cited in reports from SFT (The Norwegian State Pollution Control Authority, 1987) and the Inspectorate of Chemicals in Sweden (KEMI, 1989), which cause problems or present a potential hazard in Norwegian waters (fresh water and marine areas).

The basis for the classification (upper limit for class I) is:

### Presumed high background level at only diffuse loading.

This is a rough estimate of the "upper limit" of the concentration interval which has been derived from measurements at sites remote from the influence of point sources. The observation material which forms the basis for this "limit value" has varying degrees of completeness and reliability (see below for details and remarks on individual substances/substance groups). At present, there is no basis for supporting the limit value statistically, as with, for example, chemical/physical eutrophication parameters. Comprehensive surveys would be required to achieve this and these are only partially in progress. The basic material is derived from observations both in Norway and other countries (Knutzen and Skei, 1990, with references), and in some cases is supplemented here with more recent data.

Besides the incomplete statistical documentation, the main argument against "presumed high background level" as a reference, is that the limit will vary regionally (with the proximity to industrial and population centres, atmospheric transport routes, ocean currents and climate). The "diffuse background level" for PCB in mussels will probably be different in the southern part of the North Sea from that on remote coasts of the North Atlantic.

As an alternative reference it is perhaps possible to consider the "natural background level". However, this is non existent for anthropogenic substances, and would also be impractical as a reference level for mercury, lead and some other metals where inputs to global and regional cycles are predominantly caused by human activities. At present, only pre-industrial sediments may be used for the purposes of obtaining "background levels", though here too there are difficulties (i.e. from dating, bioturbation, etc).

# 3. PRINCIPLES OF CLASSIFICATION

The two main principles of classification are (1) according to occurrence (excess concentrations in relation to "normal concentrations") and (2) according to effect (proven damage to organisms, problems or hazards to user interests).

Owing to the relationship between concentration and effect, and because the real interest lies in the effects, it would be logical and most relevant to have a system of classification which includes both principles. A system with 4 classes could, for example, be based on the following upper limits (concentrations in water) for classes I-III:

Class I: Up to 75 (90,95) percentile of observations of substances with natural occurrence and correspondingly for observations of anthropogenic compounds, but then limited to places remote from the influence of particular point sources.

Class II: Up to the water quality criterion for protection and exploitation of aquatic communities.

Class III: Up to the limit beyond which considerable damage or problems are caused.

Class IV would then include the concentrations which cause great damage and problems, without an upper limit.

The upper limit for Class III will necessarily be a very rough estimate, whereas comprehensive field observations and knowledge about effects (limits of tolerance) are required to achieve reliable limits for classes I and II.

The knowledge basis is more or less inadequate, both with regard to the number of observations as well as their reliability. This is partly the consequence of problems in measuring low concentrations of many substances in water (not only organic substances with low solubility in water, such as polychlorinated biphenyls (PCBs), etc., but also metals such as mercury, lead and cadmium). In addition, the water quality criteria in different countries may vary considerably, depending on the premises for their setting and the observation material on which they were based (jfr. Knutzen and Skei, 1990).

Another difficulty which should be mentioned is the definition of what is actually measured, or is intended to be measured (eg. the definition of the total content or fraction, and the chemical form of metal in "solution").

Currently the most important objection to using both contaminant levels and effects in a system of classification with practical applications, is that for micropollutants this often results in an enormous breadth to class II. Even the strictest criteria for metal contents in water, based on sources in USA and Canada (table 1 below), would give upper limits for class II of 5-200 times the upper limits for class I. An increase in the metal content of 1-2 orders of magnitude can hardly be described as "moderate", except in the primary dilution zone of a discharge.

For organic substances with low solubility it is probably not possible to base the classification on concentrations in water, because there are insufficient reliable data from waters with only diffuse loading and certainly none from Norwegian coastal waters. In any case it would be impractical to conduct the necessary analyses to cover the interval of variation at the particular sites. There are, at best, only a few qualified laboratories in Norway, and the result could be a plethora of uninterpretable information.

The conclusion is that the concentration intervals for the classes above class I, at least for the present, cannot be directly related to damage and problems. Consequently, the degrees of pollution ("moderate", "marked", "strong") are defined only as increases in concentration beyond the reference value (upper limit for class I). However, in determining the limits for classes II and III, there has been some assessment of the hazards and accumulation properties of individual substances.

Furthermore, only for metals there is a basis for classification according to the concentration in water. For the predominantly particle-bound organic compounds with low solubility, the content in sediments and organisms is used. Another reason not to link the classification with effects, is that few efforts have yet been made to define the limits of damage as regards concentrations in sediments and organisms (i.e. damage to the particular species or higher trophic levels).

