Water Protection in Europe

KARL-GEERT MALLE, BASF AG, D-6700 Ludwingshafen, West Germany

ABSTRACT

In addition to national regulations, there are supranational as well as international conventions for protection of European waters. Supranational directives have been passed by the European Community concerning, for instance, the quality of bathing water and of fish as well as shellfish waters, on the quality of drinking water and surface waters for production of drinking water. The directive on "pollution caused by certain dangerous substances discharged into the aquatic environment" is of special importance. A number of international conventions with special purviews correspond to this directive. The purpose of all the regulations is to control pollution caused by dangerous substances. With regard to substances of "list I", pollution is to be eliminated by fixing emission standards for all discharges. To reduce pollution by substances of "list II", member states shall lay down emission standards which are based on standardized quality objectives. These standards shall be harmonized by the European Commission. The conventions contain only lists of families and groups of substances, among which certain individual substances first have to be selected. Meanwhile, 46 substances are under examination; for 83 more substances, discussion is proposed. This procedure is rather complicated. Technological aspects such as amounts, production processes, use and treatment technology are taken into account as well as ecological properties like toxicology, persistence and bioaccumulation. Examination also includes the economic problems involved. The proposals for emissions standards and quality objectives thus resulting have to pass through the normal legislative procedure before becoming legally binding on the respective states. The first implementing directive is limiting the mercury discharges from the chlor-alkali electrolysis (amalgam process). Furthermore, there are proposals for a drins as well as a cadmium directive. The first substance of list II under examination is chromium with its compounds.

REVIEW ON SUPRANATIONAL AND INTERNATIONAL REGULATIONS

In Western Europe, trans-boundary protection of the waters is of special importance. The Rhine basin is not the only area in Europe where states are situated so closely together that pollution of the waters in one state inevitably has consequences for the adjoining states. Therefore, for several years there have been supranational and international regulations for water protection in addition to the respective national laws.

Directives in the European Community

During the past years, several supranational directives have been passed by the European Community (Table I). Within a fixed period of time, they have to be implemented on a national basis by the member states. If the states fail to take the necessary action within the prescribed period, the Commission may bring the matter before the International Court of Justice. This already has happened several times.

However, the effectiveness of most of the EEC directives is limited. For instance, it is left to the states to decide which surface waters are to be used for the production of drinking water and for fish- or shellfish-farming. Only then are these waters subject to the EEC regulations on limit values and their control. Furthermore, the directives often state different numerical values as guide values. And only the least stringent one obtained by a compromise is fixed as imperative value. Directive 76/464/EEC on "pollution caused by certain dangerous substances discharged into the aquatic environment of the Community" of 4 May, 1976, is the only directive of great importance. This directive is to improve the protection of the surface waters against individual substances.

International Conventions

To this directive correspond quite a number of international conventions with varying purviews and signatory states (Table II). Among these conventions, the Rhine Protection Convention is of special importance for Middle Europe. It is practically identical to the EEC directive and it also incorporates Switzerland in this system of conventions. In the meantime, the EEC additionally acceded to most of the international conventions. In this way, the practical implementation of these various conventions has been largely harmonized. The policy on the EEC level has a kind of signal effect, because here the work has made the most progress. Therefore, the following will deal with this directive.

PROTECTION OF THE WATERS FROM DANGEROUS SUBSTANCES

It is the purpose of the EEC directive to control "pollution" of surface waters. "Pollution" is defined as the discharge by man, directly or indirectly, of substances or energy into the aquatic environment, the results of which are such as to cause hazards to human health, harm to living resources and to aquatic ecosystems, damage to amenities, or interference with other legitimate uses of water. Although this definition may seem rather extensive, it becomes clear at

TABLE I

EEC Directives on Water Protection

CODE	Name	Issued on
75/440/EEC	Quality of surface water for drinking water	16.06.1975
76/160/EEC	Quality of bathing water	08.12.1975
76/464/EEC	Discharge into the aquatic environment	04.05.1976
78/176/EEC	Waste from the titanium industry	20.02.1978
78/659/EEC	Quality of fresh water for fish life	18.07.1978
79/869/EEC	Sampling and analysis of drinking water	09.10.1979
79/923/EEC	Quality of shellfish waters	30.10.1979
80/68/EEC	Protection of ground water	17.12.1979
80/778/EEC	Quality of water for human consumption	15.07.1980
82/176/EEC	Mercury from chlor-alkali electrolysis industry	22.03.1982

