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HYDROGEN PEROXIDE

CAS No. 7722-84-1

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THE ECETOC SCHEME FOR THE

JOINT ASSESSMENT OF COMMODITY CHEMICALS

This report has been produced as part of the ECETOC programme for preparing critical reviews of the toxicology and ecotoxicology of selected existing industrial chemicals.

In the programme, commodity chemicals, that is those produced in large tonnage by several companies and having widespread and multiple uses, are jointly reviewed by experts from a number of companies with knowledge of the chemical. It should be noted that in a JACC review only the chemical itself is considered; products in which it appears as an impurity are not normally taken into account.

ECETOC is not alone in producing such reviews. There are a number of organisations that have produced and are continuing to write reviews with the aim of ensuring that toxicological knowledge and other information are evaluated. Thus a Producer, Government Official or Consumer can be informed on the up-to-date position with regard to safety, information and standards. Within ECETOC we do not aim to duplicate the activities of others. When it is considered that a review is needed every effort is made to discover whether an adequate review exists already; if this is the case the review is checked, its conclusions summarised and the literature published subsequent to the review assessed. To assist ourselves and others working in this field we publish annually a summary of international activities incorporating work planned, in hand, or completed on the review of safety data for commodity chemicals. Interested readers should refer to our Technical Report No. 30 entitled "Existing Chemicals: Literature Reviews and Evaluations".

This document presents a critical assessment of the toxicology and ecotoxicology of Hydrogen Peroxide (CAS No. 7722-84-1).

JACC REPORT NO. 22 - HYDROGEN PEROXIDE

CONTENTS

SECTION 1. SUMMARY AND CONCLUSIONS

Hydrogen peroxide (H_2O_2) and its aqueous solutions (up to 70% concentration) are clear, colourless, weakly acidic liquids with a distinctive and mildly pungent odour, and a low vapour pressure. Pure solutions of H_2O_2 are stable. Small quantities of stabilisers are added to commercial H_2O_2 solutions to prevent catalytic decomposition caused by impurities or contaminants. When decomposition occurs, heat is evolved and large quantities of oxygen are generated. The saturated vapour concentration over a 90% H_2O_2 solution is 3,049mg/m^3 at 25°C.

World-wide about 1,000kt/y H_2O_2 (100% basis) are used, mainly for the production of chemicals, for bleaching of cellulose pulp and textiles and for other purposes such as waste water treatment. Minor quantities are used in applications (food processing, disinfection, drinking water treatment and hair bleaching) in which there is direct contact with human beings.

H_2O_2 occurs naturally as a consequence of photochemical processes and may also be formed through oxygen reduction by iron and copper. Emissions of H_2O_2 from industrial and domestic sources are limited due to its rapid decomposition in the waste water.

Concentrations H_2O_2 found in the atmosphere vary with the intensity of solar radiation, humidity and temperature and the presence of precursors and scavangers of free radicals. The tropospheric lifetime of H_2O_2 is 10-20h. During day-time H_2O_2 concentrations range from 0.4-4μg/m^3, falling to below 0.01μg/m^3 at night. H_2O_2 in the atmosphere tends to concentrate into cloud droplets (where concentrations can reach 8,000μg/l) and is removed by rain-out. During fog and severe smog, atmospheric concentrations may rise to 4,000μg/m^3.

H_2O_2 is produced in water and soil, the amount depending upon the intensity of light, concentration of promoters and dissolved oxygen. Decomposition in water and soil takes minutes or several hours depending on the mineral content and the concentration of micro-organisms. Surface waters generally contain less than 100μg/l, dropping to below 1μg/l at 100m depth. Levels up to 3μg/l are found in ground water.

Human beings may be exposed to H_2O_2 via food. In certain vegetables naturally occurring levels of up to 8,000μg/l have been found. Environmental exposure by inhalation is less than the levels of H_2O_2 normally found in exhaled air; environmental exposure becomes significant only in foggy conditions. No exposure data are available from the uses of H_2O_2.

The acute toxicity of H_2O_2 to aquatic organisms is low. Effects have been observed only in certain marine algae below 1mg/l. Concentrations below 200mg/l affect freshwater algae, microcrustaceans, snails, bacteria, some fish species and certain aquatic plants, whilst aquatic insects, vegetative growth,

seed germination and early seed growth of terrestrial plants are not affected. The H_2O_2 present in cloud water and fog may be harmful to spruce and beech trees.

H_2O_2 is produced during normal aerobic cell metabolism, it involves a number of enzymatic reactions, especially superoxide dismutase. H_2O_2 is decomposed to oxygen and water by enzymes such as catalase, peroxidase and selenium dependent glutathione peroxidase. The activity of these enzymes varies between tissues and between different animal species or strains. For example, duodenal catalase levels in rats are orders of magnitude greater than those found in mice. In human jejunum, catalase levels were found to be several times higher than in mice. H_2O_2 exposure induces catalase activity in bacteria. This induction is less apparent in tissues of rats and mice. H_2O_2 can also be decomposed by transition metals (e.g. iron, copper) to highly reactive hydroxyl radicals capable of inducing various toxic effects.

After contact with organs and tissues, H_2O_2 undergoes decomposition to water and oxygen. This may lead to small gas embolies and reversible blanching of the exposed tissue area. Larger volumes of gaseous oxygen can lead to detachment of cell layers and the rupture of tissues and organs. The increase in oxygen content in the blood results in a hyperbaric response.

The acute oral toxicity of H_2O_2 in experimental animals varies with the strength of its solution, the lethal dose varying from 75 to 2,000mg/kg body weight. In human beings, death has resulted from the accidental ingestion of unknown quantities of 30-40% solutions. Toxic effects were generally related to the corrosive action on the gastrointestinal tract and the generation of large volumes of oxygen. There was complete recovery within 2-3 weeks even in near fatal cases.

Dermal toxicity is low. H_2O_2 solutions of less than 35% are not classified as irritant to the rabbit skin solutions of 50% and higher are corrosive. Effects on the mucosa of the gingiva and tongue of dogs were found after direct contact with a 1% solution, whilst in human beings mouth washes with up to 3% neutralised H_2O_2 did not cause mucosal irritation. Therapeutical/ clinical use of 1-3% solutions in contact with the intestinal mucosa induced colitis and inflammation.

H_2O_2 solutions of 10% or more cause irreversible damage to the eye, including blindness. Solutions of less than 5% are not classified as irritant to the rabbit eye. The first effects on the rabbit cornea are observed with a 1% solution. In human beings 1-3% solutions have been used for eye treatmen without significant injury. However, solutions containing more than 200ppm cause hyperaemia and down to 100ppm pain and stinging.

Acute exposure to saturated vapour induces only minor clinical signs in rodents. Brief exposure to aerosols at 9,400mg/m^3 H_2O_2 was lethal to mice with effects limited to the respiratory tract and the eyes. After repeated exposure, mortality in mice was observed at 80mg/m^3. In rats and dogs

respiratory irritation and transient skin thickening have been observed at 1-10mg/m^3 after prolonged exposure.

In human beings exposed for 4h the irritation threshold for the respiratory tract was 10mg/m^3 and for the skin 20mg/m^3. At these concentrations eye and throat irritation as well as gradual bleaching of hair have been reported. Under conditions of occupational exposure, when respecting a limit value of 1.4mg/m^3, no adverse effects have been reported.

Exposure to H_2O_2 at concentrations above 1% in drinking water was lethal to mice and rats within weeks. After prolonged exposure, decreased body weight gain was observed in mice with concentrations of 0.4% and in rats with 0.25% and above. In mice, 0.1% induced inflammation of the gastro-intestinal tract. In certain studies, hydropic changes in the liver, haemosiderin deposition in the spleen and epithelial degeneration of kidney tubuli have been reported, but it is unclear whether these changes were treatment-related.

H_2O_2, at concentrations which induce significant inflammation of the exposed tissue, has been shown to be a weak tumour promoter, the tumours being localised in the exposed organs. H_2O_2 itself induced an increase of duodenal tumours in mice exposed to 0.1-0.4% in drinking water. The tumour incidence correlated with a specific inflammatory response in this tissue and was more pronounced in those mice which have a low catalase activity. Rats exposed to near lethal concentrations in their drinking water developed forestomach papilloma but no tumours of the glandular stomach and duodenum. The absence of tumours in these organs correlates well with the high catalase levels found and demonstrates the protective role of this enzyme. Repeated topical application of 15% H_2O_2 to Sencar mice did not induce skin tumours.

In *in vitro* tests without metabolic activation, H_2O_2 induces gene mutations in bacteria sensitive to oxidative stress, in yeast and in mammalian cells. Primary DNA damage was observed in bacteria and mammalian cells. H_2O_2 induced chromosome aberrations and micronuclei in mammalian cells and morphological cell transformations. In general, the addition of exogenous metabolic activation or catalase reduced or abolished the genotoxic response.

Little information is available concerning the *in vivo* genotoxic potential of H_2O_2. No chromosomal aberrations or micronuclei were observed in the bone marrow of rats and mice after oral administration. In contrast, gene mutations in bacteria and chromosomal aberrations in tumour cells were observed in a host-mediated assay with mice. Overall, H_2O_2 has been shown to be genotoxic only to the cells with which it comes in direct contact.

Reproductive toxicity data are limited. Spermatozoa in mice and rabbits were unaffected and male mic
were fertile after treatment with 1-3% H_2O_2 in drinking water. Data on the teratogenic potential of H_2O
are too limited to allow any evaluation.

SECTION 2. IDENTITY, PHYSICAL AND CHEMICAL PROPERTIES, ANALYTICAL METHODS

2.1 IDENTITY

Name:	Hydrogen peroxide (H_2O_2)
IUPAC name:	Hydrogen peroxide
Synonyms:	Hydrogen dioxide Hydrogen superoxide
D	Wasserstoffperoxid
F	Eau oxygenée Peroxyde d'hydrogène
I	Perossido di idrogeno
J	過酸化水素
NL	Waterstofperoxyde
S	Vaeteperoxid
CAS name:	Hydrogen peroxide
CAS registry No.	7722-84-1
EEC No.	008-003-00-9 (<5% not classified)
EINECS No.	231-765-0
MITI No.	GN 1-149 SN 1-334
TSCA inventory:	Listed
Formula:	H_2O_2
Molecular weight:	34.0
Structural formula:	H-O-O-H

2.2 PHYSICAL AND CHEMICAL PROPERTIES

H_2O_2 is normally handled as an aqueous solution, in concentrations ranging from dilute (<5%) to >90% by weight. Commercial grade solutions up to 70% H_2O_2 by weight are generally available; solutions over 70% are produced for specific applications such as the manufacture of organic peroxides and caprolactone; there are also some military applications.

