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PREFACE

GESAMP, the Joint Group of Experts on the Scientific Aspects of Marine Pollution, was established in 1969 and is today co-sponsored by the International Maritime Organization (IMO), Food and Agricultural Organization of the United Nations (FAO), United Nations Educational, Scientific and Cultural Organization (UNESCO), World Meteorological Organization (WMO), World Health Organization (WHO), International Atomic Energy Agency (IAEA), United Nations and United Nations Environment Programme (UNEP). According to its present terms of reference, the functions of GESAMP are:

- to provide advice relating to the scientific aspects of marine pollution 1/; and

- to prepare periodic reviews of the state of the marine environment as regards marine pollution and to identify problem areas requiring special attention..

Since its beginning GESAMP involved a large number of experts as members of GESAMP or GESAMP Working Groups and produced, at the request of the sponsoring organizations, numerous reports 2/.

This document reproduces the substantive part of the report of the GESAMP Working Group on Review of Harmful Substances, approved by the sixteenth session of GESAMP (London, 17 - 21 March 1986).

Under the chairmanship of Prof. L. Friberg draft evaluations were prepared for effects on marine biota by Dr. A. Jernelov and for human health aspects by Dr. L. Magos. Editorial responsibility for the entire document was assumed by Dr. L. Magos. Their efforts and contributions were most helpful in this review and are gratefully acknowledged by GESAMP.

The activities of the Working Group were organized by WHO, acting as the "lead agency". The Working Group was jointly sponsored by WHO, FAO and UNEP.

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

2/ V. Pravdic: GESAMP, The First Dozen Years. UNEP, 1981.

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1 INTRODUCTION

1.1 Background

The Working Group on the Review of Potentially Harmful Substances (WG.13) was established at the Eighth Session of GESAMP (Rome, 21-27 April 1976) and worked since then under the subsequent chairmanship of Messrs. B.H. Ketchum, A. Jernelov and L. Friberg in order to:

- update the Review of Harmful Substances (GESAMP Reports and Studies No. 2) with greater emphasis on the human health aspects of marine pollution; and to
- continue to include consideration of the other aspects of the subject, namely, harm to living resources, reduction of amenities, and interference with other uses of the seas.

During the subsequent sessions of GESAMP, the organizations sponsoring the work of WG.13 (UNEP, FAO, WHO) requested modification of the terms of reference of the Working Group so that its products could be used by governments which are parties to various global and regional agreements, as guidance in dealing with the control of marine pollution caused by specific potentially harmful substances. Consequently, at the Tenth Session of GESAMP (Paris, 28 May - 2 June 1979) the following terms of reference were adopted:

(a) To prepare short referenced reviews on selected substances which will include an assessment of the following factors:

  (i) the total amount of the particular substance(s) which reach(es) the marine environment (on a local, regional and global scale) with particular attention to the relative importance of land-based sources;

  (ii) the fate (transport, distribution, transformation) in the marine environment; and

  (iii) the effects on the marine environment and adjacent coastal areas, including direct and indirect effects on living resources, human health and amenities;

(b) Produce a scientific evaluation of the harmful effects of substances released into the marine environment on living resources, human health, amenities and other legitimate uses of the marine environment and adjacent coastal areas.

On the basis of the intersessional work of the Working Group, including the use of data profiles by UNEP's International Register of Potentially Toxic Chemicals (IRPTC), a report covering cadmium, lead and tin has been prepared and its publication was approved by the Thirteenth Session of GESAMP (Geneva, 28 February -4 March 1983).

The present report covering organosilicons (silane and siloxanes) has been prepared using the same methodology and its publication was approved by the Sixteenth Session of GESAMP (London, 17-21 March 1986).

1.2 Evaluation Mechanism

The method and approaches applied by the Working Group were discussed and agreed upon at a planning session in Stockholm, 24-25 September, 1982. This was attended by the the chairmen of GESAMP and of the Working Group, and by international agency representatives.

The collaboration and support of IRPTC was offered at GESAMP XII and an IRPTC Data Profile on Organosilicon Compounds was issued in June 1983. The marine data collection and extraction was carried out by the Marine Biological Association of the U.K., Plymouth, United Kingdom.

From an examination of this and other data profiles, and available critical reviews of published data, significant papers were selected for thorough evaluation. These papers, together with recent and pertinent publications, then formed the basis of this review. It is

recognised, however, that these papers provide only a partial coverage of the world literature. Information was lacking in several areas essential to an environmental hazard evaluation of these substances, and these areas were identified in the reviews.

A first discussion on organosilicons took place at the second session of the Working Group which was held at the Monitoring and Assessment Research Centre (MARC) at Chelsea College, London, from 30 January - 3 February 1984. The composition of two groups is given in Annex I. As requested by GESAMP, the Working Group undertook a review of organosilicons, starting with the preparation of draft sections on marine environment and human health aspects. It was noted with great concern that the data base available largely related to the producing industry and that very little reference could be made to research findings published in the open literature. Any conclusions reached would therefore have to be qualified accordingly. Concern was also expressed over the large and open-ended group of substances which the organosilicons represent. A meaningful hazard assessment would therefore have to be limited to defined groups of organosilicons which are presently of significance with regard to production and usage.

Following the preparation of a draft evaluation of organosilicons with regard to marine organisms and to human health, an evaluation discussion took place at the fourth session of the Working Groups at WHO Geneva, 4 - 8 November 1985. The composition of this is given in Annex II.