TABLE II

Conventions for the Protection of Surface Waters

Scope	Origin of pollution	Convention	Signatory countries
Open sea	By ship or aeroplane	London	Seafaring nations
North Atlantic North Sea	By ship or aeroplane	Oslo	N, S, DK, SF, D, NL, B, F, E, P, GB, JRL, JS
Biscay, British Channel, Irish Sea, North Sea	By land-based sources	Paris	B, DK, D, GB, F, JRL NL, L, J, N, S
Baltic Sea	By ship, aeroplane, land-based sources	Helsinki	Countries bordering the Baltic Sea
Mediterranean	By ship, aeroplane, land-based sources	Barcelona	Countries bordering the Mediterranean
International watercourses	By discharge	Strassburg	Countries in the Council of Europe
Surface waters of EC	By discharge	EC directive (ENV 131)	Countries of the EC
Rhine	By discharge	Rhine protection convention	NL, F, D, CH, L, EC
Danube	By discharge	Danube convention	Countries bordering the Danube

TABLE III

Discharge of Certain Dangerous Substances

Elimination of pollution (list I)	Emission standards (GB: quality objectives)	Best technical means available (protocol: economic availability)
Reduction of pollution (list II)	Quality objectives (basis for emission standards)	Latest economically feasible technical developments

the same time that it does not aim at a zero emission, as at times the directive incorrectly has been interpreted. With regard to substances of list I, "pollution" is to be eliminated (Table III).

For this purpose, all respective discharges require prior authorization, which may be granted for a limited period only. The authorization has to specify emission standards, i.e., maximum concentraion and maximum quantity. The measures for prevention of pollution have to be based on "the best technical means available", while, according to a protocol minute, the "economic availability" has to be taken into account, too. With regard to substances within list II, "pollution" shall be reduced via national programs, which are to fix quality objectives for the respective waters (emission limit values). Here, with regard to the measures for prevention of pollution, the "latest economically feasible technical developments" have to be considered.

TABLE IV

List I of Families and Groups of Substances

1. Organohalogen compounds and substances which may form such compounds in the aquatic environment.
2. Organophosphorus compounds.
3. Organotin compounds.
4. Substances in respect of which it has been proved that they possess carcinogenic properties in or via the aquatic environment.
5. Mercury and its compounds.
6. Cadmium and its compounds.
7. Persistent mineral oils and hydrocarbons of petroleum origin.

Selection of Substances

Nevertheless, it has been a long way from the principal agreement to actual measures. We had a mere framework directive. Actual legal consequences could be effected only by implementing directives. As often with political agreements, the actual detail work had been reserved to subsequent investigations by experts. The EEC directive, like

TABLE V

List II of Families and Groups of Substances

1. The following metalloids and metals and their compounds:

1. zinc	6. selenium	11. tin	16. vanadium
2. copper	7. arsenic	12. barium	17. cobalt
3. nickel	8. antimony	13. beryllium	18. thalium
4. chromium	9. molybdenum	14. boron	19. tellurium
5. lead	10. titanium	15. uranium	20. silver

2. Biocides and their derivatives not appearing in list I.
3. Substances which have a deleterious effect on the taste and/or smell of the products for human consumption derived from the aquatic environment.

   and compounds liable to give rise to such substances in water.
4. Toxic or persistent organic compounds of silicon, and substances which may give rise to such compounds in water, excluding those which are biologically harmless or are rapidly converted in water into harmless substances.

all the other conventions on water protection, does not mention individual substances. It merely contains two lists of families and groups of substances in an annex. (Tables IV and V).

Among these families and groups, individual dangerous substances have to be selected "mainly on the basis of their toxicity, persistence and bioaccumulation."

For a quick and practicable start, national experts in a first stage had proposed for examination those substances obviously presenting risks for the aquatic environment (Table VI).