Physical and chemical properties of H_2O_2 solutions are given in Table 1.

H_2O_2 and its aqueous solutions are clear, colourless liquids with a low viscosity and low vapour pressure. The odour is distinctive and mildly pungent. The partial vapour pressure of H_2O_2 increases as its concentration in water increases; the total vapour pressure of a solution is due to both H_2O_2 and water and decreases with the concentration of H_2O_2.

2.2.1 Stability

A pure solution of H_2O_2 is slightly acidic (pH 3.5-4.5). It is relatively stable if stored in the dark in a clean, inert container. At a fixed pH more concentrated solutions appear to be more stable than diluted solutions. The decomposition reaction is strongly exothermic (Delta H = -98.3kJ/mol), and large quantities of oxygen gas are evolved (e.g. one litre 70% solution of H_2O_2 yields about 250 litres oxygen at 0°C and 1,013hPa) (Becewa, 1984). The decomposition of H_2O_2 is generally a catalysed reaction. Common catalysts are dissolved transition metals (e.g. copper, iron, manganese), solid metals (e.g. platinium, osmium or silver), solid metal oxides and hydroxides (e.g. manganese, iron, copper oxides), activated carbon and enzymes (Schumb *et al*, 1955; Goor *et al*, 1989). H_2O_2 is also decomposed by alkaline impurities sufficient to raise the pH to 7 or above. Heat and sunlight can induce photochemical decomposition with the formation of free radicals.

Stabilisers are added to the commercial product to prevent its decomposition into oxygen and water (section 2.3.1). In the gas phase, H_2O_2 at high vapour concentrations (≥26vol.%) may be exploded by an electric spark or by heating to ≥150°C (Schumb *et al*, 1955).

H_2O_2 is miscible with many polar organic solvents, e.g. low molecular weight alcohols, glycols, ketones. Concentrated aqueous H_2O_2 solutions may become explosive with these solvents (Merrifield, 1988).

2.2.2 Chemical Reactivity

H_2O_2 oxidises compounds such as nitrites, cyanides, sulphites and hydrogen sulphide. The oxidising ability of H_2O_2 is greater at low pH. H_2O_2 can also reduce compounds such as hypochlorites, permanganates and cerium salts (Ce^{4+}).

TABLE 1

PHYSICAL AND CHEMICAL PROPERTIES OF H_2O_2 SOLUTIONS

Property	Concentration of H_2O_2 (by weight)					Reference
	10%	45%	50%	70%	90%	
Density at 20°C (kg/m^3)	1.034	1.113	1.195	1.288	1.387	MCA, 1969
Freezing Point (°C)	-6	-33	-52	-40	-11	Schumb *et al.* 1955
Boiling Point (°C)	102	108	114	125	141	MCA, 1969
Flash Point (°C)	Not applicable					
Ignition Point (°C)	Not applicable					
Solubility in Water	Miscible at any ratio					
Viscosity at 20°C (10^3kg/m.s)	1.01	1.11	1.17	1.24	1.26	MCA, 1969
Surface tension at 20°C (N/m)	0.073 1	0.074 6	0.075 7	0.077 3	0.079 2	Schumb *et al*, 1955
Vapour Pressure (Pa)						
Total (H_2O_2+H_2O) at 20°C	-	1.700	1.300	800	-	Atochem 1989a-e, 1990
Total (H_2O_2 + H2o) at 22°C	-	-	1.486	873	375	Solvay, 1991
Partial (H_2O_2) at 20°C	-	-	46	98	178	Solvay, 1991
Vapour pressure at 30°C (Pa).						
Total (H_2O_2+H_2O)	-	3.070	2.400	1.470	667	MCA, 1969
Partial (H_2O_2)	-	48	99	200	333	MCA, 1969
Vapour saturation in air at 25°C (mg/m^3)	-	-	787	1.685	3.049	Solvay, 1991
Henry's Law Constant at 20°C (Pa.m^3/mol)	-	-	$1x10^{-3}$	-	-	Hwang and Dasgupta, 1985

H_2O_2 oxidises organic compounds such as alcohols, olefins and amines and also forms organic peroxides (Schirmann and Delavarenne, 1979).

2.3 ADDITIVES AND IMPURITIES

Commercial H_2O_2 solutions normally contain added stabilisers and some impurities from production process.

2.3.1 Stabilisers

Common stabilisers are phosphoric or other mineral acids (to keep the product acidic), sodium pyrophosphate (a complexing agent to inhibit metal-catalysed decomposition), sodium stannate (a colloid-forming inhibitor) and organic stabilisers such as 8-hydroxyquinoline, pyridine carboxylic acids, tartaric acid and benzoic acids (mainly complexing agents and radical inhibitors) (Schumb *et al*, 1955). Stabilised H_2O_2 solutions normally lose <2%/y of their H_2O_2 content, when stored at ambient temperature.

Nitrate salts can be added as passivators to improve the chemical resistance of stainless steel and aluminium against H_2O_2.

2.3.2 Impurities

Commercial H_2O_2 solutions contain 0.005-0.10% organic impurities (total organic carbon). These impurities are aromatic hydrocarbons and other organic compounds used during purification of the crude product (section 3).

The amounts of inorganic impurities are low; the total concentration does not normally exceed 10ppm (total) with total heavy metals usually <2ppm.

2.3.3 Grades of Hydrogen Peroxide

In technical and chemical grades, the total stabilisers and impurities (total non-volatile compounds) range from of 0.01-0.25%; chemical grades having the lower and technical grades the higher levels.

"Food Grade" H_2O_2 (30-50%) meets the US Food Chemical Codex requirements and contains ≤0.006% non-volatile compounds (FCC, 1981). "Electronic Grade" H_2O_2 (30%) is extremely pure. Typically, the total concentration of non-volatile impurities is 0.001% (L'Air Liquide, 1990a). "Cosmetic Grade" H_2O_2 (35, 50 and 70%) contains more stabilisers (≤0.5%) added by individual customers. This is because the product is diluted with water before use in cosmetics, e.g. to a 12% solution in hair care products, 4% in skin care and 2% for nail hardening. In general, the cosmetic user industry complies with the European Specification for 3% and 30% H_2O_2 (Pharmacopée Européenne, 1985; COLIPA, 1991).

2.4 CONVERSION FACTORS

Conversion factors at 20°C and 1,013hPa:

1ppm = 1.414mg/m^3
1mg/m^3 = 0.707ppm

2.5 ANALYTICAL METHODS

2.5.1 Product Analysis

Titration with permanganate (ISO, 1984) is normally used during the production of H_2O_2. Density measurement is an alternative method. Aqueous solutions which contain components in addition to H_2O_2, such as bleaching liquids and waste water, are analysed preferably by an iodometric method (Kolthoff *et al*, 1969).

2.5.2 Environmental Media

Sakugawa *et al* (1990) reviewed a large number of studies of the H_2O_2 content of air and rain/cloud water and stated that the different analytical procedures used to measure atmospheric concentrations gave different results. Further improvements in H_2O_2 sampling and analysis would be needed. Sampling presents a special problem at low concentrations in air. Thus, Lee *et al* (1991) found that for low atmospheric levels (2ppb) as much as 90% of the gaseous H_2O_2 could be lost by surface reactions at the inlet of the sampling line.

Examples of methods for the determination of H_2O_2 in air are summarised in Table 2. In ambient air, a sensitive, direct fluorescence method is available (Lazrus *et al*, 1985, 1986). Other methods involve trapping H_2O_2 in wash traps or on filters, followed by analytical determination. The lowest detection limit, using a colorimetric method, is approximately 3ppt (v/v) (Ferm, 1988).

Methods for the determination of H_2O_2 in water are summarised in Table 3. The most sensitive method is used for ground-water (Holm *et al*, 1987).

2.5.3 Biological Media

A summary of methods for the determination of H_2O_2 in biological media including the analysis of plant tissues, animal tissues, blood, food and milk, is given in Table 4.

TABLE 2

ANALYSIS OF AIR

Sample Preparation	Analytical measurement	Limit of detection (ppb)	Reference
Ambient Air			
Collect in impingers containing distilled water; react with luminol using alkaline Cu^{2+} catalyst	Chemilumi-nescence	0.5 (0.7ng/l)	Kok *et al*, 1978b Das *et al*, 1983
Collect in aqueous gas washing traps; react with scopoletin and horseradish peroxidase	Flourescence decay at 365nm and 490nm	At least 70ng/l in trap water	Zika and Saltzman, 1982
Decomposition of H_2O_2 by catalase	Automatic flourometry	0.010-0.100	Lazrus *et al*, 1986
Trap in Ti^{4+} + H_2SO_4 on glass filter	Colourimetry at 475nm	0.003	Ferm, 1988
Workplace Air			
Absorption in water containing $TiCl_4$/HCl	Colourimetry at 415nm	10	Pilz and Johann, 1974
Absorption in acidic potassium titanium oxalate	Colourimetry at 400nm	140-2,800	Interox, 1991

TABLE 3

ANALYSIS OF WATER

Sample preparation	Analytical measurement	Limit of detection (µg/l)	Reference
Surface Water			
Add leuco crystal violet, horseradish peroxidase and acetate buffer	Spectro-photometry at 596nm	50	Draper and Crosby, 1983
Boil, cool, filter and irradiate	Thin-layer chromatography with peroxidase-catalysed leuco crytsal violet spray	50	Draper and Crosby, 1983
Rain and Cload Water			
React with alkaline luminol	Chemilumi-nesence	1	Kok, 1980
Acidify, cool to 5°C	Liberation of O_2, conversion of O_2 to CO_2	A few	Holt and Kumar, 1986
Sea Water			
Unknown	Flourescence decay	≤1	Kieber and Helz, 1986
Ground Water			
Add scopoletin, measure flourescence; add horseradish peroxidase, measure flourescence	Flourescence decay	A few (0.034)	Holm *et al*, 1987
Cooling Water			
Mix with phenolphtalein leuco base	Photometry	Unknown	Zabelin and Karbovnichii, 1983