Local or regional variations in the natural content of metals in water and various degrees of diffuse loading of mainly airborne metals and organic micro-pollutants, may warrant specific local/regional specific classifications. In principle this is a valid point of view, though with our present state of knowledge (and limited data), it is not possible to consider. In reality the problem is about the justification, necessity or purpose of operating parallel systems, with different class limits, for more or less definable water masses or coastal areas (e.g. markedly brackish fjord water versus water from the open coast, or Skagerrak versus the Norwegian West Coast and the Gulf Stream-influenced coast of Northern Norway).

On several points, therefore, in evaluating environmental contamination data, some judgement and caution are required. In practical terms this means that all conclusions should be accompanied by an acknowledgement of the uncertainties and reservations which are associated with the classification, or a specific evaluation of these in individual cases.

In addition to the system based mainly on excess concentrations one might have a parallel system where the class limits were related to the various degrees of ecological damage or interference with user interests. (The principle difference between the two could be denoted respectively "degree of contamination" and "degree of pollution".) However, sufficiently detailed information is generally not available on the relationship between concentration and effect to enable the association of objective data - e.g. indices of diversity - with the class limits.

An argument against a system based on effect is also that its purpose would be restricted. For most of the substances in question, and as a consequence of the way in which micropollutants have been defined here, all excesses of the criterion value would be unacceptable in a larger volume of water. If only class I is used for regulatory purposes, much of the reasoning for further classification becomes redundant. (It is somewhat different in the case of fresh water, where there are many cases of pollution from disused mines, and also generally in cases where the main problem is acute toxicity).

A classification system based on effect is, therefore, considered to be of doubtful value as far as micropollutants are concerned. Better assessments of manifest damage or risks can be made from direct observations at the locations in question, and/or by linking registered or theoretically calculated concentrations with lists of quality criteria provided in the following chapter.

It may be possible in future to classify effects of micropollutants by physiological and biochemical stress reactions. The application of such methods will depend partly on whether they are sufficiently specific to each substance and partly on the extent to which the response can be associated with the concentration of the particular contaminant in edible organisms and/or damage to populations.

# 4. WATER QUALITY CRITERIA

Tables 1 & 2 provide a collation of the quality criteria for seawater from various sources abroad known to date. The aim of the criteria is, as stated, the protection of marine communities, higher levels (birds, mammals) in food chains originating in the sea, and the exploitation of edible species for food (except the WRC-criteria, which do not include exploitation for food).

The tables give summary presentations of the conclusions from work involving highly complex questions on sometimes uncertain grounds. Evaluation and decision making in specific cases may therefore require closer studies of the literature referred in the foundation material regularly and in more detail Knutzen and Skei (1990). The criteria should be considered as a guide and cannot replace a particular evaluation of the individual case.

The criteria apply partly to the total content (all organic micropollutants and organic compounds of tin) and partly to the soluble fraction (passed through a filter with pore size  $0.45~\mu m$ ). In cases where the same source provides different values for the limit, the lower of these is used.

For a number of the organic micropollutants fresh water criteria are referred, as no marine criteria are available. Some of the contaminants listed in table 2 are not among the substances mentioned in SFT (1987) or KEMI (1989), but have been included here for the sake of completeness (aldrin, chlordane, endosulphane, endrin, heptachlor).

As regards the criteria for groups of substances such as PCB and Toxaphene, it must be emphasized that limit values should have been given for the individual compounds with the greatest hazard potential. This stage has not yet been reached, because it is only during later years that analyses of specific substances (only PCB) have become common practice.

From the tables it can be seen that there may be considerable differences between criteria values from various sources. In general this may be explained partly by somewhat of differing aims, premises and methods of data interpretation, though perhaps most important is the continuing lack of knowledge particularly about the organic environmental contaminants. For these substances the question arises as to whether criteria, expressed as concentrations in water, on the whole are useful management tools.

Table 1. Water quality criteria for selected elements and organo-tin compounds in salt water. Cf. text and Knutzen and Skei (1990) with references. Concentrations in μg/l.

SOURCES	EPA <sup>1</sup> )	WRC <sup>2</sup> )
SUBSTANCES	(Total content)	(Soluble fraction, except <sup>6</sup> ))
Arsenic (total)		25 <sup>3</sup> )
Arsenic III	36 <sup>3</sup> )	
Cadmium	9.3	- <sup>4</sup> )
Copper	2.9 5)	5
Chromium (total)	ŕ	15
Chromium VI	50	
Lead	5.6	25
Mercury	0.025	- <sup>4</sup> )
Nickel	8.3	30
Silver	2.3 5)	-
Tin (inorganic)	ĺ	10
Tributyl-tin		0.001 6)
Triphenyl-tin		0.008 6)
Zinc	86	40