TABLE VI

Substances Already Selected for Investigation

First series		Progress made
1.	Mercury, chlor-alkali electrolysis Mercury, other industries	Directive 22.03.82 Directive in preparation
2.	Cadmium and cadmium compounds	Proposal for a Directive 17.02.81
3–5.	Aldrin, dieldrin, endrin	Proposal for a Directive 16.05.79
Second series		
16, 17	Chlordane, heptachlor (heptachlorepoxide)	No action necessary 18.07.80
8, 9	DDT, hexachlorocyclohexane (all isomers)	Proposal in preparation
10, 11	PCB (PCT) Hexachlorobenzene	Discussion under way
Third series		
12, 13	Endosulfan, hexachlorobutadiene	Discussion under way
14, 15	Pentachlorophenol, trichlorophenol	
Fourth series		
16–18.	Benzene, carbon tetrachloride, chloroform	Studies in progress
Carcinogens		
19–21.	Arsenic (and mineral compounds), benzidine, PAH	Studies in progress
Fifth series		
22–36.	1,1-Dichloroethane, 1,2-dichloroethane 1,2-dibromethane 1,1,1-trichloroethane 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane 1,1-dichloroethene, 1,2-dichloroethene, trichloroethene tetrachloroethene, chlorobenzene, trichlorobenzene dichloromethane, 1,2-dichlorpropene, malathion	
Sixth series		
37–46.	2-Chloroaniline, 3-chloroaniline, 4-chloroaniline 1-chloro-2-nitrobenzene, 1-chloro-4-nitrobenzene, 2,4-dichlorophenol 2-chloroethanol, 1,3-dichloropropanol, epichlorhydrin, parathion	

Simultaneously, the EEC Commission had charged the firm of Biokon to list all respective substances as completely as possible. Thus, ca. 1,500 substances were named. From this "Biokon list," those substances then have been preselected which are first to be examined. The EEC has found that, of these 1,500 substances, 1,000 are produced or used in the community in quantities of less than 100 tons/year, 186 more than 1,000 tons/year, 44 more than 10,000 tons/year and only 25 in excess of 100,000 tons/year. The risks to the aquatic environment from discharges of these substances have been examined by means of a mathematical model for evaluation. In this way, 129 substances have been specified (Table VII).

Eventually these substances will be studied. As a result of this examination it surely will become evident that several of them are less important.

Examination of the Substances

The actual examination of the substances is rather time-consuming. First, the EEC Commission for each substance orders three expertises from scientists or institutes with regard to ecology, technology and economic impact (Table VIII).

These papers then are discussed in detail together with reports from all member states, before the proposal for an implementing directive can be introduced into the legislative procedure. This procedure, too, needs the usual period of time. In addition to the scientific and technical problems, there are a lot of fundamental juridical problems which have to be solved with the very first implementing directive. Therefore, it is not surprising that studies have been completed for only a few substances so far.

Quality Objectives

Above all, the British "quality objectives" proved to be a drag on efficient proceeding. Naturally, the British Isles are important for the ecological situation of the North Sea and it seemed necessary to include Great Britain in the conventions. Therefore, the continental states have conceded that Great Britain may apply limit values for emission, the so-called "quality objectives," instead of the continental emission standards which are relatively easy to convey. This means that, for each individual substance,

TABLE VII

List of Substances Additionally Proposed for Investigation

2-Amino-4-chlorophenol, anthracene, azinphos-ethyl, azinphos-methyl, benzyl chloride, benzylidene chloride, biphenyl, chloral hydrate, chloroacetic acid, 1-chloro-2,4-dinitrobenzene, 4-chloro-3-methylphenol, 1-chloronaphthalene, chloronaphtalenes, 4-chloro-2-nitroaniline, 1-chloro-3-nitrobenzene, 4-chloro-2-nitrotoluene, chloronitrotoluenes, 2-chlorophenol, 3-chlorophenol, 4-chlorophenol, chloroprene, 3-chloroprene, 2-chlorotoluene, 3-chlorotoluene, 4-chlorotoluene, 2-chloro-P-toluidine, chlorotoluidines, coumaphos, cyanuric chloride, 2,4-D, demeton, dibutyltin dichloride, dibutyltin oxide, dibutyltin salts, dichloroanilines, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, dichlorobenzidines, dichlorodilsopropyl ether, dichloronitrobenzenes, 1,3-dichloropropene, 2,3-dichloropropene, dichloroprop, dichlorvos, diethylamine, dimethoate, dimethylamine, disulfoton, ethylbenzene, fenitrothion, fenthion, hexachloroethane, isopropylbenzene, linuron, MCPA, mecoprop, methamidophos, mevinphos, monolinuron, naphthalene, omethoate, oxydemeton-methyl, phoxim, propanil, pyrazon, simazine, 2,4,5-T, tetrabutyltin, 1,2,4,5-tetrachlorobenzene, toluene, triazophos, tributyl phosphate, tributyltin oxide, trichlorfon, 1,1,2-trichlorotrifluoroethane, trifluralin, triphenyltin acetate, triphenyltin chloride, triphenyltin hydroxide, vinyl chloride, xylenes