TABLE 4

ANALYSIS OF BIOLOGICAL MEDIA

Sample preparation	Analytical measurement	Limit of detection (µg/l)	Reference
Plant Tissue			
Transfer frozen sliced tissue into 5% thyrocalcitonin; homogenise; centrifuge; pass over anion exchange resin; add to ammoniacal luminol; add potassium ferri-cyanide	Chemilumines-cence	At least 1ng (corresponding to 0.1-1g fresh tissue)	Warm and Laties, 1982
Animal Cells and Tissue			
Mix tissue homogenates or subcellular fractions with catalase	Spectrophotometry (640-660nm)	Unknown	Sies, 1981
Blood Serum			
Add sodium azide, ascorbate oxidase, catalase and 1,4-piperazine-diethane-sulphonic acid or phosphate buffer	Hydrogen peroxide-selective electrode with oxidase meter	Unknown	Nakane and Kosaka, 1980
Plasma			
Blood centrifuged, deproteinated	HPLC and spectrometry	Unknown	Nahum *et al*, 1989
Food			
Extract with 0.5% $KBrO_3$ at pH 7.0	O_2 release by catalase, oxygen electrode	0.01mg/l (liquid) 0.1mg/kg (solid)	Toyoda *et al*, 1982
Milk			
Treat with trichloro-acetic acid; filter	Colourimetry ($TiCl_4$/HCl) 415nm	2mg/l 0.4mg/l	Matz and Dietze, 1971 Gupta *et al*, 1977

SECTION 3. PRODUCTION, STORAGE, HANDLING, TRANSPORT AND USE

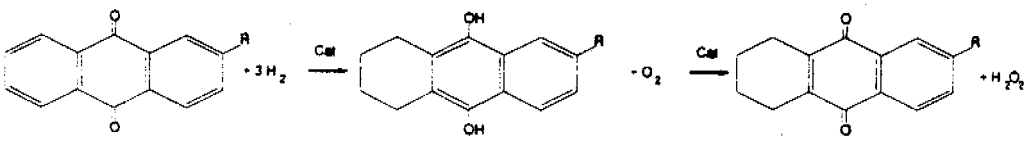
3.1 PRODUCTION METHODS

3.1.1 Anthraquinone Autoxidation

The predominant industrial method of H_2O_2 manufacture is by anthraquinone autoxidation involving two main steps (SRI, 1988; Goor *et al*, 1989; Figure 1). The first step is catalytic hydrogenation of 2-alkyl-9,10-anthraquinone or other anthraquinone derivatives to corresponding anthrahydroquinones using a palladium or nickel catalyst and separation of the solid catalyst from the "working solution". The second main step is oxidation of anthrahydroquinones by bubbling air or oxygen through the solution, when the anthrahydroquinones are oxidised back to anthraquinones and H_2O_2 is formed. The crude H_2O_2 is extracted with water from the organic solution which is returned to the first hydrogenation step producing a cyclic process.

FIGURE 1

ANTHRAQUINONE AUTOXIDATION METHOD (Goor *et al*, 1989)



R = alkyl -

The extracted crude aqueous solution contains about 20-40% H_2O_2 and is normally purified in two or three stages by extraction with organic solvents, such as xylene and/or methyl cyclohexanol acetate (Goor *et al*, 1989). An optional treatment with activated carbon or absorbent resin can be applied to reduce the organic carbon content. Finally, the aqueous solution is distilled to give 50-70% H_2O_2 solutions.

3.1.2 Other Production Methods

Small quantities are produced by older methods using electrolysis of aqueous ammonium sulphate or sulphuric acid solution in water (Goor *et al*, 1989). An organic process based on 2-propanol is in use in the Soviet Union (Goor *et al*, 1989).

3.2 HANDLING, STORAGE AND TRANSPORT

To prevent the decomposition of H_2O_2 solutions, measures are taken to avoid contamination during storage and transport. Tanks of aluminium (≥99.5%) or stainless steel (AISI 316L or 304L) are used for the bulk storage of ≤70% H_2O_2 solution. Before use the metal surfaces must be cleaned and passivated (the metal oxide layer on the surface improved). High density polyethylene tanks are also used for ≤60% H_2O_2. Aluminium (min 99.5%) or stainless steel is mainly used for concentrations >70%. Smaller quantities (concentration ≤60%) are mainly stored in drums or bottles of high density polyethylene.

Storage vessels are vented to the atmosphere in order to avoid pressure build-up resulting from decomposition.

Regulations for rail, road and sea transport are in force for the transport and packaging of >8% H_2O_2 solutions (Table 5).

TABLE 5

CLASSIFICATIONS FOR TRANSPORT AND PACKAGING

Regulation	Concentration (wt %)		
	8-20	20-60	>60
RID/ADR	8, No. 62c	8, No. 62b	5.1, No. 1
IMDG code (sea)	5.1	5.1	5.1
DOT (rail, road, sea)	Corrosive	Corrosive + oxidiser	Corrosive + oxidiser
UN No.	2984 pack. group III	2014 pack. group II	2015 pack. group I

RID European Rules for International transport of Dangerous goods (by rail).

ADR Agreement concerning international carriage of Dangerous goods by Road (class 8, Corrosive; class 5.1, Oxidising). Classes marked with an * have been reclassified to class 5.1, No. 1c and 1b respectively (effective in Europe on 1/1/1993).

IMDG International Maritime Dangerous Goods, vol III (1989).

DOT US Department of Transportation (<8% not regulated).

3.3 USES

3.3.1 Quantities Used and Produced

The estimated world consumption of H_2O_2 in 1989 was 1,023kt/y, distributed between Europe 49%, North America 23%, South America 5%, Asia 20% and Africa/Middle East 3% (Interox, 1990).

H_2O_2 is produced at approximately 40 production sites world-wide, each site having a production capacity in the range of 2-90kt/y (100% basis). In Western Europe, there are about 20 production sites.

3.3.2 Usage

There are three main uses [percent total world consumption in 1987 (ECN, 1988)]:

Production of chemicals (39%). Chemical or technical grade 35-70% H_2O_2 is used for the production of chemicals such as detergent raw materials (sodium perborate and sodium percarbonate), epoxidised soybean oil (stabiliser for PVC), cathecol and hydroquinone, hydrazine, organic peroxides (hardeners and initiators for the polymer industry), peracetic acid (a disinfectant and oxidising agent), caprolactone (a polyester raw material) and fatty amine oxides (detergent chemicals).

Bleaching of cellulose pulp (29%). Technical grade 50-70% H_2O_2 is used for bleaching mechanical pulp, chemi-thermo-mechanical pulp (CTMP) and chemical (kraft and sulphite) pulp and for de-inking waste paper. This use is expected to continue to increase.

Bleaching of textiles (19%). Technical grade 35-70% H_2O_2 is used for the bleaching of textile and cotton.

The remaining 13% of the world consumption is used for applications such as environmental control (waste water, waste gas and ground water treatment), metal etching (printed circuit boards), mining (gold ore leaching) and semiconductor chips manufacturing (cleaning). Most of these applications require a technical grade H_2O_2 (35-70%), except for semiconductor chips for which a special, highly pure electronic grade (30%) has been developed.

A relatively small quantity (≤2%) is used in applications which are particularly relevant to human exposure (section 5.2); namely: disinfectant in aseptic packaging of juice, milk, etc. (food grade), disinfection of drinking water (food grade), bleaching of certain foodstuffs, e.g. tripe, herring (food grade), sanitisation of chemical instruments, disinfectant for eye contact lenses, disinfection of wounds, mouthwashing and hair bleaching (cosmetic grade).

SECTION 4. ENVIRONMENTAL DISTRIBUTION AND TRANSFORMATION

4.1 SOURCES

There are natural, industrial and domestic sources of H_2O_2.

4.1.1 Natural Sources

H_2O_2 is produced naturally in each environmental compartment.

Surface water. H_2O_2 is generally produced in surface water by a photochemical process involving dissolved light-absorbing organic matter and molecular oxygen (Schumb *et al*, 1955; Cooper and Zika, 1983; Zika *et al*, 1985a).

$$Org + h\nu \rightarrow Org^{\cdot} \quad (290\ nm < \lambda < 385\ nm)$$

$$Org^{\cdot} + O_2 \rightarrow Org^{\cdot -} + \cdot O_2^-$$

$$2 \cdot O_2^- + 2H^+ \rightarrow H_2O_2 + O_2$$

A large number of organic compounds such as glycerol, glucose, acetic acid, benzoic acid, aniline, quinone, tryptophan, humic acid and tyrosine can serve as promoters (Draper and Crosby, 1983). In river and lake waters, terrestrial humic promoters are responsible for the photo-sensitisation process, while in sea-water the photo-reactive chromophores have not been identified.

In sea-water, the Weiss mechanism may also be responsible for the production of H_2O_2 due to the oxidation of iron and copper ions (Moffet and Zika, 1987):

$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + \cdot O_2^-$$

$$Fe^{2+} + \cdot O_2^- + 2H^+ \rightarrow Fe^{3+} + H_2O_2$$

Laboratory experiments with deep water (250m) and surface water samples from the Mediterranean showed similar H_2O_2 production rates of between 1-10nmol/l/h after illumination. In deep water no H_2O_2 is found under natural conditions (section 5.1.1) (Johnson *et al*, 1989).

Concentrations in surface water are also influenced by precipitation of rain, snow or fog, which have a relatively high H_2O_2 content (section 5.1.3). The higher concentrations at the surface are attributed to input by precipitation rather than dry deposition of gaseous H_2O_2

(Cooper and Zika, 1983). As an example, in the case of France, with an average precipitation of 630mm/y, containing 10µg/l H_2O_2 (Table 9 -Section 5.1.3.), the annual input of H_2O_2 would be 3,500t/y (Chemoxal, 1992).

Ground water. Ground water samples taken from wells in a shallow sand and gravel aquifer at depth of 11, 15, 21 and 32m were examined. The H_2O_2 concentration was related to the content of dissolved oxygen through the O_2:H_2O_2 redox couple activity, indicating the possibility of a Weiss type oxidation mechanism in the soil (Holm *et al*, 1987).

Atmosphere. The formation of H_2O_2 in ambient air requires the presence of one or more free radical species.

In an unpolluted atmosphere, the formation of H_2O_2 is ultimately due to the photolysis of ozone (O_3) to give oxygen atoms. The latter are converted to free radical species, including ·OH, ·RO, $\cdot HO_2$ and $\cdot RO_2$, which initiate the breakdown of organic species and give rise to $\cdot HO_2$ radicals which are precursors of H_2O_2 (Wayne, 1988):

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \qquad (\lambda \leq 310nm)$$

$$O(^1D) + H_2O \rightarrow 2\cdot OH$$

$$\cdot OH + CH_4 \rightarrow \cdot CH_3 + H_2O$$

$$\cdot CH_3 + O_2 + M \rightarrow \cdot CH_3O_2 + M$$

$$\cdot CH_3O_2 + NO \rightarrow \cdot CH_3O + NO_2$$

$$\cdot CH_3O + O_2 \rightarrow HCHO + \cdot HO_2$$

$$\cdot HO_2 + \cdot HO_2 \rightarrow H_2O_2 + O_2$$

($k=3.1 \times 10^{-12} cm^3 molecule^{-1} s^{-1}$; Jacob *et al*, 1987)

In polluted air, the most important source of free radicals, especially $\cdot HO_2$, is by photolysis of aldehydes, mainly formaldehyde (Calvert and Stockwell, 1983).

$$HCHO + h\nu \rightarrow \cdot H + \cdot HCO \qquad (\lambda \leq 370nm)$$

$$\cdot HCO + O_2 \rightarrow CO + \cdot HO_2$$

$$\cdot H + O_2 + M \rightarrow \cdot HO_2 + M \quad (M \text{ is a molecule acting as a catalyst})$$

$$2\cdot HO_2 \rightarrow H_2O_2 + O_2$$

The reaction of ·OH and ozone with olefins such as isoprene and terpenes, emitted by trees can result in the formation of H_2O_2. Measurements of gaseous H_2O_2 in a conifer forest showed considerably higher concentrations within the forest than outside.