- <sup>1</sup>) EPA = U.S. Environmental ProtectionAgency. EPA (1986a) + update from 1/5 1987 (includes nickel) and EPA (1986b, 1987).
- <sup>2</sup>) WRC = Water Research Centre, Great Britain, several criteria documents for the ECs list II substances, cf. Knutzen and Skei (1990).
- 3) Does not take into account the high toxicity of As V to marine benthic algae (cf. Blanck et al., 1989).
- <sup>4</sup>) For the ECs list I substances the environmental quality standards are decided by the ECs council. For cadmium the EC limit in coastal water is 0.5 and for mercury 0.3 ug/l, cf. The European Economic Community's Times no. L. 291 24/10-83 (cadmium) and L 81 27/3-82 and L 74 17/3-84. Note: Outdated limits.
- 5) Limit for acute toxicity, criterion for chronic toxicity not set.
- 6) Total content.

Outside the USA and Great Britain, it is worth mentioning the activity in the EC to set concentration limits ("quality objectives") for micropollutants in water. However, until 1990, for the presumed most hazardous - list I substances - the only directives from the Council are for HCH, in addition to mercury and cadmium in the marine environment. (For the 15-20 substances where proposals for quality objectives are available, see Knutzen and Skei, 1990).

For the substances whose concentrations in water are difficult to measure, a better way of achieving objectives would be to use criteria based on contents in sediments and organisms. This applies not only to organic substances which have a low water solubility, but also to metals such as mercury and lead, which are still technically difficult to analyze (owing to contamination of samples) and require such low levels of detection that it may cause problems in practical monitoring.

However, too little is known about which concentrations cause hazards. In several countries studies are being undertaken to set sediment criteria based partly on equilibria distributions between the particular substances in water, sediments and organisms, partly on data from biological testing. The task is complicated and so far no country has concluded in the form of official criteria for the

marine environment. There is even less knowledge about which levels in organisms would represent a danger to the species concerned, or to higher trophic levels in the food chains to which the species belongs (for more details see Knutzen and Skei, 1990).

Table 2. Water quality criteria for selected organic micropollutants <sup>1</sup>). Cf. text and Knutzen and Skei (1990) with references. Concentrations in μg/l (total content).

SOURCES	EPA <sup>2</sup> )	CCREM <sup>3</sup> )	NICHOLSON
SUBSTANCES	•	ĺ	(1984) <sup>4</sup> )
Aldrin	1.3	6)	0.01
Atrazine	-	2	-
Chlordane	0.004	0.006	0.004
Chlorinated phenols	-	0.2 - 18	**
DDT <sup>5</sup> )	0.001	0.001	0.0005
Dieldrin	0.0019	0.004	0.002
Endosulfan	0.0087	0.02	0.0007
Endrin	0.0023	0.0023	0.003
HCB <sup>5</sup> )	-	0.0065	•
HCH <sup>5</sup> ) (see lindane)	See lindane	0.01 7)	0.003 7)
Hexachlorobutadiene	-	0.1	-
Heptachlor	-	0.01	0.0003
Lindane	0.16 8)	See HCH	0.001
Total PCB <sup>5</sup> )	0.03	0.01 <sup>9</sup> )	0.004
Pentachlorophenol	7.9	0.5	-
Tetrachloroethylene	-	260	-
Toxaphene	0.0002	0.008	0.002
1,2,4-trichlorobenzene		0.5	-

- 1) Includes fresh water criteria (CCREM), see text.
- 2) US Environmental Protection Agency, quoted salt water criteria.
- <sup>3</sup>) Canadian Council of Resource and Environment Ministers, 1987. Canadian Water Quality Guidelines with updates, freshwater (except-PCB).
- <sup>4</sup>) Australian water quality criteria, mainly based on the same data as the EPA-criteria. Applies to both fresh and salt water. Quoted criteria are for the protection of aquatic communities generally; limits for exploitation of fish for food often are an order of magnitude lower.
- <sup>5</sup>) DDT: Dichlorodiphenyltrichloroethane. HCB: Hexachlorobenzene, HCH: Hexachlorocyclohexane, several isomers, including lindane. PCB: Polychlorinated biphenyls.
- 6) Converts into dieldrin (see this).
- 7) Sum of all isomers. 0.02 ug/l within the EC (cf. The European Community's Times no. L 274 Oct. 17, 1984).
- 8) Only acute criterion.
- 9) Salt water criterion, update April 1991, 0.001 ug/l in freshwater.

# 5. CLASSIFICATION

Classification systems have been devised for both contents in water (table 3) and for the levels in sediments (table 4) and organisms (tables 5-12).

Several factors support operating with additional classifications for media other than water:

- Difficulties of measuring some of the substances in water (especially fat soluble, bioaccumulating substances which have a low solibility in water), as well as problems in obtaining representative data for water.
- Sediments are the main store of most micropollutants.
- The need to cover different parts of the marine environment (free water masses, shallow water communities, sediments) and organisms with different modes of life and hence various exposure routes (plants, mussels, snails, fish).
- The particular concern associated with the content of contaminants in edible species.