After further revision, including comments received from GESAMP members through the draft circulation process, the final report was submitted to GESAMP XVI for consideration and adoption. This was followed by its formal publication and general distribution.

2 ORGANOSILICONS IN THE MARINE ENVIRONMENT.

2.1 Background and references documentation.

Reports presented through the European Council of Chemical Manufacturers' Federation (CEFIC) to various scientific and policy groups, documents and reviews written by scientists working in the organosilicon industry (eg Fry, 1980; Firmin et al., 1984) with independent reviews prepared for the US Environmental Protection Agency by Howard et al. (1974) and for the EEC by Vonk et al. (1984) were consulted. A selection of studies circulated as company reports (eg Hill et a., 1983) or published in open literature were used and these are listed in the reference section.

2.2 General facts

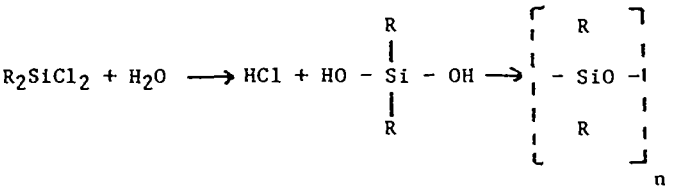
A silylation of organic compounds by the replacement of hydrogen with a trimethylsilyl group or the substitution of carbon atom by silicon can increase in principle the number of organosilicon compounds above the number of organic compounds. The introduction of silicon into these organic compounds does not render a specific set of toxicological properties, but rather the silicon analogues simulate the biological activity of parent compounds (Wannagat, 1977). This report is not concerned with these so called sila-pharmacons, but concentrates on those commercially produced organosilicons which are synthesised in the following steps:

1. Silicone is reacted with alkylhalide at high temperature in the presence of copper catalyst:

$$Si + RCl \xrightarrow{Cu} R_3SiCl,\ R_2SiCl_2,\ RSiCl_3$$

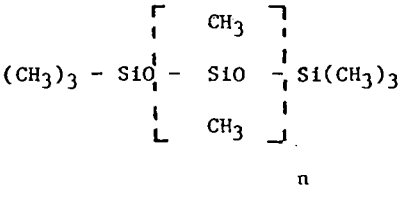
(chlorosilanes which have to be separated by fractional distillation)

2. The hydrolysis of chlorosilanes gives HCl and unstable reactive silanol which yields condensed polysiloxane, eg



silanol polysiloxane

The most commonly produced polysiloxane (silicone) is trimethyl end-blocked polydimethylsiloxane (PDMS):



The characteristics of a polymer depend on the number of siloxane blocks and on the organic radical attached to the silicon atom. Polymers containing up to 2000 siloxane blocks remain fluid, though with increasing viscosity and decreasing volatility. The viscosity of organosilicon fluids is given in kinematic viscosity (= viscosity/density) units, usually cSt (centiStoke),which shows some degree of correlation with the number of siloxane units per molecule (Howard et al., 1974). Cyclic polysiloxanes are mainly formed with n = 3-5. In the production of some linear and cyclic polysiloxanes methyl groups are partially substituted with longer alkyl chains or phenyl radical. To avoid the formation of oestrogenic phenylmethylcyclotetra-siloxanes, polymethylphenyl fluids are now synthetised from diphenyldimethyl instead of phenylmethyl intermediates.

The introduction of polyethers (polyoxyethylene and polyoxypropylene) gives block and graft silicone polyether copolymers. In block copolymers a block of siloxane polymer is attached to a block of polyether polymer and in graft copolymers polyoxyalkylene side chains are grafted on a polymethylsiloxane backbone. The production of elastomers and resins is based on the presence of reactive (eg H, OH or vinyl) radicals which allows cross linking between linear polymers and the formation of a more rigid matrix.

The subdivision of such a large group of heterogeneous compounds is a prerequisite for any meaningful discussion. The following groups have been chosen for the evaluation of their behaviour in the marine environment:

silanes and silanols
polydimethylsiloxanes (PDMS) fluids
silicone polyether and other copolymer fluids
polyphenylsiloxane fluids
silicone elastomers and resins

2.3 Sources

2.3.1 Production and use

The annual world production of organosilicons was about 500,000 tons in 1983 (Vonk et al., 1984). According to an earlier estimate (Howard et al., 1974) about 45-50% of the total production went into silicon fluids (two thirds PDMS and one third polyether copolymers), 33% into elastomers and 11% into resins. A small amount (about 3%) of silanes was not used for polymerization. According to a later estimate for the USA, the proportion of silicon fluids, elastomers; resins is 11.2:4.5:1 (Vonk et al., 1984).

Organosilicons have found numerous applications. The fluids are used in waxes and polishes, polyurethane foams, lubricants and water repellents and as antifoams. Some of them are used for coating of textiles and glass, in cosmetics, pharmaceuticals and pesticide formulations, in surgery for dressing granulating wounds (foam elastomers). Resin and elastomer protheses are implanted in plastic and orthopaedic surgery. PDMS is replacing PCB as a dielectric coolant.