Levels of H_2O_2 were raised by 70% when the air temperature increased from 10-30°C with other meteorological factors and air pollutant concentrations remaining constant (Sakugawa *et al*, 1990).

High solar radiation intensity enhances peroxide production, which is consequently higher during the day than at night, higher in summer than in winter and higher at low latitudes than at high latitudes. Because the rate of H_2O_2 production from $\cdot HO_2$ is second order and the generation of ozone is only first order, larger amounts of H_2O_2 will be generated photochemically, especially with high solar UV irradiation. Unlike ozone, photolysis of H_2O_2 is slow and of minor importance. As a consequence, the evolution and concentration profiles of ozone and H_2O_2 are not parallel and the compounds have different tropospheric half-lives: 10-20h (Kleinman, 1986) for H_2O_2 and 10-100d for ozone (Liu *et al*, 1987) have been reported.

Thompson *et al* (1989) suggested that a 10% decrease in stratospheric ozone content would result in a >100% increase of H_2O_2 in the troposphere.

Water vapour is involved in another process of H_2O_2 formation, namely, the production of hydrated hydroperoxyl radicals ($HO_2 \cdot H_2O$), which rapidly react with $\cdot HO_2$ radicals to generate H_2O_2. About twice as much H_2O_2 is formed at 100% relative humidity than at 50% humidity (ambient temperature 25°C) (Calvert and Stockwell, 1983).

H_2O_2 accumulates in the atmosphere during extended dry periods (Jacob and Klockow, 1987). High concentrations of volatile organic compounds (VOC) in the atmosphere aid H_2O_2 generation, because of greater photochemical production of free radical species.

In an unpolluted atmosphere, about 70% of ·OH radicals react with CO and 30% with CH_4 to form ·H radicals, and yield H_2O_2.

$$\cdot OH + CO \rightarrow \cdot H + CO_2$$

$$\cdot H + O_2 + M \rightarrow \cdot HO_2 + M \quad \text{(M is a molecule acting as a catalyst)}$$

$$2 \cdot HO_2 \rightarrow H_2O_2 + O_2$$

The reaction with methane (CH_4) has been given above (Jacob *et al*, 1987).

A doubling of the emission rate of CO or CH_4 caused the concentration of H_2O_2 to increase by 30% (for CO), or 15% (for CH_4), in an unpolluted continental mid-latitude atmosphere (Thompson *et al*, 1989).

H_2O_2 formation may be inhibited in various ways, particularly by SO_2 and NO_x which are scavengers for H_2O_2.

A high concentration of NO_x inhibits H_2O_2 formation by scavenging $\cdot HO_2$ and its free radical precusors from the air.

$$NO + \cdot HO_2 \rightarrow \cdot OH + NO_2$$

H_2O_2 levels were inversely related to NO levels in polluted air. The production rate of H_2O_2 was extremely sensitive to the reaction of NO_2 with the $\cdot OH$ radical, because this removes both NO_x and $\cdot OH$ radicals from the pool of photochemical reactants. NO levels were relatively low in marine air, giving enhanced H_2O_2 production compared to continental air. It should also be noted that the concentration ratio of VOC/NO_x together with their absolute concentrations, influences the formation of H_2O_2 (Stockwell, 1986).

Living organisms. H_2O_2 is produced naturally by many living organisms (Section 7), either by the organism itself or by its surrounding medium. Examples of organisms capable of producing H_2O_2 are blue-green algae under light irradiation, at a rate of 1-50µg H_2O_2/l/h (Zepp *et al*, 1987); for *Nostoc muscorum* the rate was 0.9nM/µl cells (Stevens *et al*, 1973). *Hymenomonas carterae* (phytoplankton) formed H_2O_2 at 0.034-0.068µg/l/h (Johnson *et al*, 1989). The bombardier beetle (*Brachinus crepitans* (L.)) has been shown to produce H_2O_2 in solution at concentrations up to 28.5% (Schildknecht and Holubek, 1961). H_2O_2 has been detected in human exhaled breath at relatively high concentrations (300-1,000µg/m^3) (Williams *et al*, 1982).

H_2O_2 may also be formed in the medium surrounding an organism where certain metabolites from the organism act as promoters, e.g. riboflavin, excreted by a number of marine organisms. Laboratory experiments showed a H_2O_2 production of 0.34µg/l for every 1nM/l of riboflavin added to seawater (Moffet and Zika, 1987).

4.1.2 Industrial Sources

Plants manufacturing or using H_2O_2. Total losses of H_2O_2 during production are estimated to be 0.3%, the main release being in works waste water where the concentration can be 200mg/l. Following biological or Fenton based treatment, the maximum concentration in the final effluent is normallly in the range of 0-50mg/l or 0-30mg/l respectively for a plant using

H_2O_2 (Chemoxal, 1992) and 0-10mg/l for a manufacturing plant (Interox, 1990). The emission of H_2O_2 to the atmosphere from manufacturing plants is limited by its high Henry's Law constant and because it is processed in closed systems. In all, it is estimated that 0.1% of the produced quantity of H_2O_2 is released to the (aquatic) environment.

In the pulp industry, the amount of H_2O_2 lost to waste water is 2-10kg/t pulp for plants using mechanical processes, 0-2kg/t pulp for chemical processing plants and <1kg/t pulp from de-inking. H_2O_2 could not be detected in the effluent leaving these plants because of its rapid decomposition (Eka Nobel, 1990).

Nuclear power plant cooling water contains traces of H_2O_2 formed by radiochemical processes (Giguère, 1975; IARC, 1985).

Sterilisation of drinking water and food packaging. A potential source of H_2O_2 is from drinking water which has been treated with ozone and UV radiation. The authorised residual concentration of H_2O_2 in potable water is 0.1mg/l in the USSR (Antonova, 1974) and Germany (Bundesminister, 1990) and 0.5mg/l in France (Ministère de la Solidarité, de la Santé et de la Protection Sociale, 1990).

4.1.3 Domestic Sources

The domestic release of H_2O_2 is mainly from the use of sodium perborate (tetrahydrate and monohydrate) and sodium carbonate peroxyhydrate for laundering. The H_2O_2 concentration in the outlet of a washing machine ranges from 0-5mg/l, assuming that 4kg clothing, 80l water and 120g washing powder containing 15% tetrahydrate perborate (with 10% unreacted H_2O_2) are used in the whole washing cycle. In the case of France, with a perborate consumption of 80,000t/y, the amount of H_2O_2 released would be 1,700t/y (Chemoxal, 1992). The decomposition resulting from the mixing of washing effluents with other domestic waste water greatly reduces the H_2O_2 concentration in the inflow to municipal sewage treatment works.

4.1.4 Evaluation

H_2O_2 occurs naturally as a result of photochemical processes involving free radicals, organic matter and molecular oxygen.

H_2O_2 production in fresh and marine water depends upon the intensity of daylight and the concentration of promoters and dissolved oxygen. In the absence of light, H_2O_2 may be formed through the oxidation of iron and copper. Its concentration in soil depends on the presence of these metals and the dissolved oxygen content.

H_2O_2 concentrations in the atmosphere vary with temperature, solar radiation, humidity and the presence of precursors (CH_4, CO, volatile organic compounds) and inhibitors (SO_2, NO_x).

H_2O_2 is produced naturally by living organisms.

H_2O_2 emissions to the environment from industrial and domestic sources are limited due to its rapid decomposition in the waste water.

The amount of H_2O_2 deposited by rain-water into surface waters is greater than that from industrial and domestic sources together.

4.2 TRANSFORMATION

4.2.1 Aquatic Fate

H_2O_2 is subject to various reduction or oxidation processes in the environment and decomposes into water and oxygen at rates which depend on contact with catalytic materials and other factors (section 2.2.1). The actual concentration of H_2O_2 in the environment results from a dynamic equilibrium between its production and degradation (Figure 2). As a first approximation, degradation kinetics are generally assumed to be of a first order.

At ambient temperatures and concentrations, the rate of formation and degradation of H_2O_2 in sea-water varies widely, from 0.34-17µg/l/h (Johnson *et al*, 1987). Similar rates, 2-12µg/l/h, were found in freshwater (Cooper and Lean, 1989).

In sea-water, the oxidation of organic substrates by H_2O_2 catalysed by metals, under certain conditions, may be an important factor in the increase its degradation rate.

The catalytic action of iron and copper salts on the degradation of H_2O_2 is unlikely to affect the H_2O_2 content because at the same time it is formed by the oxidation of iron and copper (Weiss Mechanism) (Moffet and Zika, 1987).