A difficulty with using several bases for classification is the risk that an area will be given different classifications according to different scales.

Expressed in a simple manner the below proposals for classification schemes represent the following degrees of contamination/pollution:

Class I: None or insignificant

Class II: Moderate
Class III: Marked
Class IV: Strong

### **5.1.** Contents in water

The classification proposal in table 3 is based on heterogenous and limited data material with respect to define the "high background level" in the Baltic, Skagerrak and North Sea and oceanic water (cf. references in Knutzen and Skei, 1990), as well as unpublished NIVA observations from 40 metres depth in the Oslo fjord. The classification is aimed at covering fjord and coastal waters without a pronounced influence from fresh waters, i.e. with clearly marine organism communities. A proper basis for such a classification - sufficient numbers of data to calculate, e.g. reliable 90% percentiles for the concentrations - are not available. In addition, the fact that the waters along the various parts of the coast are influenced to varying extents by sea currents with different diffuse loading has not been taken into account.

The general basis for the classification in table 3 is that a 10 (5)-fold increase compared to the presumed "high background level" (upper limit for class I) must be seen as a "strong" contamination and therefore be set as the limit to class IV. The result of such a schematic view is then compared with the strictest criteria values in table I, or later information about damage thresholds. This has resulted in a downward adjustment of the limit between classes III and IV for arsenic (Blanck et al., 1989), fluoride (Knutzen, 1987) and mercury. (For fluoride consideration has also been taken of the much higher natural concentration in sea water than that of the other substances).

The above procedure has resulted in that all concentrations which exceed the criteria values in table 1 fall into class IV. This consequence can be justified by the following facts:

- In the case of at least some of the substances, lower criteria values can be expected as knowledge about the effects improves.
- Mobilization of the substances in question is generally unwanted owing to the hazards of accumulation in the surroundings.
- Because the substances accumulate in organisms, a method of assessment is required which is more rigorous than simply looking at the toxic effects from water exposure.

Table 3. Proposals for water quality classes for the total content of selected metals, arsenic and fluoride in fjord and coastal waters,  $\mu g/l$ .

SUBSTANCES	CL. I	CL. II	CL. III	CL. IV
Arsenic 1)	< 2	2 - 5	5 - 10	> 10
Cadmium	< 0.05	0.05 - 0.15	0.15 - 0.5	> 0.5
Chromium	< 0.15	0.15 - 0.5	0.5 - 1.5	>1.5
Copper 1)	< 0.2	0.2 - 0.5	0.5 - 1	> 1
Fluoride	<1.3 · 10 <sup>3</sup>	$1.3 - 4 \cdot 10^{3}$	4 - 10 · 10 <sup>3</sup>	> 10 4
Lead	< 0.05	0.05 - 0.15	0.15 - 0.5	> 0.5
Mercury 1)	< 0.005	0.005 - 0.015	0.015 - 0.03	> 0.03
Nickel	< 0.7	0.7 - 2.2	2.2 - 7	> 7
Silver	< 0.01	0.01 - 0.03	0.03 - 0.1	> 0.1
Zinc	< 0.05	0.05 - 1. 5	1.5 - 5	> 5

<sup>1)</sup> Partly revised compared with Knutzen and Skei (1990).

### 5.2. Contents in sediments

The classification of metals and PAHs in table 4 is based on data from studies of aerobic Norwegian fjord sediments, and estimates of the upper limit of concentrations not traceable to point sources. The values for organic chlorine compounds are partly based on foreign data (cf. ref. in Knutzen and Skei, 1990) and are among the most dubious, owing to the lack of observations. Besides, the same objection concerning PCB applies here as previously stated about the criteria in Chapter 4: the classification should preferably have been for the most toxic of the compounds within the group.

The micropollutant concentrations in sediments depend on a number of factors, which emphasizes the need for standardization of sampling, treatment, and methods of analysis and interpretation, as well as normalization with respect to aluminium, grain size or organic carbon. (In specific cases consideration must also be given to redox conditions and the geology in the catchment area of the fjords.) Such a standardization has not been fully achieved. In all probability the system should be based on values which were at least normalized for grain size (<63 um) and content of organic carbon (the latter particularly important for organic micropollutants).

The class intervals in table 4 are in principle derived in the same way as for water, although "presumed high background level" (upper limit Cl. I) is multiplied by 20 instead of 10 to

determine the limit between class III/IV (except for fluoride). In practice an increase of 20 times in the sediment will present a considerably smaller hazard than a 10-fold increase in water.