TABLE VIII

Examination of Substances

- Ecology
  - Toxicity
    - To man
    - In waters
  - Persistence
    - Physicochemical degradation
    - Biological degradation
  - Bioaccumulation, biomagnification
- Technology
  - Production, use, processes, amounts
  - Analytics
  - Discharges into the waters
  - Wastewater treatment technology
  - Emission standards
- Economy
  - Impact of the substance
  - Costs of treatment technology
  - Consequences of substitution

TABLE IX

Mercury (Chlor-alkali Electrolysis) EEC Directive

Emission standards			Quality objectives
Load (g Hg/ton chlorine production capacity)			Fish flesh 0.3 mg Hg/kg wet flesh
Recycled brine			Inlaid surface waters 1 μg/L total Hg
Effluent from production unit 1983	monthly average	0.5	
	daily average	2.0	Estuary waters 0.5 μg/L dissolved Hg
discharge into the waters	monthly average 1983	1.5	
	1986	1.0	Territorial sea waters, internal coastal waters 0.3 μg/L dissolved Hg
Lost brine			
Effluent from production unit 1983	monthly average	2.5	
Discharge into the waters	monthly average 1983	8	
	1986	5	

time-consuming studies of the emission situation are necessary before the quality objectives can be specified. Furthermore, Great Britain insisted on fixing these quality objectives not for fresh water, salt water and high sea only, but also for ecological secondary media. As a consequence the average mercury content of samples of fish flesh from the Liverpool fish market now is representing the limit value for the British chlor-alkali electrolysis. The weak points of this regulation are obvious. When are the limit values really exceeded? How long will it take until a discharge of mercury is causing an increase in fish mercury content? Which interrelations exist between cause and consequence? Therefore, on ratification of the directive, the continental states have declared their intention not to claim the alternative of quality objectives themselves.

PRESENT STATE OF PROCEEDINGS

The first implementing directive is dealing with mercury discharges by the chlor-alkali electrolysis (amalgam process) (Table IX).

Emission standards have been fixed for the recycled brine as well as for the lost brine. The differing limit values for concentrations in the discharges of a production unit or the site of an industrial plant, respectively, take into account the so-called "historical mercury" (residues of mercury or mercury compounds from earlier activities in the sewers). Parallel to the emission standards now there are quality objectives for different surface waters and for fish flesh, as requested by Great Britain.

However, the number of limit values in the proposal of the EEC Commission for a cadmium directive is even greater (Table X). These examples may show how complicated the regulations inevitably will become, if you try to do justice to the different situations of all industrial dischargers.

Exemplarily among the substances within list II, the element chromium has been studied. In this case, the experts have agreed on a quality objective of less than 50 μg/L chromium at the fresh water border line. Currently, national programs for meeting and maintaining this value are being compiled and will be presented to the EEC Commission.

PRACTICAL CONSEQUENCES FOR THE WATERS

These procedures are extremely time-consuming and the results are complicated and difficult to control. Nevertheless, the work accomplished so far has already had positive consequences for the quality of surface waters. This may best be illustrated by data of the thoroughly controlled Rhine (Table XI).

TABLE X

Cadmium EEC Directive (Proposal)

	Emission standards monthly average: concentration (mg Cd/L) 1983	concentration (mg Cd/L) 1986	load (g/kg Cd handled) 1983	load (g/kg Cd handled) 1986	Quality objectives	(μg Cd/L) 1983	(μg Cd/L) 1986
Mining, nonferrous metal industry	0.5	0.3	–		Fresh water in relation to increasing hardness of the water	1.2–3.0	0.6–1.5
Manufacture of pigments			0.7	0.3			
Manufacture of stabilizers			0.8	0.5			
Manufacture of batteries			2.5	1.5			
Electroplating	1.0	0.5	0.5	0.3	Salt water	2.0	1.0
Manufacture of cadmium compounds			1.0	0.5			
					Sediments, molluscs or fish may be controlled alternatively		
Other industries			–	–			

Maximum daily average up to twice the respective montly average.