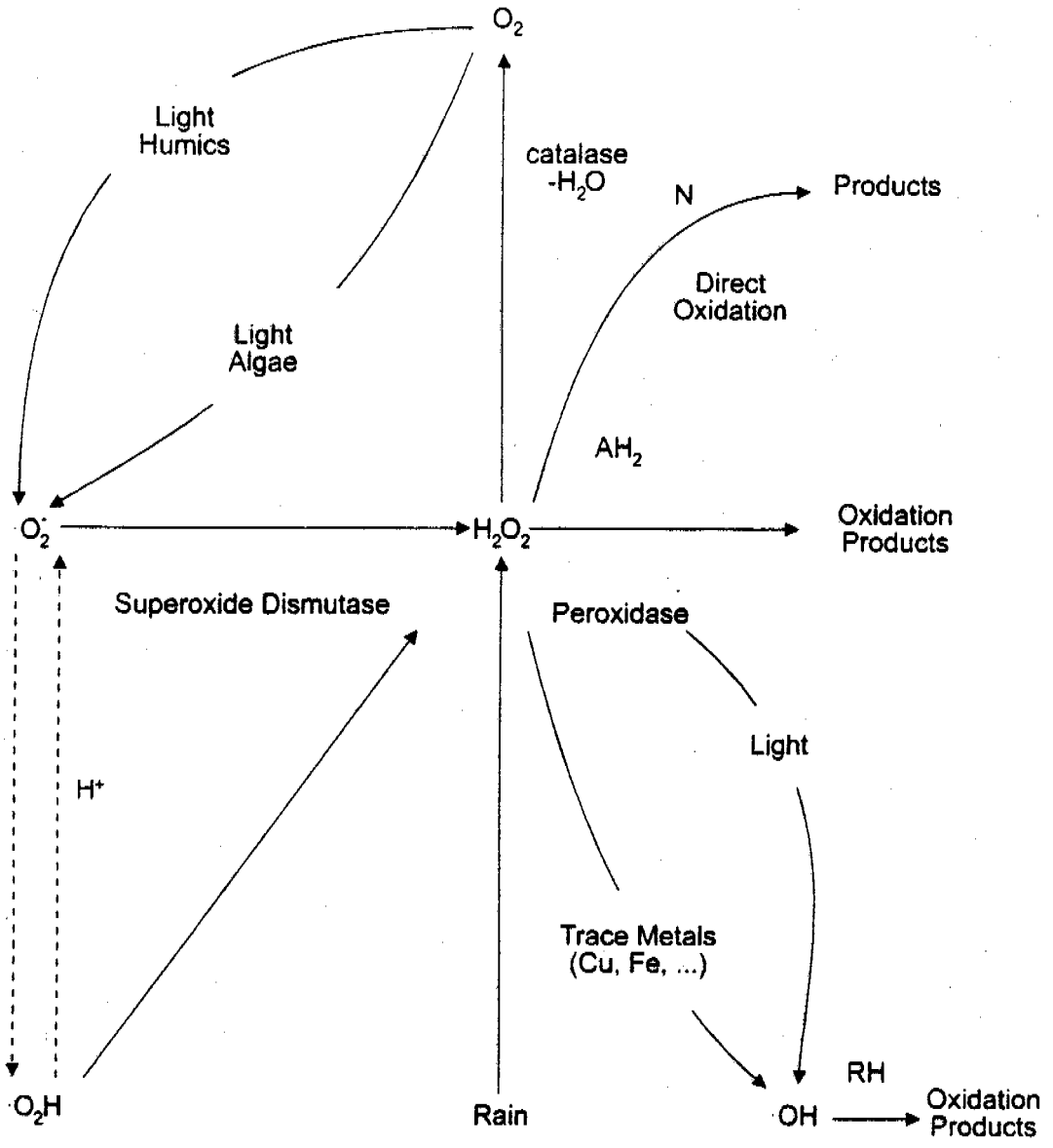
The half-life of H_2O_2 in sea-water samples from the Bay of Biscay (filtered 0.2µm) was 60h (Petasne and Zika, 1987).

The degradation of H_2O_2 in freshwater has been studied in Jacks Lake (Ontario). The half-life of H_2O_2 (initial concentration of 3.4µg/l) was:

7.8h (unfiltered lake water)
8.6h (filtered, 5µm)
31h (filtered, 1µm)
>24h (filtered, 0.45µm).

FIGURE 2

FORMATION AND DECAY IN AQUATIC ENVIRONMENTS (Zepp *et al*, 1987)



N Nucleophile that reacts with H_2O_2;

AH_2 Substrate capable of oxidation by peroxidases (horseradish peroxidase) and H_2O_2, e.g. phenols, anilines;

RH Organic chemical

These results indicate that the fraction containing picoplankton (defined as 0.2-2µm) contains the major proportion of the biological agent responsible for the degradation of H_2O_2. The fraction <1µm contained roughly 90% of the bacterial and <5% of the phytoplankton biomass (Cooper and Lean, 1989).

Laboratory studies on water from the River Saône showed that H_2O_2 degradation kinetics were of a first order and that half-lives were dependent on the initial H_2O_2 concentrations (Table 6). Filtering out particles over 0.2µm had little effect. Similar studies with de-ionised water containing 500mg/l H_2O_2 showed an increase in concentration, probably due to the influence of daylight. The decay of H_2O_2 appeared to be slower at initial concentrations <500mg/l (L'Air Liquide, 1991).

The half-life of H_2O_2 decreases with increasing size of the microbial population in water (Table 7).

TABLE 6
DEGRADATION IN THE RIVER SAÔNE
(L'Air Liquide, 1991)

Initial concentration (mg/l)	$t_{½}$ (days)	
10,000	2.5	
1,000	8.1	
500	8.2	±2*
250	15.2	±2.5*
100	20.1	

* Higher values for filtered samples

TABLE 7
DEGRADATION AND SIZE OF MICROBIAL POPULATION
(Degussa, 1991)

	Fresh Water	Process Water	Waste Water	Sludge
Cells/ml	$\leq 10^3$	$\leq 10^6$	$>10^6$	10^8-10^{10}
$t_{½}$	h-d	h-d	min-few h	few s

Catalase is a powerful decomposing agent: when 5µg of a 1µg/ml solution of catalase was added to 20ml of sun-lit water from the Patuxent River (saline, estuarine water), the degradation rate of H_2O_2 was sharply increased and the half-life reduced from >24h to 20min; in freshwater (River Paint Branch) without photolysis but with catalase, the half-life was 5min (Kieber and Helz, 1986). Similar results have been obtained in waste waters containing catalase, where H_2O_2 half-lives of 0.3-9min were measured (Barenschee, 1990).

Algae can photoproduce and decompose H_2O_2 (Zepp *et al*, 1987). For example, H_2O_2 in the dark was decomposed in the supernatant of an algal culture, the rate of decay being first order:

$$-\frac{d[H_2O_2]}{dt} = k_{bio}\, C_a\, [H_2O_2]$$

where C_a is the concentration of chlorophyl-*a* (Chl-*a*) and the median values of k_{bio} is $4.4 \times 10^{-3} m^3/mg$ Chl-*a*/h. Assuming that C_a is $100 mg/m^3$, the half-life of H_2O_2 in an euphotic zone of a eutrophic lake in the dark is estimated to be about 1.5h.

After exposure of a eutrophic water sample to sunlight for 3h, H_2O_2 concentrations (50-250µg/l) reached a plateau, indicating a steady state. In the dark, the half-life of H_2O_2 was measured as 1h with approximately first order kinetics (Draper and Crosby, 1983).

Ground-water. The half-life of H_2O_2 in ground-water, taken from wells in a shallow sand and gravel aquifer at 11-32m below ground level was <1h (Holm *et al*, 1987).

4.2.2 Atmospheric Fate

The tropospheric half-life of H_2O_2 is normally 10-20h (section 4.1.1). The reaction of H_2O_2 with ·OH radicals in the gas phase and subsequent photolysis are thought to be major degradation pathways in air (Sakugawa *et al*, 1990).

Photolysis. Photolysis of H_2O_2 leads to the formation of ·OH radicals. The photodecomposition of H_2O_2 in air occurs within a light spectrum of 380nm >λ >280nm. The extinction coefficient is independent of H_2O_2 concentration in air. The rate of decomposition for moderate light intensities (<1,017quanta/ls) is directly proportional to the concentration of H_2O_2 and to the square root of light intensity. The mechanism may be summarised (Schumb *et al*, 1955) as:

$$2H_2O_2 + h\nu \rightarrow H_2O + \cdot OH + \cdot HO_2$$

The ·OH radical is a scavenger for $\cdot HO_2$ according to:

$$\cdot OH + \cdot HO_2 \rightarrow H_2O + O_2$$

Reactions.. Formation of organic hydroperoxides (R-OOH) appears to be a pathway for the decomposition of H_2O_2 in the atmosphere. They are formed by ·OH-induced oxidation of hydrocarbons or by direct oxidation of aldehydes by H_2O_2 under acidic conditions (e.g. in clouds).

$$\text{aldehydes} + H_2O_2 \xrightarrow{\textit{acidic}} \text{hydroxyalkyl hyproperoxides}$$

Conversely, hydroperoxides can also produce H_2O_2 (section 4.1.1). The hydroperoxide content is 1-10% of the atmospheric H_2O_2 concentration (Hellpointner and Gaeb, 1989).

In clouds and aerosols the fate of H_2O_2 as an oxidising agent depends strongly on the pH of atmospheric water (Heikes, 1987). Measurements in cloud water made at the top of Whiteface Mountain (USA) showed that the degradation rate of H_2O_2 was 5.8%/h at a pH of 5.3-5.9 (Lazrus *et al*, 1985). Under more acidic conditions (pH <4.5) H_2O_2 may act as a replacement for ozone and oxidises sulphite to sulphate in the liquid phase; the oxidation rate of S^{4+} can be 100%/h. In humid air, the atmospheric level of sulphur dioxide varies inversely with the level of H_2O_2, especially during haze and fog, suggesting that H_2O_2 also contributes to the oxidation of sulphur dioxide. The rate of oxidation (a few percent of S^{4+}/h) in the gaseous phase is slower than in the liquid phase (Sagukawa *et al*, 1990).

A marked depletion of H_2O_2 has been shown to occur inside a cloud, both in the vapour and the liquid phase. For example, gaseous H_2O_2 concentrations were 0.4-0.5ppb inside a cloud and 1-1.25ppb outside, with SO_2 concentrations of 2-3ppb (Heikes *et al*, 1987). In a cloud, liquid phase H_2O_2 concentrations were 2-4 times lower than those resulting from the equilibrium with gaseous concentrations according to Henry's Law. The reactions are thought to be controlled by mixing of H_2O_2 from above the cloud with SO_2 from below (Barth *et al*, 1989).

Under strongly acidic conditions (pH <2), airborne H_2O_2 oxidised nitrite (HNO_2) to nitrate (HNO_3), which is also a substantial component of acid precipitation. At pH 2 and a H_2O_2 level of about 1ppb, 1% of the total amount of nitrous acid (gas and liquid) was converted within one hour; 1,5% was converted at pH 1 (Damschen and Martin, 1983). The reaction is:

$$HNO_2 + H_2O_2 \rightarrow HOONO + H_2O$$

$$HOONO \rightarrow H^- + NO_3^-$$

In conclusion, H_2O_2 plays a role in the generation of sulphate and, to a lesser extent, of nitrate in the atmosphere, either in clouds and aerosols or in dry air. Some researchers claim that ≥40% of sulphate acidity of precipitation derives from the reaction of sulphur dioxide with H_2O_2.