In other words, to conform to the water classification, the intervals should have been greater. On the other hand it was desirable to emphasize that, for many substances, a 4-5 times or greater increase in the "background level" (lower limit Cl. III) must be viewed as being "markedly polluted". More concrete meaning of the terms "moderately", "markedly" and "strongly" polluted can only be attained when the concentration intervals can be related to risks of damage.

Note that the basis for the classification in table 4 is presumed high background levels in "fine-grained" fjord sediments (ie. mostly silt and clay, cf. Knutzen and Skei, 1990, table 15). As the concentrations do not relate to normalized values, some judgement must be used when comparing data with class intervals. This is necessary for instance in decisions regarding dredging, dumping or disturbances of e.g. sediments which belong to class IV for one or more contaminants. Another factor to be considered is the size of the affected area.

Table 4. Proposal for classification of micropollutant contents in upper layers of fine-grained fjord sediments. Concentrations in mg/kg dry weight for elements.; μg/kg dry weight for organic compounds.

SUBSTANCES	CL. I	CL. II	CL. III	CL. IV
ELEMENTS				
(mg/kg dry wt.)				
Arsenic	< 20	20 - 80	80 - 400	> 400
Cadmium	< 0.25	0.25 - 1	1 - 5	> 5
Chromium	< 70	70 - 300	300 - 1400	> 1400
Copper	< 35	35 - 150	150 - 700	> 700
Mercury	< 0.15	0.15 - 0.6	0.6 - 3	> 3
Fluoride 1)	< 800	800 - 3000	3000 - 8000	> 8000
Lead	< 30	30 - 120	120 - 600	> 600
Nickel	. < 30	30 - 130	130 - 600	> 600
Silver	< 0.3	0.3 - 1.3	1.3 - 6.0	> 6
Zinc	< 150	150 - 650	650 - 3000	> 3000
		·		
ORGANIC COMPOUNDS			•	
(μg/kg dry wt.)				
PAH <sup>2</sup> )	< 300	300 - 1000	1000 - 6000	> 6000
B(a)P	< 5	5 - 25	25 - 100	> 100
PCB <sup>4</sup> )	< 5?	5 - 25	25 - 100	> 100
HCB <sup>5</sup> )	< 0.5?	0.5 - 2.5	2.5 - 10	> 10
EPOCl 1, 6)	< 100?	100 - 500	500 - 2000	> 2000
2,3,7,8-TCDD equiv. <sup>7</sup> )	< 0.03 ?	0.03 - 0.12	0.12 - 0.6	> 0.6

<sup>1)</sup> Revised compared with Knutzen and Skei (1990).

<sup>2)</sup> Sum polycyclic aromatic hydrocarbons.

<sup>3)</sup> Benzo(a)pyrene (one of several potentially carcinogenic PAH compounds).

<sup>4)</sup> Sum polychlorinated biphenyls.

<sup>&</sup>lt;sup>5</sup>) Hexachlorobenzene.

<sup>6)</sup> Extractable persistent organically bound chlorine.

Num of the toxicity potential for polychlorinated dibenzofurans/dioxins, measured as equivalents of the most toxic of these compounds (2,3,7,8-tetrachlorodibenzo-p-dioxin) after Ahlborg et al. (1989); cf. Næs and Oug (1991) for "background values".

## 5.3. Contents in organisms

In addition to the need to study extent of contamination in organisms with different modes of life, ways of exposure, accumulation properties and relation to various user interests, there are practical reasons for a classification based on the accumulation in several species. A preferred indicator species, such as the blue (common) mussel, may be lacking in an area and then be replaced by others, e.g. the knotted wrack (metals only) or the common periwinkle (metals, PAH). With the use of two or more indicator species in the same area, it is unavoidable that one may risk inconsistent classification, but the risk of such "errors" can be reduced by comparative studies of the accumulation properties of the species concerned. So far results from such studies are rare.

The determination of "presumed high background level" is also open to conjecture. This element of uncertainty varies both with substance and species, and can only be estimated with a closer view into the studies referred by Knutzen and Skei (1990).

For several potential indicator species (e.g. the edible crab) studies of "background" concentrations are lacking or inadequate. If the classification systems are to be made more reliable and usable, the recording of "background levels" and updating of the knowledge base remain key factors.

For some substances and groups of chemicals classification is prohibited by lack of data. This applies to some organochlorine and organobromine compounds - single substances as well as sum variables. As stated, it is only partially meaningful to use the sum of PCB instead of the most toxic congeners or a sum of identified compounds. To some extent such a change in the registration and monitoring of PCB has now been introduced and will soon require new classification systems for PCB in organisms.

A more detailed treatment of variation factors is found in Knutzen and Skei (1990). As with water and sediments, warnings are made against using the below proposal for classification without taking into account the presuppositions and reservations.