2.3.2 Sources of environmental contamination

Environmental presence of organosilicons is exclusively anthropogenic. According to Howard et al.(1974) the contribution of manufacturing operations and transport to environmental contamination is not significant. The only reported large scale accident was the spill of 4500 l tetrachlorosilane through the ruptured tank-coupling unit of a storage tank. Rapid hydrolysis on the moist ground resulted in the formation of HCl and silicic acid (H_4SiO_4). The inorganic silicon compound formed a 150-200 m high cloud and spread over more than a mile (Kizer et al., 1984). Siloxanes are not corrosive and volatility sharply decreases with the degree of polymerization, and these two characteristics decrease tendencies to escape. So far no significant accidental spill into natural waters has been reported (Firmin et al., 1984). Whether this was because there were none or whether they simply remained unnoticed was not made clear. Loss of organosilicons into the environment is mostly from their use (Howard et al., 1974). Organosilicons in waxes and cosmetics are eventually washed off. Antifoams especially when used in sewage plants can enter the water system with sludge and effluent. Silicone fluids used as lubricants, shock absorbers, heat exchange and dielectric fluids may be released into the environment through leaks or intentional disposal. The treatment bath for coating of textiles or glass with silicone may be the source of environmental contamination. Silicone polymers in polyurethane foams, elastomers, resins and coated textiles are either incinerated or disposed in land fill. Incineration decomposes organisilicons to CO_2 and SiO_2 but disposal of fluids in land-fills may allow small amounts to escape into aquatic systems.

2.4 Transport, transformation and bioaccumulation

2.4.1 Transport and transformation

2.4.1.1 Silanes and silanols

Chlorosilanes, but also alkoxy-, acetoxy, amino-, and epoxysilanes undergo rapid hydrolysis in water with the formation of silanol and siloxane compounds. Degradation of chlorosilanes also produces HCl. In the marine environment the acid is dispersed and neutralised. Diethoxydimethylsilane, as the single source of energy,was able to maintain the growth of a strain of Pseudomonas, several bacilli and gram negative rods (Heinen, 1977), probably from ethanol liberated from the hydrolysis of the Si-O bond. Dimethylsilanediol $(Me_2Si(OH)_2$ and other water-soluble methylsilaxonols, irradiated with 254 nm UV light, sun lamps giving 365 nm UV light or natural ground level sun light, broke down in water to CO_2 and silicic acid. Traces of $NaNO_3$ or $NaNO_2$ (10 ppb) acelerated decomposition (Frye, 1980; Buch et al., 1983).

2.4.1.2 Polydimethylsiloxane (PDMS) fluids

Linear, branched and cyclic polydimethylsiloxanes have densities below 1. Nevertheless they do not form lasting surface films on natural waters, but become adsorbed onto particles and sink to the sedimental layer where mobility is low (Pellenbarg, 1979a; Gettings and Lane, 1982). Thus 430 l seawater, percolated slowly through 200 g sediment siliconised with 2.0 g DC 561 (50 cSt) PDMS, removed only 5% silicone (CEFIC,1983, Eales and Taylor, 1983).

At present there is no evidence for biodegradation in the aquatic environment (Vonk et al., 1984), though non-biological decomposition has been demonstrated. Under the influence of UV light the atmospheric decomposition of volatile methylsiloxanes, like hexamethyldisiloxane or octamethylcyclotetrasiloxane was faster than the decomposition of n-octane (Frye, et al., 1980). The siloxane bond of PDMS undergoes hydrolysis and rearrangement in contact with the clay components of soil when the moisture content is more than 2.0%. Contact with kaolinite results in the formation of volatile cyclics while montmorillonite attacks trimethylsiloxy ends in preference to the dimethylsiloxy chain sites (Buch and Ingebrigtson, 1979; Frye, 1980).

2.4.1.3 Silicone polyether copolymer fluids

Depending on the polyether composition these surfactant materials may be soluble, miscible or insoluble in water. The water soluble or miscible copolymers are expected to behave differently from PDMS. Some biodegradability may be expected but has not been reported. On theoretical grounds nitrate mediated photodegradation is possible.

2.4.1.4 Polymethylphenylsiloxane fluids

Environmental properties of this group are expected to be similar to those of PDMS and on theoretical grounds the same degradation mechanism is likely. The utilization of phenylsilane by a Pseudomonas strain (Heinen, 1977) and the conversion of 2,6-cis-diphenylhexamethylcyclotetrasiloxane to hydroxyphenyl derivative (LeVier et al., 1977) have been suggested, but without any documentation. Moreover, at least in rats phenyltrimethylsilane and phenyldimethylsilane are not decomposed but converted to disiloxanes (Fassenden and Hartman, 1970).

2.4.1.5 Organosilicon elastomers (rubbers) and resin.

These materials are cured solids; they are insoluble in water and non-biodegradable. The suggestion that silicon rubber can be used as food source by Streptomyces was not supported by the demonstration of degradation (Calderon and Staffeldt, 1965). Other publications reviewed by Vonk et al. (1984) showed that silicon resins and rubber are resistant to fungal decay and deterioration by microorganisms.

2.4.2 Bioaccumulation

2.4.2.1 Octanol-water partition coefficient

Bioconcentration factors (BCF) of organic substances are determined under steady state conditions, and can be predicted on the basis of partition coefficient [K_{OW}] (GESAMP 1984, Chiou 1981). Based on the measured [K_{OW}] values of 59 chemicals and their BCF values in fathead minnow, bluegill, mosquito fish, rainbow trout and green sunfish, Veith et al., 1979, found that BCF can be prediced from the following equation:

$$\log BCF = 0.85 K_{OW} - 0.70$$

The predicted BCF may be lower than the actual BCF when biomagnification via food chain occurs and higher when the compound is biodegraded (GESAMP 1984). BCF, calculated from the water concentration of the chemical at the beginning of exposure, is also too high when aqueous concentration declines (Chiou, 1981), e.g. the chemical undergoes hydrolysis (like silanes), evaporation (like cyclic siloxanes) or sedimentation (like PDMS). Long accumulation time increase the importance of these factors. Though bioconcentration increases with K_{OW}, the time to reach the steady state is increased with decreasing water solubility. Thus the more soluble trichlorobenzene reached the steady state concentration in fish in two days and the less soluble pentachlorobenzene in 7 days (Chiou, 1981). Another exception, important for polymers, is that diffusion through membrane can be impeded by the structure or size of the molecule (Roberts and McGarrity, 1985).