Deposition. Airborne H_2O_2 shows a strong tendency to dissolve in the aqueous phase. Henry's Law constant is $H = 10^{-3}Pa.m^3/mol$ at 20°C. This is valid for H_2O_2 concentrations of 5.1-5,100mg/l (Hwang and Dasgupta, 1985). On the other hand, evaporating clouds can release considerable amounts of gaseous H_2O_2, a phenomenon which occurs even at night. The appearance of clouds lowers the gas-phase H_2O_2 mixing ratio. During wet deposition, H_2O_2 is efficiently removed from the atmosphere.

The above-mentioned reactions have been summarised in a one dimensional model, in which altitude is the only dimension (Thompson *et al*, 1988):

$$[H_2O_2] = \frac{k[\cdot HO_2]^2}{J\text{-}H_2O_2 + k[\cdot OH] + RO}$$

where $J\text{-}H_2O_2$, $k[\cdot OH]$, and RO are first order coefficients for H_2O_2 photolysis, reactions with the hydroxyl radical and rain-out phenomena respectively.

Tropospheric H_2O_2 concentrations vary by two orders of magnitude, depending on the geographical latitude (intensity and duration of light irradiation), altitude (intensity of UV radiation), water vapour content and the presence of precursors (CH_4, CO, VOC) and inhibitors (NO_x, SO_2). Deposition by rain-out and transport by wind naturally influence local H_2O_2 concentrations.

4.2.3 Fate in Soil

The fate of H_2O_2 in soil is determined by the following decomposition reaction:

$$H_2O_2 \xrightarrow{k_1} H_2O + \tfrac{1}{2}O_2$$

The rate of decomposition of H_2O_2 injected into, or spilled on soil depends on the microbiological flora and mineral composition of that soil.

Half-lives of H_2O_2 in soil have been shown to vary from 15h in soils without microbiological activity and few minerals, to several minutes in soils with 10^8-10^9cells/g total solids and in the presence of iron and manganese (Barenschee, 1990).

Studies have been made of the clean-up of polluted soils by enhancing the oxidation processes using H_2O_2 as a source of oxygen by injection into the infiltration water. When a 30% solution of H_2O_2 was added to recirculated soil water, the half-life was only 25 minutes (Spain *et al*, 1989).

A k_1 in the range of 0.1-0.01/min is expected for decomposition rates of H_2O_2 concentrations of about 300mg/l in ground-water (Hinchee and Downey, 1988). The half-life of H_2O_2 varied from 7-70min (Barenschee, 1990).

When k_1 is <0.01/min, only 1.3% of the available oxygen is used for microbial respiration. Thus, more than 98% of the oxygen produced by decomposition is present in the form of bubbles which escape to the surface either directly or dissolved in percolation water.

4.2.4 Bioaccumulation

H_2O_2 is decomposed by enzymatic action (section 7) and does not accumulate in cell systems.

4.2.5 Effects on Biological Treatment Plants

At concentrations ≤200mg/l in waste water, H_2O_2 does not affect the performance of biological treatment works (activated sludge process) (Solyom, 1973). It is partly degraded and has even been shown to stimulate biodegradation in waste water treatment works (activated sludge process) (Interox, 1990). At higher concentrations (>200mg/l) H_2O_2 becomes toxic to micro-organisms (section 6).

4.2.6 Evaluation

H_2O_2 formed in the atmosphere tends to condense and is removed by wet deposition. Reactions with hydroxy radicals and subsequent photolysis give a troposphere life of 10-20h.

Decomposition in water and soil takes minutes to several hours, depending on the mineral content and the concentrations of micro-organisms.

SECTION 5. ENVIRONMENTAL LEVELS AND HUMAN EXPOSURE

5.1 ENVIRONMENTAL LEVELS

5.1.1 Natural Waters

Sea-water. H_2O_2 has been detected in sea-water at concentrations ranging from 0.14-58µg/l (Table 8). The concentration of H_2O_2 is determined by several factors (section 4.1.1).

TABLE 8

LEVELS IN NATURAL WATERS

Location	Concentration (µg/l)	Reference
Sea Water		
Western Mediterranean Sea	> 3.4	Johnson *et al*, 1989
Gulf of Mexico	3.4 - 9.5	Zika *et al*, 1985a
Gulf of Peru	0.27 - 0.17	Zika *et al*,1985b
Chesapeake Bay	1.0 - 58	Helz and Kieber, 1985
	1.8 - 2.9	Kieber and Helz, 1986
Texan coastal waters	0.5 - 5.8	Van Baalen and Marler, 1966
North Atlantic	0.14 - 5.1	Zika, 1978*
Biscayne Bay/Florida	2.7 - 7.1	Zika, 1980*
Bahama bank	1.7 - 6.5	Zika, 1980*
Fresh Water		
Lakes Ontario, Erie, Jacks	0.34 - 27.2	Cooper and Lean, 1989 Cooper *et al*, 1989
Patuxent River	1.0 - 16	Kieber and Helz, 1986
Volga River	44.0 - 109	Sinel'nikov, 1971*
reservoir, Russia	24 - 44	Sinel'nikov, 1971*

* Quoted in Cooper *et al*, 1988

Spatial and temporal variations of H_2O_2 are principally due to changes in its photochemical production. For example, the concentration level dropped from 9.9µg/l at the surface to 1.1µg/l at 30m depth at a coastal station and from 5µg/l to 0.3µg/l at 100m depth at an ocean station. Variation of H_2O_2 concentrations occurred throughout the day, with mid to late afternoon maxima (9.9µg/l at 6p.m.) and pre-dawn minima (6.2µg/l at 6a.m.) at a coastal station. In oligotrophic open oceanic waters, photochemical generation still occurred at a depth of 75m, where the H_2O_2 concentration was 1.7µg/l; vertical mixing probably contributed to this. In coastal waters, where light attenuation is relatively greater, the rate of

photochemical formation of H_2O_2 decreases sharply with depth, resulting in concentrations dropping from 8.5-9.9µg/l at the surface to 0.7-1.1µg/l at 30m. The lifetime of H_2O_2 in coastal waters was relatively short, probably due to higher concentrations of transition metals and organic compounds. Thus, diel variations are more pronounced in coastal surface waters than in oligotrophic waters (Zika *et al*, 1985a).

Similar profiles and diel cycles have been observed in the western Mediterranean (Johnson *et al*, 1989). In waters off the coast of Peru, depth profiles and diel cycles were less pronounced and H_2O_2 levels did not increase nearer to the coast as in the Gulf of Mexico. The authors related this phenomenon to a lack of coastal vegetation (Zika *et al*, 1985b).

Freshwater. Surface levels of H_2O_2 in freshwater ranged from 0.34-109µg/l (Table 8). H_2O_2 concentrations declined with increasing depth (6µg/l at the surface to <0.7µg/l at 20m in lake Erie) and followed attenuation of light intensity. It has been suggested that bacteria and algae may also have had a role. Diel fluctuations in H_2O_2 levels indicate that photochemical processes could be involved in its formation (Cooper *et al*, 1989; Cooper and Lean, 1989).

5.1.2 Sewage - Waste Water

The concentration of H_2O_2 in a sample of raw sewage exposed to sunlight was 85µg/l. When samples from sewage stabilisation ponds were exposed to sunlight, concentrations of 420-1,100µg/l were encountered (Draper and Crosby, 1983).

5.1.3 Atmosphere (Table 9)

It should be noted that the analytical methods reported in the literature need further development (section 2.4).

Ambient air. In rural air, H_2O_2 concentrations ranged from 0.3-3ppb during day-time but could not be detected at night (<0.01ppb) (Das *et al*, 1983). Other results from a variety of locations ranged from 0.02-2.4ppb (Sakugawa and Kaplan, 1987; Slemr *et al*, 1986; Tanner *et al*, 1986; Barth *et al*, 1989). At the summit of Whiteface mountain (NY), Mohnen and Kadlecek (1989) found <2.7 to <6.1ppb H_2O_2. H_2O_2 concentrations were highest in the afternoon (Dollard *et al*, 1988; Possanzini *et al* 1988; Sakugawa and Kaplan, 1989).

Latitude dependency has been found with a concentration increase from north to south of 0.04-0.05ppb per degree of latitude (Van Valin *et al*, 1987). Values ranging from 0.2-3.9ppb in Brazil have been compared with those obtained using similar techniques in West Germany ranging from 0.01-0.6ppb (Jacob *et al*, 1987; Jacob *et al*, 1990). Heikes *et al* (1987) have also noted an increase of H_2O_2 concentration with latitude decrease near the surface layer (0.05ppb/degree of latitude) and above cloud top (0.1ppb/degree of latitude), but with an uniform distribution above 3,000m.

TABLE 9

LEVELS IN THE ATMOSPHERE

Sampling site, time, height	Concentration (ppb)	Reference
Ambient Air		
Rural air, day, ground	0.3-3	Das *et al*, 1983
night, ground	< 0.01	
Canada, Ontario, summer 1984-85, ground	< 0.3-2.1	Slemr *et al*, 1986
Upton, NY, summer-autumn 1985, ground	< 0.1-1.2	Tanner *et al*, 1986
Carolina coast, Jan.-Mar. 1986, cloud	< 0.2-2.4	Barth *et al*, 1989
Whiteface Mountain, NY, (1,500m), summer 1986 (463 samples)	< 2.7 (mean 0.6)	Mohnen and Kadlecek, 1989
summer 1987 (673 samples)	< 6.1 (mean 0.8)	
Southern England, Apr. 1987, ground	< 1.8	Dollard *et al*, 1988
Rome, Italy, Jan.-Mar. 1988, ground	< 0.2	Possanzini *et al*, 1988
Southern California, summer-autumn, 1985, ground	0.03-2.04	Sakugawa and Kaplan, 1987
1985-88, ground	0.02-1.2	Sakugawa and Kaplan, 1989
Dortmund, Germany, Oct. 1984-Jul. 1985, ground	0.03 (mean)	Jacob *et al*, 1987
Brazil, Mar.-Apr. 1988, ground	0.2-3.9	Jacob *et al*, 1990
Eastern USA, autumn 1984, cloud (150-3,700m)	0.2-4.1	Heikes *et al*, 1987
South central USA, Feb. 1987, cloud (1,700-2,600m)	< 0.1-1	Van Valin *et al*, 1987
Central USA, Jun. 1987, ground to 5.5km	< 0.2-7	Daum *et al*, 1990
Northeastern USA, Jun. 1987, ground to 4km	0.6-3.6	Van Valin *et al*, 1990
Summit of Whitetop Mountain, VA, (1,689m), summer 1986	< 0.02-2.6	Olszyna *et al*, 1988
fall 1986	< 0.02-0.57	
Central USA, 1987, (1,450-2,450m)	< 0.3-4.8	Boatman *et al*, 1989
Riverside, CA Hoboken, NJ, summer 1970, ground (smog)	40-180	Bufalini *et al*, 1972
California, south coast, summer 1970, ground (smog)	10-30	Kok *et al*, 1978a