Depending on substance and indicator species, the following class limits imply that a 3- to 5- fold increase in the "presumed high background level" should be considered a "marked" and a 10- fold increase as a "strong" contamination, and hence these (rounded off) values are used as the upper limits for classes II and III.

The reason for somewhat variable sizes of the class intervals is mainly practical. In some cases the high natural levels of individual elements (e.g. arsenic, fluoride, copper and zinc) have been taken into consideration.

For metals in the generally most used indicator species, the concentrations are given on a dry weight basis. For commercial edible species, a fresh weight basis is used. Spatial and temporal comparisons of organic micropollutant levels require recalculation to fat weight basis.

### 5.3.1. Metals

In shallow water environments the most used metal indicators in Norway are benthic algae (table 5) and mussels (table 6), although the common periwinkle (table 7) has also been used. The main basis for the classification - information about "background level" - is somewhat variable, and the same applies to the species' indicator properties in relation to different metals (cf. Knutzen and Skei, 1990).

As regards other marine sub-environments, an adequate data base for metal classification has only been found for mercury in fish.

**Table 5.** Proposal for classification of marine environmental quality based on the content of metals, arsenic and fluoride in bladder wrack (*Fucus vesiculosus*) and knotted wrack (*Ascophyllum nodosum*), mg/kg dry weight. Particular uncertainty regarding the upper limit of class I is marked with?

ELEMENTS	CL. I	CL. II	CL. III	CL. IV
Arsenic	<50	50 - 150	150 - 350	> 350
Cadmium	< 1.5	1.5 - 5	5 - 20	> 20
Chromium	< 2?	2 - 10	10 - 30	> 30
Copper	< 10	10 - 25	25 - 75	> 75
Fluoride	< 15	15 - 50	50 - 100	> 100
Lead	< 3	3 - 10	10 - 30	> 30
Mercury	< 0.05	0.05 - 0.15	0.15 - 0.5	> 0.5
Nickel	< 10	< 10 - 50	50 - 100	> 100
Silver	< 0.5?	0.5 - 1.5	1.5 - 3	> 3
Zinc	< 200 ¹)	200 - 500	500 - 1500	> 1500

<sup>1)</sup> Young tissue of knotted wrack often contains less than 100 mg/kg.

To table 5 may be added that the "high background levels", on which the limit for Cl. I is based, apply to the upper 10-15 cm in bladder wrack and shoots cut just under the second bladder from the top in knotted wrack. Hence this tissue is up to about 2 years old. The possibility that the metal content is systematically dependent on age is only clearly established for zinc in knotted wrack, where the youngest tissue often contains <100 mg/kg dry weight.

Some recent results from Northern Norway (NIVA, unpubl.) indicate considerably lower "background" concentrations than the above upper limits for class I, thus possibly illustrating the need to operate with regional reference values.

**Tabell 6.** Proposal for classification of marin environmental quality in marine waters based on the content of metals, arsenic and fluoride in the blue mussel (*Mytilus edulis*), mg/kg dry weight. Uncertainty as to the upper limit for class I is marked with?

ELEMENTS	CL. I	CL. II	CL. III	CL. IV
Arsenic	< 10	10 - 30	30 - 100	> 100
Cadmium	< 2	2 - 5	5 - 20	> 20
Chromium	< 3	3 - 10	10 - 30	> 30
Copper 1)	< 10?	10 - 30	30 - 100	> 100
Fluoride	< 15?	15 - 50	50 - 150	> 150
Lead	< 5	5 - 20	20 - 50	> 50
Mercury	< 0.2	0.2 - 0.5	0.5 - 2	> 2
Nickel <sup>2</sup> )	< 5	5 - 20	20 - 50	> 50
Silver	< 0.3?	0.3 - 1	1 - 2	> 2
Zinc	< 200	200 - 500	500 - 1500	> 1500

<sup>1)</sup> Dubious indicator of copper.

**Table 7.** Proposal for classification of marine environmental quality based on the content of metals and arsenic in the common periwinkle (*Littorina littorea*), mg/kg dry weight. Uncertain upper limit for class I marked with ?.

ELEMENTS	CL. I	CL. II	CL. III	CL. IV
Arsenic	< 30?	30 - 75	75 - 300	> 300
Cadmium	< 5	5 - 15	15 - 30	> 30
Chromium	< 3	3 - 10	10 - 30	> 30
Copper	< 150	150 - 300	300 - 750	> 750
Cobalt	< 5?	5 - 15	15 - 50	> 50
Lead	< 10	10 - 25	25 - 75	> 75
Mercury	< 0.5?	0.5 - 2	2 - 5	> 5
Nickel	< 10?	10 - 30	30 - 100	> 100
Silver	< 3?	3 - 10	10 - 20	> 20
Zinc	< 100	100 - 300	300 - 1000	> 1000

Apart from mercury and (partly) arsenic in fillet and lead/cadmium in liver, fish are generally unsuitable as indicators of metals owing to their ability to regulate the uptake and to excrete most of the metals (cf. references in Knutzen and Skei, 1990).