2.4.2.2 Silanes and silanols

There are no environmental data on the bioaccumulation of silanes or silanols, but their environmental instability makes significant bioaccumulation unlikely. The lack of bioaccumulation in fathead minnows (Pimephales promelas) exposed from eggs through adult stages for 60 to 90 days to a maximum of 10 ppm dimethylsilandiol were in agreement with this view (Annelin and Buch, 1978).

2.4.2.3 Polydimethylsiloxane (PDMS) fluids

Bioconcentration experiments (Annelin, 1984) with octamethylcyclotetrasiloxane indicated that fathead minnows (Pimephales promelas) take up this cyclic oligomer (m.w. = 296, water solubility = 0.5 mg/l) rapidly. The average bioconcentration factor was near to the predicted 1200 calculated from log K_{OW} = 4.45 estimated by Bruggeman et al., (1984).

About 90 % of the body burden cleared with a half time of 16.8 h and 10% with a half time of 120 h (Annelin, 1984).

In feeding experiments (Bruggeman et al., 1984) with linear and cyclic oligomers and DC 200 fluid (5 cSt) the volatility of low molecular weight oligomers, including octamethylcyclotetrasiloxane, prevented supplementation with measurable concentration in food but authors were able to estimate the uptake of cyclosiloxanes with 6 and 9 silicon atoms and the uptake of linear siloxanes from 5 to 14 silicon atoms. Only the two cyclic siloxanes and from the linear groups those with 6 to 12 silicon atoms gave measurable concentrations in guppies (Poecilia reticulata) after the 10 weeks treatment period. The detection limit was 0.3 µg/g tissue. The apparent biomagnification factor (the ratio of concentration in fish to concentration in food) for linear octosiloxane was 0.16 and for all others less than 0.1. These factors did not show any correlation with the octanol-water partition coefficient and were 10-30 times lower than those of PCB compounds.

Similar low bioconcentration and biomagnification factors were obtained with more viscous preparations, eg with 50 cs PDMS fluid in bullheads, Ictalurus melas (Annelin, 1979) and with 300 cSt fluid in bluegill sunfish, Lepomis macrochirus (Hobbs et al., 1975). Aubert et al. (1985, 1985) exposed four food-chain pairs to 200 mg/l PDMS (47 cSt) oil. Worms in the presence of bacteria and plankton, or fish and crustacea fed on exposed annelid worms had a bioconcentration factor (concentration in tissue per concentration in water) of 0.05. Both phytoplankton and plankton had about 2.0 bioconcentration factor, but molluscs (Mytilus edulis) fed on phytoplankton or fish (Carassius auratus) fed on plankton had low bioconcentration factors, 0.24 and 0.1 respectively.

Contrary to these observations Watanabe et al (1984a) reported significantly higher bioconcentration factors in silver carp. Water concentrations (and solubility) for the 1200, 6000, 2500 and 56000 m.w. PDMS preparations were 1.6, 0.56, 0.17 and 0.076 ppm and after 72 h exposure tissue silcone concentrations were 4.1, 3.5, 48.0 and 75.3 ppm. It is not clear that concentrations refer to the whole fish or to muscle, but surface contamination is the most likely explanation for the following reasons. Firstly diffusion of molecules through membranes cannot increase with molecular weight and secondly from the gastrointestinal tract even linear methylsiloxane with 6 silicon atoms are not absorbed (Le Vier et al., 1977).

2.4.2.4 Silicone polyether copolymers and polymethylphenylsiloxane fluids.

Polyether copolymers due to their surface active properties may behave somewhat differently from PDMS, and polymethylphenylsiloxane fluids are expected to behave like PDMS with the same molecular weight. However it must be pointed out that phenyl groups are not only enlarge but modify the structure of molecule.

2.4.2.5 Elastomers and resins

No data on aquatic bioaccumulation have been found, but based on experience of their use in medicine, the probability of bioaccumulation is extremely unlikely.

2.5 Concentrations in sea water, sediments and marine biota.

Low solubility limits the aqueous concentration of organosilicons but they can form a microlayer on aqueous surfaces. In two marinas microlayer samples, which filled an aluminium mesh screen in contact with the surface, contained 20-40 ppb silicone (Pellenbarg, 1979a). Such a layer is highly permeable to oxygen (Clark and Gollan, 1966), and both low solubility and low surface tension promotes adsorption on particles. Thus Pellenbarg (1979a) and Ann Arbor Technical Services (1985) measured 1.0 to 4.8 ppb organosilicon concentrations in the effluent of different sewage disposal plants, while concentrations in filter cake and sludge ranged from 8.0 to 104 ppm. In the New York Bight, near to the dumping site of sludge, sediments contained up to 50 ppm organosilicons (Pellenbarg, 1979b), while in the sediments of the Potomac river near to a sewage disposal plant the maximum concentration was only 3.1 ppm and in the Delaware river Bay it was below 1.0 ppm (Pellenbarg, 1979b). No octamethylcyclotetra- siloxane (detection limit: 0.05 ppm dry weight) was detected in sediments collected in the Curtis Bay, Delaware Bay and Potomac river areas (Ann Arbor Technical Services Ltd., 1985). No data have been found for organosilicon concentrations in sediments

outside estuaries or in seawater and biota. Extractable organosilicon concentrations in fish from the Nagara river area, highly contaminated with municipal and industrial sewage, were below 1.0 ppm (Watanabe et al., 1984b).