TABLE XI

Substances in the Rhine (Yearly Averages, German-Dutch Border)

	1976	1977	1978	1979	1980
Mercury (μg/L)	0.5	0.4	0.3	0.3	0.2
Cadmium (μg/L)	3.0	2.0	1.5	1.2	0.9
Chloroform (μg/L)	67	28	22	8.4	4.5
Dichloromethane (μg/L)	–	18	15	0.09	nn
1,1,1-Trichloroethane (μg/L)	2.2	0.27	0.08	<0.1	0.2
Trichloroethylene (μg/L)	0.56	0.50	0.32	0.13	0.23
HCB (μg/L)	0.051	0.051	0.024	0.019	0.01
α-HCH (μg/L)	0.026	0.025	0.015	0.007	0.01
Hexachlorobutadiene (μg/L)	–	0.063	0.023	0.008	nn
Nitrobenzene (μg/L)	–	0.38	0.12	<0.01	–
Fluoranthene (μg/L)	–	0.21	0.21	0.096	0.076
3,4-Benzopyrene (μg/L)	–	–	0.058	0.041	0.033
Amount of water (m^3/s)	1341	2208	2361	2541	2552

The industry is forced to plan on a long-term basis. Therefore, waste reduction measures obviously have been taken even without actual administrative regulations.

OUTLOOK ON FUTURE DEVELOPMENTS

However, possible risks of these proceedings become more and more obvious. Again and again, additional substances are brought into discussion by various groups. For a sensible examination, first their content in the surface waters as well as in possible discharges has to be ascertained via analysis. For this purpose, the authorities – as, of course, the dischargers, too – have to make series analyses in the trace range. With regard to these substances, possible points of discharge, waste reduction techniques, control measures, etc., have to be found. All this has to be done at a time when the extensive sanitation measures become evident, as shown at the Rhine. There is a danger that bureaucratic perfectionism is liable to turn this necessary EEC directive into an end in itself. The selection of substances should be reasonable and implementation of the directive should still be possible. Therefore, selection should strictly concentrate on those substances for which an ecological necessity for regulation is definitely recognizable.

Large-Scale Production and Application of Highly Concentrated Ozone

HANS-PETER KLEIN, BBC Brown Boveri & Cie., CH-8050, Zürich, Switzerland

ABSTRACT

With the new, very efficient generating plants, ozone can be produced in high concentrations, at low cost and with high reliability. This versatile reagent is therefore destined, in the near future, to play a more important role in the oleochemical industry than today, since it can help to solve different problems in the synthesis of chemicals as well as in the treatment of waste.

INTRODUCTION

Ozone is an extraordinarily powerful oxidizing agent which has been used in drinking water treatment for more than 80 years. Its outstanding properties–high oxidation potential (2.07 V), high reactivity even below room temperature, pronounced selectivity and no residues after reaction–make ozone a reagent which can be used to solve various problems. Ozone has many possible applications in synthesis and in the treatment of wastewater, and off-gases are being studied in laboratory and pilot plant experiments. Nevertheless, ozone lacks large-scale application in the chemical industry. The only known process, where ozone is used in amounts of hundreds of kilograms per hour, is the ozonolysis of unsaturated long-chain fatty acids for the production of bifunctional compounds such as dicarboxylic acids, aldehydes, ketons and alcohols (1,2). There are several reasons for this shortcoming:

Ozone is very often considered to be an expensive, dangerous substance which cannot be produced with the reliability demanded for industrial production processes. The concentrations in which ozone could be produced in the feed gas were restricted to about 1.5 wt-% in air and 3 wt-% in oxygen. This resulted in the handling of large gas volumes and an unfavorable reaction kinetic. Moreover, ozone cannot substitute for other oxidants without an adaption of the whole process.

It is the aim of this paper to show that modern large-scale ozone generating plants can produce ozone according to the requirements of the oleochemical industry, i.e., cheaply, reliably and in high concentrations.

PRINCIPLES OF OZONE PRODUCTION

Today ozone is produced on a commercial scale exclusively by a silent electrical discharge in an oxygen-containing gas. An alternating current with a high voltage is applied between 2 electrodes separated by a dielectric of glass and a narrow gap. While the feed gas is flowing through the gap, the silent electrical discharge produces ozone in it. The discharge causes a dissociation of oxygen molecules into 2 oxygen atoms, which recombine with oxygen molecules and form ozone.