In the case of mercury it is well documented that the content in fish fillet increases with age and size. A classification should therefore be based on a normalization according to weight (age or length). However, for mainly practical, descriptive purposes, the limits shown below (table 8) should be generally adequate and may be used not only for cod, but also for whiting, haddock, flounder and plaice.

<sup>&</sup>lt;sup>2</sup>) Partly revised compared with Knutzen and Skei (1990).

**Tabell 8.** Proposal for the classification of marine environmental quality based on the content of mercury in fillet of cod (mg/kg fresh weight).

CL. I	CL. II	CL. III	CL. IV
< 0.1	0.1 - 0.3	0.3 - 0.5	> 0.5

In Norway species of soft bottom fauna have only rarely been analyzed for metal content. A practical reason for this is that the bottom environment in deeper waters can be more easily classified through analyses of sediments.

### 5.3.2. Polycyclic aromatic hydrocarbons (PAH)

Preferably the blue mussel (Mytilus edulis), is used as an indicator of PAH, with the horse mussel (Modiolus modiolus), common periwinkle (Littorina littorea) or limpets (Patella vulgata) as substitutes. The accumulation properties of the latter three seem to differ somewhat from those of the blue mussels, although the class division in table 9 can still provide a useful indication of the degree of pollution. In this respect the least reservations are associated with the sum of PAHs.

Recent results (cf. Knutzen and Green, 1990 and Næs et. al., 1991) partly suggest that the previously assumed upper limit for diffuse background level (Knutzen, 1989) has been overestimated. Therefore new and systematic studies are required to establish reliable reference values. Until such studies have been conducted the proposal for classification in table 9 must be seen as merely indicative. A comprehensive survey will also make it possible to use the sum of the potential carcinogenic PAH as a classification variable, and not just benzo(a)pyrene as a representative for this group.

Observe that the main guideline which defines a 10-fold increase in "high background level" as a "strong" degree of pollution, has not been found applicable to the sum of PAH and especially not to benzo(a)pyrene. This is because mussels (and snails) show an extreme accumulation of these substances. An increase of between 100- and 1000- fold is usual between levels in areas of only diffuse loading and registration in smelter recipients, and excess concentrations of four orders of magnitude have been recorded.

Tabell 9. Preliminary proposal (see text) for classification of marine environmental quality based on contents of polycyclic aromatic hydrocarbons (PAH) and the potential carcinogenic compound benzo(a)pyren (B(a)P) in mussels (Mytilus edulis), ug/kg fresh weight.

SUBSTANCES	CL. I	CL. II	CL. III	CL. IV
Total PAH 1)	< 100	100 - 300	300 - 2000	> 2000
B(a)P 1)	< 1	1 - 5	5 - 25	> 25

<sup>1)</sup> Revised compared with Knutzen and Skei (1990).

The high variability and the difficulties in interpreting the results of PAH in fish, together with rapid uptake/excretion, render fish unsuitable as a PAH indicator. In any case thorough reference studies are required. This is also desirable for the edible crab.

### 5.3.3. Organo-chlorine compounds

Examples of suitable indicators of the degree of pollution by these substances are mussels (table 10) and several species of fish (table 11). The same probably applies to the edible crab, though there are insufficient data at present (except for polychlorinated dibenzofurans/dioxins).

The classification is based mainly on recent results from the Norwegian State Pollution Monitoring Program and the international monitoring under the direction of the Oslo/Paris Commission's Joint Monitoring Group (JMG). Collection of the JMG data from reference areas started in 1990 and the data are only partially evaluated.

Consequently, a re-appraisal of the class limits may soon be required. This applies particularly to PCB, where instead of the somewhat dubious calculations of the total content, future limits should be based on the sum of identified compounds, both the assumed main components of commercial mixtures and sum variable for the most toxic congeners based on TEF-values (TEF = Toxicity Equivalence Factors). For cod and flounder comprehensive comparative studies are already available (Marthinsen et. al., 1991), which showed that the sum of 7 single compounds (PCB no. 28, 52, 101, 118, 153, 180 - "the 7 Dutch") made up about 60% of the total PCB determined by previous methodology. An introductory analysis of 50 reference data for mussels in the JMG programme showed the sum of these 7 PCBs to be just less than 50% of the "total". This would suggest about a halving of the figures in tables 10-11, which apply to total-PCB.

The JMG data may also require a moderate downward adjustment of the limits for some of the other substances. As an example, the average/standard deviation for HCB in mussels at about 50 observations of reference values in 1988 - 1990 was as low as 0.10/0.06 ug/kg fresh weight.