3. EFFECTS ON MARINE BIOTA

The paucity of data on marine organisms made it essential to include data on freshwater species.

3.1 Reference documentation

The review of Vonk et al. (1984) especially the tabulated data on toxic effects served as a basis for this part. Other reviews consulted were those by Firmin et al. (1984) and by Cabridenc (1985).

In two thirds of the entries in the comprehensive toxicity tables prepared by Vonk et al., (1984) the highest organosilicon concentrations used by the investigators had no injurious effect on marine organisms or were below the corresponding LC_{50} values. The arbitrariness in the choice of the highest concentration makes the grading of organosilicons for toxic potential difficult. Moreover as most of the experiments with polymers were carried out at a concentration level well above water solubility, differences in the dispersion and sedimentation of the insoluble substance may have caused differences in actual concentrations from experiment to experiment.

3.2 Silanes and silanols

3.2.1 Microorganisms, algae and crustaceans.

In microcosm experiments 50 to 60 ppm dimethylsilanediol did not alter community structure of bacteria, algae and protozoa (Getting and Lane 1982). Fourteen days exposure to 1000 to 2000 ppm trimethylsilanol, dimethylsilandiol or methylsilanetriol did not affect the growth of green (Selenastrum capricornutum) and blue algae (Anabaena flos-aquae), but different methoxysilanes in the concentration range of 100 to 300 ppm caused a 50% inhibition (IC_{50}) in algal growth (Vonk et al., 1983).

Chlorosilanes at around 200-300 ppm level killed 50% (LC_{50}) of European brown shrimp (Crangon crangon). As hydrochloric acid from the hydrolysis of silane was the toxic agent the extension of exposure time from 1 h to 96 h did not increase mortality (Franklin, 1981). The 96 h LC_{50} values for dimethylsilanediol were 471 ppm in shore crab (Pachygrapsus crassipes), and 604 ppm in marsh shrimp (Palaemonetes vulgaris), while in waterflea (Daphnia magna) 72 h exposure to 1000 ppm trimethylsilanol, dimethylsilanediol or methylsilanetriol did not cause mortality (Vonk et al., 1983). For the same species epoxysilane had 324 ppm as 48 h LC_{50}. Alkoxytrimethoxysilane and acetoxysilane were not toxic in concentration up to 100 ppm.

3.2.2 Molluscs and fish

No toxicity data are available for molluscs. Fish (armed bullhead, Agonus cataphractus) with 1 hr LC_{50} values of 180 to 300 ppm have the same sensitivity to chlorosilanes as crustaceans (Franklin, 1981). No LC_{50} values could be established for silanols, as eg 96 h exposure to 1000 ppm dimethylsilanediol did not cause any mortality in rainbow trout (Salmo gairdneri), bluegill sunfish (Lepomis macrochirus) or killifish (Fundulus heteroclitus) (Vonk et al., 1984). Exposure to 10 ppm dimethylsilanediol for 280 days did not affect survival, growth and weight of fathead minnows (Pimephales promelas). Of three oxysilanes vinyltriacetoxysilane had the lowest LC_{50}, 51 ppm for rainbow trout and 68 mg ppm for bluegill sunfish. In the same two species glycidoxypropyltrimethoxysilane and an aminopropyltrimethoxysilane had LC_{50} values between 200 and 300 ppm and vinyltrimethoxysilane was not toxic to bluegill sunfish even at 1000 ppm (Vonk et al., 1984).

3.3 Polydimethylsiloxanes (PDMS) fluids

3.3.1 Microorganisms, algae and crustaceans

Community structure of a microcosm, including bacteria, algae and protozoa, was not affected by 24 weeks exposure to ^{14}C-labelled 55 cs hydroxy endblocked PDMS. The microcosm system consisted of 9.1 l water and 2.4 l lake sediment and 84 mg PDMS was either spread on the surface of water or mixed with the sediment. Water concentrations in the first case ranged from 17 to 260 ppb with 144 ppb median and in the second case from below detection limit to 14.5 ppb with 9 ppb median (Gettings and Lane, 1982). Sea water saturated with different PDMSs (100, 350 or 12,000 cSt) did not affect the growth of flagellates or diatoms, or the mortalities of brine shrimp and hermit crab (Clinobarius misanthropus) (Maggi and Alzieu, 1977). Aubert (1983) found the 120 h LC_{50} of a 30% PDMS emulsion (47 cSt) 2000 ppm for flagellates, while an Annelid (Nereis diversicolor) and brine shrimp (Artemia salina) tolerated longer exposure time or higher concentrations.