TABLE 9 (continued)

Sampling site, time, height	Concentration (µg/l)	Reference
Rainwater		
Strasbourg, France	2-38	Lagrange and Lagrange, 1990
Dortmund, Germany, 1983-84, summer	25-2,200	Klockow and Jacob, 1986
winter	0-290	
Netherlands, Apr.-Jun. 1986	< 279	Keuken *et al*, 1987
North Sea, summer 1982	17-2,414	Roemer *et al*, 1985
winter 1981	0.34-6.8	
Florida and Bahama Islands, 1981	340-2,380	Zika *et al*, 1982
California, LA basin, 1978-79	1-159.8	Kok, 1980
Gulf of Mexico	390-2,800	Cooper *et al*,1987
Florida	130	
Summit of Whitetop Mountain, VA (1,689m), spring-autumn 1986	< 1.36-1,353	Olszyna *et al*, 1988
Eastern USA, summer 1982-83	3.4-2,142	Kelly *et al*, 1985
Ontario, Canada, Jan.-Feb. 1984	< 17-170	Daum, 1990
Brazil, Mar.-Apr. 1988	578-6,766	Jacob *et al*, 1990
Tokyo, Japan, 1981-82	6.8-1,064	Yoshizumi *et al*, 1984
Cloudwater		
Cumbria, Great Dun Fell, autumn	< 34	Dollard *et al*, 1988
spring	> 34	
North Sea, summer 1982, (150-3,000m)	< 41-3,000	Roemer *et al*, 1985
Eastern US, summer 1982-83, (< 3,000m)	3.4-3,400	Kelly *et al*, 1985
Eastern US, 1982-83, (450-1,500m)	< 2,550	Daum *et al*, 1984
California, LA basin, May 1982	31-2,992	Richards *et al*, 1983
California, LA basin, May-Jun. 1985	408-5,678	Richards, 1989
Carolina coast, US, Jan.-Mar. 1986	10.2-3,808	Barth *et al*, 1989
Summit of Whitetop Mountain, VA, spring-autumn 1986, (1,689m)	< 1.36-8,398 (mean: 880.6)	Olszyna *et al*, 1988

An increase of H_2O_2 concentration with increasing altitude has been observed by several workers (Heikes *et al*, 1987; Van Valin *et al*, 1987; Daum *et al*, 1990; Van Valin *et al*, 1990).

Seasonal differences in H_2O_2 concentration have been studied by Olszyna et al (1988) and Boatman *et al* (1989). The latter observed that the average H_2O_2 concentration varied by a factor of 16 (0.3-4.8ppb) between winter and summer.

Ice cores, drilled in Greenland and West-Antarctica, give an archive of solid precipitation over the past 50,000-100,000 years. H_2O_2 was one of the dominant trace components of the ice, indicating that it was the main trace species in clouds over remote and unpolluted areas. In the Greenland ice cores, the H_2O_2 level decreases from 92 ±76 to <0.5µg/kg ice with increasing depth from 26 to 25,000m and was extremely low during the last glaciation. In Antarctic cores, a H_2O_2 concentration was observed in the ice deposited 6,000-12,000 years ago, decreasing from 17.3 ±1.0µg/kg ice at 650m to 2.8 ±0.24µg/kg ice at 22,000m below the surface. The annual deposition rate of H_2O_2 at Greenland was calculated to be 30 times higher than at Antarctica (Neftel *et al*, 1984, 1986). Seasonal variations can be detected for both recent and ancient times.

H_2O_2 is a significant, active component of photochemical smog. Levels as high as 0.18ppm (0.25 mg/m^3) have been reported in severe smog (Bufalini *et al*, 1972). Concentrations during periods of moderate smog ranged from 10-30ppb (Kok *et al*, 1978a).

Stratosphere. At an altitude of 38.3km, the H_2O_2 level was 0.68 ±0.21ppb, while at 29.3km, the level was about 0.08ppb. Measured increases in H_2O_2 concentration with altitude were in disagreement with profiles obtained by mathematical modelling. The discrepancies were believed to be due to incomplete current knowledge of the stratospheric chemistry of H_2O_2 (Chance and Traub, 1987).

Rain-water and cloud-water. H_2O_2 is present in rain-water and cloud-water at a wide range of concentrations. In rain-water, levels ranged from 0-2,414µg/l in Europe, 1-2,800µg/l in the USA/Canada, 578-6,766µg/l in Brazil and 6.8-1,064µg/l in Japan (Table 9). The concentrations in summer were often much higher than those found in winter (Roemer *et al*, 1985; Klockow and Jacob, 1986). Concentrations in cloud-water in the USA ranged from 3.4-8,398µg/l. Measurements in cloud water 150-3,000m above sea level in background or barely polluted air masses from the North Sea, gave values from <41-3,000µg/l H_2O_2 (Table 9).

5.1.4 Soil

H_2O_2 was found in concentrations of 0.034-2.2µg/l in ground-water taken from wells 11, 15, 21 and 32m deep in a shallow sand and gravel aquifer (Holm *et al*, 1987).

5.2 HUMAN EXPOSURE

5.2.1 Non-Occupational Exposure

Human beings may be exposed to H_2O_2 as a result of its use in non-prescriptive pharmaceuticals (antiseptics, cleaning agents), cosmetics (hair bleaches, dentifrices, deodorants, mouthwashes), food, drinking water and because of its use as a sterilising agent for polymeric food packaging and for juice and wine processing.

Data on the quantity used per capita from preparations containing H_2O_2 are not available. It is generally only permitted for food processing if residual quantities are removed by appropriate physical and chemical means or if the residual level in food directly after aseptic packaging is 0.05% (500ppm) (US FDA, 1990).

Recent studies or other information on human exposure to H_2O_2 via foodstuffs are not available.

It should be noted that endogenous H_2O_2 levels in plant tissues are relatively high. For example, the concentration in tomatoes was 3.1-3.5ppm, in castor beans 4.7ppm and potato tubers 7.6ppm (Warm and Laties, 1982).

In Japan, H_2O_2 has been used as an antiseptic and bleaching agent for food manufacturing for several decades and was designated as a food additive with the enforcement of the Food Sanitation Act (1948). Since 1969, the residue level of H_2O_2 has been limited to 100ppm in noodles, kamaboko (fish sausage) and chikuwa (fish paste cooked in a bamboo-like shape) and 30ppm in other foods. During a survey in 1977-78, H_2O_2 was present in 1% of fish paste products, and in 30-50% of boiled noodles. In another study in 1977, high levels of H_2O_2 (≥30ppm) were found in 32% of boiled wheat-noodles. The intake per capita from these residues was calculated to be 4.3-13.6µg/kg (Koseishyo, 1980a). From October 1980, H_2O_2 should be decomposed or eliminated completely from the final food products (Koseishyo, 1980b).

Evaluation. Exposure of the general population from ambient air is usually <4µg/m^3. However, exhaled air contains 300-1,000µg/m^3 (section 4.1.1). Therefore ambient air is not a significant source of exposure, except in foggy conditions. Total human exposure cannot

be assessed due to a lack of data on foodstuffs, drinking water, non-prescriptive pharmaceuticals and cosmetics.

5.2.2 Occupational Exposure

The national regulations and guidelines on occupational exposure limits for H_2O_2 are listed in Table 10. In general, the time-weighted average concentration over an 8h working day which should not be exceeded is 1ppm (1.414mg/m^3); this level should not be higher than 2-3ppm (2.8-4.2mg/m^3) for any short period of exposure (5-15min).

The maximum concentration from which one could safely escape within 30 minutes without a respirator (or in the event of respirator failure) has been estimated to be 75ppm; this concentration is thought not to cause any impairment or irreversible health effects "immediately dangerous to life and health" (NIOSH, 1990).

The US-National Institute for Occupational Safety and Health estimated that 52,800 US-workers were potentially exposed to H_2O_2 in 18 different industry sectors in 1982 (OSHA, 1989a).

Limited data on work exposure levels are reported in Table 11.

TABLE 10

NATIONAL OCCUPATIONAL EXPOSURE LIMITS

Country, year of enforcement	TWA (8h) concentration (mg/m^3)	Short-term exposure or excursions (mg/m^3)	Ceiling value (mg/m^3)	Legal status	Reference
Australia, 1990	1.4	-	-	R	ILO, 1991
Belgium, 1990	1.4	-	-	R	Cardinaels, 1990
Bulgaria, 1971	-	-	1	R	IARC, 1985
Canada, 1989	1.4	3	-	R	Québec, 1989
Denmark, 1988	1.4	-	-		Arbejdstilsynet, 1988; ILO, 1991
Finland, 1990	1.4	4.2 (15 min)	-	G	ILO, 1991
France, 1988	1.4	-	-	G	INRS, 1987
Germany, 1991	1.4	3 (5 min)	-	G	DFG, 1991
Italy, 1990	1.4	-	-	G	ACGIH, 1991
Netherlands, 1989	1.4	-	-	G	Arbeidsinspectie, 1989
Norway, 1990	1.4	2.8 (15 min)	-	G	Arbeidstilsynet, 1989
Switzerland, 1990	1.4	-	-	R	CNA, 1987; ILO, 1991
UK, 1991	1.4	3 (10 min)	-	R	UK HSE, 1991
USA,					
- OSHA, 1989	1.4	-	-	R	OSHA, 1989b
- ACGIH, 1990-91	1.4	-	-	G	ACGIH, 1986, 1991
USSR, 1977	-	-	2	R	IARC, 1985; INRS, 1990
Yugoslavia, 1971	-	-	1.4	R	IARC, 1985
Sweden, 1991	1.4	3 (15 min)	-	R	AFS, 1990
Thailand	1.4	-	-	Unknown	Hasle, 1987

R, regulatory; G, guideline.

TABLE 11

OCCUPATIONAL EXPOSURE LEVELS

Process, location	Year of measurement	Concentration (mg/m^3)	Reference
Production plant			
general work area	1987	0.85	ECETOC, 1991
	1989	0.07-0.14	
	1989	5.7[a]	
drum filling station (during filling)	1987	2.8	ECETOC, 1991
	1989	2.8	
	1979	0.3	
	1982, 1990	0.3 - 2.0	
storage/shipping tank car loading near storage tank	1983	< 0.01	ECETOC, 1991
	1979	0.3	
	1982	1-2	
pump house (unmanned)	1982	10, 2[b]	ECETOC, 1991
Packaging machine			
coffee cream, during startup	Unknown	< 0.20	Suenaka *et al*, 1984
	Unknown	0.21 - 1.2	
milk	1987	12-42	Kaelin *et al*, 1988
		1.5, 4.5[c]	
fruit juice	1983-1988	0.2-0.66	Tetra Pak, 1991

a Over opened vessel with 70% solution.

b Before and after reparation of leaking seal box.

c Before and after installation of ventilation.