Table 10. Preliminary proposal (see text) for classification of marine environmental quality based on the content of selected persistent organo-chlorine compounds and sum variables in the blue mussel (*Mytilus edulis*), µg/kg fresh weight. For abbreviations, see table 2, note 5.

SUBSTANCES	CL. I	CL. II	CL. III	CL. IV
Sum DDT	< 2	2 - 5	5 - 20	> 20
НСВ	< 0.2	0.2 - 1	1 - 5	> 5
Sum HCH	< 0.5	0.5 - 3	3 - 10	> 10
PCB (total)	< 10	10 - 30	30 - 100	> 100
2,3,7,8-TCDD equiv. 1)	< 0.0003?	0.0003 - 0.001	0.001 - 0.003	> 0.003

<sup>1)</sup> Model after Ahlborg et al. (1988).

Table 11. Preliminary proposal (see text) for the classification of marine environmental quality based on the content of selected persistent organic chlorine compounds and sum variables in fish, μg/kg fresh weigh. Particularly doubtful limits for class I marked with ?. For abbreviations, see table 2, note 5.

SUBSTANCES	CL.	ΣDDT	НСВ	ΣΗCΗ	РСВ	2378-TCDD-
					(total)	eq. <sup>1</sup> )
Species/Classes						
Cod (Gadus morhua)	I	< 2	< 0.2	< 1?	< 10	< 0.0002
	П	2 - 5	0.2 - 0.5	1 - 3	10 - 50	0.0002 - 0.0005
Fillet	Ш	5 - 15	0.5 - 2	3 - 10	50 - 200	0.0005 - 0.002
	IV	> 15	> 2	> 10	> 200	> 0.002
	I	< 200?	< 20	< 50?	< 1000?	< 0.05
	П	200 - 500	20 - 50	50 - 200	1000 - 3000	0.05 - 0.15
Liver	Ш	500 - 1500	50 - 200	200 - 500	3000 - 10000	0.15 - 0.3
	IV	> 1500	> 200	> 500	>10000	> 0.3
Flounder (Platichthys						
flesus)	I	< 3?	< 0.3	< 2	< 20?	< 0.0003?
	П	3 - 5	0.3 - 1	2 - 5	20 - 50	0.0003 - 0.001
Fillet	Ш	5 - 20	1 - 3	5 - 20	50 - 100	0.001 - 0.003
	IV	> 20	> 3	> 20	> 100	> 0.003
Herring (Clupea						
harengus)	I	< 20	< 2	< 10	< 100?	< 0.002
	П	20 - 50	2 - 5	10 - 30	100 - 300	0.002 - 0.005
Fillet	Ш	50 - 150	5 - 20	30 100	300 - 1000	0.005 - 0.015
	IV	> 150	> 20	> 100	> 1000	> 0.015

<sup>1)</sup> After model in Ahlborg et al. (1988).

Table 12 gives a tentative proposal for classification of marine environmental quality based on the content of polychlorinated dibenzofurans/dibenzo-p-dioxins (PCDF/PCDD), measured as 2,3,7,8-TCDD-equiv. in hepatopancreas of the edible crab:

**Tabell 12.** Preliminary proposal for classification of marine environmental quality based on the content of PCDF/PCDD (TCDD-equiv. after Ahlborg et al., 1988) in hepatopancreas of the edible crab (*Cancer pagurus*), ng/kg fresh weight.

CL. I	CL. II	CL. III	CL. IV
< 25	25 - 75	75 - 150	> 150

The modest difference between "presumed high background level" and class IV for TCDD-eq. is motivated by the low dosage limits which have been set for intake by humans of these extremely toxic substances.

# 6. USE OF THE CLASSIFICATION SYSTEM

The water quality with respect to micropollutants can, in theory, be classified by anyone with access to relevant analytical data. However, in practice it should be left to qualified researchers or experts working with management authorities. This is because many factors which demand good insight and judgement are involved:

- Can the results be regarded as reliable and comparable with other data? (collection, storing, transport and treatment of samples, analytical methods).
- If the results are considered to be reliable, is the amount of data sufficient for classification? (dependent on the type of sample and place; also whether the aim of the classification is mainly descriptive or whether decissions and actions will be based on it).
- How can borderline cases be treated properly in accordance with the system's schematic structure?
- What about cases of different classification results according to different micropollutants (e.g. lead, PAH, PCDF/PCDD and PCB in mussels) or from the same parameters observed in different species.

The latter problem types cannot be solved within a system based on numerical steps and/or colours denoted to each class, but requires a method of weighting and further division of the classes.

A temporary reservation is associated with the quality and number of data which provide the basis for determining the classification's point of reference - "presumed high background level". In the future more and better data will be available, and therefore also a better overview of the spatial and temporal variations.

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