Hobbs et al. (1975) found the 48 h LC_{50} of an antifoam with 30% PDMS emulsion (350 cSt) to be 244 ppm (73 ppm PDMS) for Daphnia magna. Two other studies gave LC_{50} values near to 500 ppm (155 ppm PDMS) for the same species (Howard et al., 1977). The 12% cyclic oligomers in the PDMS used by Hobbs (1975) may have interfered in the toxicity, but authors also noted that the crustaceans became entangled with the silicone layer on the water surface. Exposure to cyclic methylsiloxanes at least up to 100 ppm concentration for 96 h did not affect the mortality of marsh shrimp (Palaemonetes vulgaris) or algal growth. Brine shrimp tolerated 24 hr exposure to 500 ppm (Vonk et al., 1984).

3.3.2 Molluscs and fish

Few data are available on soluble linear and cyclic compounds. Cyclic low molecular weight siloxanes (DC 345) were not toxic to the zebra fish (Brachydanio rerio) at least up to 96 h exposure to 500 ppm (Meurice, 1981a) or 105 days exposure to 10 ppm (Meurice, 1981b).

More data are available on high molecular weight polymers. Exposure of mussel (Mytilus edilis), periwinkle (Littorina littorea) or oyster (Ostrea edulis) for 96 h to saturated solutions of 100, 350 or 12,500 cSt PDMS solutions caused no mortality (Maggi and Alzieu, 1977). Mytilus edulis is more sensitive to the emulsifier than to PDMS and according to Aubert et al. (1985) the lethal factor is not biochemical, but the mechanical obstruction of the respiratory passages. Data tabulated by Vonk et al. (1984) indicates that mussels (Mytilus edulis) or cockles (Prothaca spaminea)can tolerate 1000 ppm PDMS.

Exposure of rainbow trout (Salmo gairdneri), bluegill sunfish (Lepomis macrochirus) and killyfish (Fundulus heteroclitus) to 1000 ppm DC Antifoam C (30% emulsion) for 96 h caused no death in the first two and 20% mortality in the third species. At and above 1000 ppm bluegill sunfish and rainbow trout became less active (Hobbs et al., 1975). Eight days exposure of minnows (Phoxinus phoxinus) to 3000 ppm emulsified PDMS caused 40% mortality (Vonk et al., 1984). Exposure time is important. In the experiments of Aubert et al. (1983) with PDMS (47 cSt) increase of exposure time from 24 to 42 h decreased LC_{50} from 10,000 to 1000 in goldfish (Carassius auratus) and from 50 h to 120 h decreased the LC_{50} of Scorpaena porcus from 2000 to 1000 ppm. These concentrations are substantially higher than the solubility of PDMS, which is in the ppb range. Maggi and Alzieu (1977) found no mortality when three-spined stickleback (Gasterosteus aculeatus) or sand goby (Pomatoschistus minutus) were exposed for 96 hr to the saturated solution of different PDMS.

Sheepshead minnow (Cyprinodon variegatus) embryos and larvae were exposed to the polydimethylsiloxane formulation of MAJ241 at five concentration levels (Hill et al., 1984). The measured concentrations of MAJ241 were 91, 200, 293, 606 and 671 ppm with 35% PDMS. An additional group was exposed to the emulsion formulation MAJ242 which has the same composition as MAJ241 but PDMS was replaced by water. The concentration of MAJ242 was 594 ppm, that is approximately the same as in the 606 ppm exposure group. Statistical comparison was made between these groups and a sixth group kept in saline water. Hatchability was significantly inhibited only in the highest exposure group, survival in the second and fourth exposure group and in the emulsion control, length decreased in the 671 ppm and emulsion groups and finally weight increased in the 200, 293 and 606 ppm exposure and decreased in the emulsion control groups. As survival was affected in the 200 ppm MAJ 241 exposure group, authors put the no-observable effect concentration (NOEC) at 91 ppm, the observed effect concentration (OEC) at 200 ppm and therefore the threshold concentration between 91 and 200

ppm (Hill et al., 1984). However this evaluation may be over zealous because the lack of graded dose response relationship range. Maggi and Alzieu (1977) found no mortality when three-spined stickleback (Gasterosteus aculeatus) or sand goby (Pomatoschistus minutus) were exposed for 96 hr to the saturated solution of different PDMS.

3.4 Silicone polyether copolymer fluids

3.4.1 Microorganisms, algae and crustaceans

Silicone polyether copolymers did not affect the biological oxygen demand of sewage organisms exposed to 1000 ppm for 20 weeks (Firmin et al., 1984). DC 193 surfactant, a silicone polyether copolymer, caused a 50% decrease in the growth rate of green algae at 16.8 ppm and that of the blue algae at 753 ppm concentration (Vonk et al., 1984). The same surfactant did not influence the reproduction of Daphnia magna exposed to 10 ppm for 21 days and for the same species the estimated 48 h LC_{50} values were 311 ppm and 486 ppm (Vonk et al., 1984) and 10% of the brine fish (Artemia salina) died when exposed to 500 ppm for 24 h (Meurice, 1981c).

3.4.2 Fish

The 96 h LC_{50} of DC 193 surfactant was 245 ppm in the rainbow trout (Salmo gairdneri) and 30% of the bluegill sunfish (Lepomis macrochirus) died by 96 h exposure to 1000 ppm (Vonk et al., 1984). No zebra fish (Brachydanio rerio) died from 96 h exposure to 500 ppm DC 190 surfactant (Meurice, 1981a) or exposure to 10 ppm for 105 days (Meurice, 1981b).