SECTION 6. EFFECTS ON ORGANISMS IN THE ENVIRONMENT

6.1 MICRO-ORGANISMS

Several authors studied the bactericidal efficiency of H_2O_2 in sterilisation of milk and food material packaging. The rate and extent of destruction varied with the organisms tested, the contact time and temperature (Table 12).

H_2O_2 has been shown to be more effective as a sporicide than as a bactericide. H_2O_2 was bacteriostatic at concentrations >5.1mg/l (Baldry, 1983).

The 16-18h EC_{10} to *Pseudomonas putida* was 11mg/l (Knie *et al*, 1983).

Of bacteria indigenous in dental plaque, *Actinobacillus actinomycetem* - comitans was more resistant to H_2O_2 (not completely killed at 34mg/l H_2O_2) than *Haemophilus aphrophilus*, which was destroyed after 1h exposure to 1.7mg/l H_2O_2 (Miyasaki *et al*, 1985, 1987).

6.2 AQUATIC ORGANISMS

6.2.1 Fish (Table 13)

Studies with several fish species showed no effects following exposure to H_2O_2 concentrations ranging from 2 to 40mg/l. The 96hLC_{50} was 37.4mg/l for Channel catfish (*Ictalurus punctatus*), and 16.4mg/l for fathead minnow (*Pimephales promelas*) with a NOEC of 5mg/l.

H_2O_2 did not affect glutamic oxalacetic transaminase activity, but inhibited lactic dehydrogenase activity in blood plasma of white sucker (*Catostomus commersoni*) exposed to 2,000mg/l for 2 weeks (Christensen, 1971/72). H_2O_2 (340mg/l) did not affect acetylcholinesterase activity prepared from muscle of a fathead minnow (*Pimephales promelas*, Rafinesque) (Olson and Christensen, 1980).

There was no evident effect on the dispersal of schooling of *Kuhlia sandvicenis*, a saltwater fish, at a concentration of 20mg/l H_2O_2 (Hiatt *et al*, 1953).

The Task Force is aware of, but unable to obtain data on acute toxicity studies with 35% H_2O_2 in Bluegill sunfish (*Lepomis macrochirus*) and Rainbow trout (*Salmo gairdneri*), submitted confidentially to the US EPA (McAllister and Cohle, 1984a,b).

TABLE 12

TOXICITY TO MICRO-ORGANISMS

Species	Duration (h)	Temperature (°C)	Lethal concentration (mg/l)	Reference
Aerobic, non-pathogenic				
Enterobacter aerogenes	4	Ambient	EC_{10} : 50	Lal *et al*, 1985
	2	Ambient	EC_{100} : 300	
pathogenic				
Salmonella typhosa	4	Ambient	EC_5 : 50	Lal *et al*, 1985
	4		EC_{13} : 300	
	30 min	54	EC_{100} : 600	Naguib, 1972
Staphylococcus aureus	4	Ambient	EC_7 : 50	Lal *et al*, 1985
	4	Ambient	EC_{26} : 300	
	30 min	54	EC_{100} : 600	Naguib, 1972
	2	Ambient	EC_{100} : 90	Yosphe *et al*, 1968
Salmonella typhimurium	15 min	54	EC_{100} : 1,000	Mahmoud *et al*, 1984
	1	5	EC_{99} : 5,000	Uenluetuerk and Turantas, 1987
Anaerobic, non-pathogenic				
Streptococcus lactis	4	Ambient	EC_{10} : 50	Lal *et al*, 1985
	4	Ambient	EC_{20} : 300	
	15 min	54	EC_{100} : 1,000	Mahmoud *et al*, 1984
Streptococcus faecalis	15 min	54	EC_{100} : 1,000	Mahmoud *et al*, 1984
non-pathogenic sporformer				
Bacillus subtilis	4	Ambient	EC_7 : 50	Lal *et al*, 1985
	4	Ambient	EC_9 : 300	
Streptococcus thermophilus	15 min	54	EC_{100} : 1,000	Mahmoud *et al*, 1984

TABLE 12 (cntd)

TOXICITY TO MICRO-ORGANISMS

Species	Duration (h)	Temperature (°C)	Lethal concentration (mg/l)	Reference
Anaerobic, pathogenic				
Escherichia coli	2	Ambient	EC_{52} : 30	Yosphe *et al*, 1986
	5	Ambient	EC_{70} : 30	
	4	Ambient	EC_{20} : 50	Lal *et al*, 1985
	5	Ambient	EC_{94} : 90	
	2	Ambient	EC_{100} : 200-300	
Clostridium botulinum	6 min	55	EC_{100} : 50	Ito *et al*, 1973
	2 min	55	EC_{100} : 200	
pathogenic sporformer				
Clostridium perfringens	15 min	54	EC_{100} : 1,000	Mahmoud *et al*, 1984
Clostridium butyricum	15 min	54	EC_{100} : 1,000	Mahmoud *et al*, 1984
	30 min	54	EC_{100} : 600	Naguib, 1972
Aerobic/anaerobic, non-pathogenic				
Lactobacillus vulgaricus	4	Ambient	EC_{16} : 50	Lal *et al*, 1985
	4	Ambient	EC_{22} : 300	
non-pathogenic sporformer				
Bacillus cereus	4	Ambient	EC_5 : 50	Lal *et al*, 1985
	4	Ambient	EC_9 : 300	
	15 min	54	EC_{100} : 1,000	Mahmoud *et al*, 1984
pathogenic				
Listeria monocytogenes	9-24	15	EC_{100} : 710	Dominguez *et al*, 1987

TABLE 13

TOXICITY TO FISH

Species	Effect	Concentration µg/l	Reference
Freshwater Fish			
Rainbow trout, fingerling *(Salmo gairdneri)*	Lethality, 48h	>40	Southgate, 1950; McKee, 1963
Squawfish *(Ptychocheilus oregonensis)* Coho salmon *(Oncorhynchus kisutch)*	No mortality LC_0, 24h	10	MacPhee and Ruelle, 1969
Channel catfish *(Ictalurus punctatus)*	LC_{50}, 96h	37.4	Kay *et al*, 1982
Mosquito fish *(Gambusia affinis)*	Unharmed (field study)	2.38-9.86	Kay *et al*, 1982
Guppy *(Lebistes reticulatus)*	Unharmed	34	Quimby, 1981
Golden orfe *(Leuciscus idus melanotus)*	LC_{50}, 24h	35	Degussa, 1977
Fathead minnow *(Pimephales promelas)*	LC_{50}, 96h NOEC	16.4 5	Shurtleff, 1989
Marine Fish			
Kuhlia sandvicenis	Behaviour not affected	20	Hiatt *et al*, 1953

6.2.2 Crustacea (Table 14)

Immobilisation by H_2O_2 of a variety of crustaceans was seen at concentrations between 2.4-7.7mg/l. Crayfish (*Procambarus clarkii*) were not affected by 64.6mg/l H_2O_2 (Kay *et al*, 1982).

6.2.3 Molluscs (Table 14)

The 96h LC_{50} for *Physa* sp., a freshwater snail, was 17.7mg/l (Kay *et al*, 1982).

In the marine environment, H_2O_2 at a concentration of 170mg/l caused synchronous spawning in male and female red abalones (*Haliotis rufescens*). The authors suggested that H_2O_2 activates the prostaglandin endoperoxide-forming cyclo-oxygenases (Morse *et al*, 1976).

6.2.4 Insects (Table 14)

Aquatic insects were unharmed at H_2O_2 concentrations of 170-218mg/l (Kay *et al*, 1982).

6.2.5 Algae (Table 15)

H_2O_2 was tested as a potential algicide for fresh aquaculture, where effects on several species were measured in terms of chlorophyll reduction at concentrations of 1.7mg/l and above (Kay *et al*, 1982).

It was highly toxic in one species of marine algae and may be a natural growth-inhibiting factor (Florence and Stauber, 1986).

6.2.6 Aquatic Plants (Table 15)

H_2O_2 is toxic to hydrilla (*Hydrilla verticillata*) and coontail (*Ceratophyllum demersum*) at concentrations ranging from 34-136mg/l, but does not affect alligator weed or water hyacinths (*Eichhornia crassipes*) (Quimby, 1981).

TABLE 14

TOXICITY TO AQUATIC INVERTEBRATES

Species	Effect	Concentration (mg/l)	Reference
Freshwater Crustacea			
Gammarus	LC_{50}, 96h mortality	4.42	Kay *et al*, 1982
Daphnia magna	$EC(I)_{50}$, 24h Immobilisation	7.7	Bringmann and Kuehn, 1982
	EC_0	3.8	
Daphnia pulex	Immobilisation 5min.	4.2	Gannon and Gannon, 1975
	LC_{50}, 48h	2.4	Shurtleff, 1989
	NOEC	1.0	
Crayfish *(Procambarus clarkii)*	LC_0 No mortality	64.6	Kay *et al*, 1982
Freshwater Snail			
Physa sp.	LC_{50}, 96h	17.7	Kay *et al*, 1982
Marine Mollusc			
Red abalones *(Haliotis rufescens)*	Induced spawning	170	Morse *et al*, 1976
Insects			
Stratiomyd fly *(Statiomis* sp.)	No effect	217.6	Kay *et al*, 1982
Dragonfly naiads *(Pachydiplax longipennis)*	No effect	170	Morse *et al*, 1976

TABLE 15

TOXICITY TO AQUATIC ALGAE AND PLANTS

Species	Effect	Concentration (mg/l)	Reference
Freshwater Algae			
Anabaena	Chlorophyll reduced to 5% after 24h	9.86	Kay *et al*, 1982
Ankistrodesmus	Chlorophyll reduced to <5% after 24h	17	Kay *et al*, 1982
Raphidiopsis	Chlorophyll reduced to <5% after 24h	6.8	Kay *et al*, 1982
Microcystis	Chlorophyll reduced to <6% after 48h	1.7	Kay *et al*, 1982
Marine Algae			
Nitzchia closterium	Cell count reduced to 50%	0.85	Florence and Stauber, 1986
Freshwater Plants			
Ceratophyllum demersum	80% necrosis continuous exposure	34	Quimby, 1981
Hydrilla verticillata	30% necrosis 1h exposure	34	Quimby, 1981
	80% necrosis	136	Quimby, 1981