3.5 Polymethylphenylsiloxane fluids

There are only few data on the toxicity of this group of compounds on aquatic organisms. The growth or yield of algae (Selenastrum capricornotum or Anabaena flos-aquae) was not influenced by 67 days exposure to 10,000 ppm polymethylphenylsiloxane (Vonk et al., 1984). Exposure to 500 ppm DC 556 (20 cSt) for 24 hr caused 20% mortality in brine shrimps (Artemia salina) (Meurice, 1981c). The 24 hr LC_{50} value for Daphnia magna and Brachydanio rerio were also in excess of 500 ppm, and 1000 ppm fluid was not toxic for the rainbow trout (Vonk et al., 1984). Exposure to zebra fish (Branchydanio rerio) to 500 ppm DC 556 for 96 h (Meurice, 1981a) or 10.0 ppm for 105 days did not increase mortality (Firmin et al., 1984).

3.6 Silicone elastomers and resins

These are insoluble in water and not toxic for marine organisms.

3.7 Some other organosilicons

Some silicon derivatives of alkyl- and aryl amino alcohols, called silatranes, are biologically active and can reduce photosynthesis in diatoms (Roth et al., 1983) or have antibacterial and antifungicidal activities (Lukevics, 1977). The extent of use of these compounds either industrially or commercially is not clear, but yearly production is unlikely to exceed 1 ton.

3.8 Summary

The comparative aquatic toxicology of four groups of silanes and siloxanes on selected species is given in Table 1.

reports of FAO/WHO (1974), Howard et al. (1975), Cosmetic Ingredient Review (CIR) Expert Panel (1982) and review papers written by Garson and Kirchner (1971) LeVier et al. (1977) and Vonk et al. (1984) have also been used.

4.2 Toxicokinetic properties

4.2.1 Silanes and silanols

There are no data on the absorption and excretion of chlorosilanes and alkoxysilanes. Chlorosilanes in contact with the humidity of mucous membranes or even skin are rapidly hydrolysed with the liberation of HCl (Rowe et al., 1948). The resulting silanol can undergo condensation to siloxanes (Heinen, 1977; Fassenden and Ahlfors, 1967; Fassenden and Hartman, 1970). Oxysilanes are also prone to hydrolysis (LeVier et al., 1977), but at a slower rate and therefore the concentration of silanol may be too low to permit condensation.

Trimethylsilanol and dimethylsilandiol labelled with ^{14}C were completely adsorbed by the gastrointestinal tract of monkeys. The elimination route for trimethylsilanol was 10-30% pulmonary, 70-85% in urine and 1.0% in faeces, while in dimethylsilanediol treated monkeys no pulmonary elimination was evident and urinary excretion correspondingly increased (Bennett and Statt, 1973).

4.2.2 Polydimethylsiloxanes (PDMS) fluids

The gastrointestinal absorption of polydimethylsiloxanes shows an inverse relationship with the number of silicon atoms per molecule. Compared with hexamethyldisiloxane, the gastrointestinal absorption of a linear trisiloxane is 75% and a linear pentasiloxane is only 20%. Linear siloxanes with 6 silicon atoms or more are not significantly absorbed. The gastro-intestinal absorption of cyclic siloxanes is 100% up to 4 Si atoms and 30% and 10% for penta- and hexosiloxanes (LeVier et al., 1977).

Silicones are less readily absorbed dermally than after ingestion (Howard et al., 1975). Dermally applied cyclic phenylmethylsiloxanes with at least one phenyl group per cyclic oligomer were absorbed in rabbits, but not in monkeys or in humans (Palazzolo et al., 1972). Blood and urine levels of silicone did not indicate any absorption from the daily application of 50 mg PDMS, tris(trimethylsiloxy)phenylsilane or trifluoropropylmethylpolysiloxane (Hobbs et al., 1972). Absorption after intraperitoneal administrations is less than after ingestion, but follows the same order (LeVier et al., 1977). From the peritoneal cavity large molecular weight polymers are mostly transported by phagocytizing cells (Rees et al., 1967).

Within 48 h of the oral administration of 20 to 80 mg/kg of ^{14}C labelled hexamethyldisiloxane to monkeys, 20% of the radioactivity was exhaled, 78% was recovered in urine and 1% in faeces. When the compound was injected intravenously, values for pulmonary and urinary excretion were reversed (Bennett and Statt, 1973) probably because this volatile compound (47 mm Hg vapour pressure at 30° C) is practically insoluble in water (Rowe et al., 1948) and therefore the initial high plasma concentration promoted evaporative loss into the alveolar space. In similar experiments with monkeys 80% of the orally administered octamethylcyclotatrasiloxane was excreted within 48 h, 20% in expired air, 63% in urine and 5% in faeces (LeBeau and Gorzinski, 1973).

Only the oligomers from C^{14}-labelled PDMS were absorbed and these were eliminated from monkeys with half-times of 4-6 hr for pulmonary and 24 hr for urinary excretion (FAO/WHO, 1974). The excretion of silicon in the urine of human volunteers increased only by the ingestion of Antifoam A, which contained about 10% low molecular weight silicons, and not by Antifoam M, which contained less than 0.2% oligomers (LeVier et al., 1977).

Faecal excretion is the only route of excretion after the oral administration of non-absorbable PDMS oligomers (LeVier et al., 1977; Dow Corning, 1967).

4.2.3 Silicon polyether copolymer fluids

No data are presently available, but the molecular weight of commercial copolymers is too high to permit absorption. Decomposition in the gastrointestinal tract could possibly

result in the absorption and urinary excretion of low molecular weight product from the polyether chains. The polydisiloxane residues would be expected to be excreted in the faeces unchanged.

4.2.4. Polymethylphenylsiloxane fluids

Within 48 h of the oral or intravenous administration of ^{14}C-labelled 2,6-cis-diphenyl-hexamethylcyclotatrasiloxane the recovery of radio activity was found respectively 3.3 and 2.8% in expired air, 60 and 65% in urine and 28 and 20% in faeces. As 45% of the dose was secreted in bile and only 20% was excreted in faeces, more than half of the secreted compound had to be reabsorbed (LeBeau and Gorzinski, 1973). In monkeys the clearance half time of this compound was 12 h and in man 18 h (Pilbrant and Strindberg). In seven male patients maximum serum concentration of 1.1 to 5.0 mg/l were obtained within4 to 7.5 h of the administration of 100 mg 2,6-cis-diphenylhexamethyltatracyclosiloxane (Pilbrant and Strindberg, 1975). No evidence of absorption of low molecular weight cyclic phenylmethyl-siloxanes through human skin was noted (Palazzalo et al., 1972).

Higher polymers probably behave as PDMSs.

4.2.5 Organosilicon elastomers and resins

These are not absorbed from the gastrointestinal tract or after implantation.

4.3 Health effects

4.3.1 Silanes and silanols

The acute effect of alkylchlorosilanes given orally or i.p. is due entirely to their rapid hydrolysis to corrosive HCl. Their lethal dose after oral administra-tion is about 1 g/kg, and ten times less after i.p. injection (Rowe et al., 1948). Phenyltrichlorosilane is somewhat less and phenyltriflurosilane is more toxic than methyltrichlorosilane (Smyth et al., 1954). The replacement of halide with ethoxy group(s) decreases toxicity. The oral LD_{50} of tetraethoxysilane in the rat is 6.3 g/kg and alkylalkoxysilanes are even less toxic (Smyth et al., 1949; 1954). Acute inhalation exposure to rats resulted in lung damage, eye and nose irritation, while diethoxysilane and ethoxytrimethyl- silane had no similar effects (Rowe et al., 1948). Besides being an irritant, tetraethoxysilane is renotoxic (Rowe et al., 1948).

4.3.2 Polydimethylsiloxanes (PDMS) fluids

4.3.2.1 General toxicology

The acute toxicity of alkylsiloxanes is very low. Thus a single oral dose of 30 ml/kg hexamethyldisiloxane had no effect on rats or guinea pigs, and the same dose of dodecamethyl-pentasiloxane had only a laxative effect (Rowe et al., 1948). Intraperitoneally and intra-dermally injected, but not dermally applied hexamethyldisiloxane was irritant. Longer siloxane chains had no irritant effect (Rowe et al., 1948).

Linear polyorganosilicones have an extremely low toxicity (Rowe et al., 1948; Parent, 1979a, b, c; Cosmetic Ingredient Review Expert Panel, 1982). PDMS (50 or more cSt) did not change growth, organ weight, or cause haematological or histopathological changes after the oral administration of 20 doses of 1.0, 2.0, 5.0, 10 or 20 g/kg within 28 days (Rowe et al., 1948) or after feeding rats on a diet containing 0.3% PDMS-silica mixture for two years (Rowe et al., 1950) or 1.0% PDMS for 90 days (MacDonald et al., 1960). Rats and rabbits showed no signs of adverse effect when fed for 8 to 12 months on 1% PDMS (50 and 350 cSt) or 1% PDMS-silica (Carson et al., 1956). Dogs had occasionally moist and loose stool during a 6 weeks treatment with daily doses of 0.3, 10 or 3.0 g/kg (Child et al., 1951).

In agreement with animal experiments, twentyseven patients tolerated 48 ml PDMS given in divided doses for 3-13 months, without significant toxic effects except occasional nausea (FAO/WHO, 1975). Neither adverse effects or intestional absorption were noted in four human volunteers fed daily 7.1 g PDMS for ten days (Howard et al., 1974).

4.3.2.2 Reproduction

Hexamethyldisiloxane, decamethyltetrasiloxane or PDMS (50, 350 or 1250 cSt) at dermal doses of 200 mg/kg/day for 28 days were without any effect on the reproductive organs of male and female rats (Hobbs et al.1, 1972). The daily subcutaneous injection of 200 mg/kg PDMS (350 cSt), given to male rats for 10 weeks (3 times weekly) before mating or to female rats from two weeks before mating until the end of lactation, had no effects on dams, pregnancy or offspring (Kennedy et al., 1976). A 7 cSt fluid was not teratogenic in rats at an oral dose of 1000 mg/kg (Kennedy et al., 1976).

4.3.2.3 Mutagenicity

In the Ames test PDMSs were not mutagenic (Marshall et al., 1981; Roidl, 1983). A 7-cSt PDMS fluid was non-mutagenic in mice at intraperitonal doses of 5 or 10 mg/kg (Kennedy et al., 1976).

4.3.2.4 Carcinogenicity

Ben-Hur and Neuman in their first experiment (1963) found in 2 of the 36 mice treated subcutaneously with 2 or 3 ml PDMS adenocarcinomas, but this finding was not confirmed by their next experiment (1965) or by Grasso et al. (1964). In a lifespan study mice were given for 76 weeks either 2.5% dietary antifoam containing 94% PDMS and 6% finely divided SiO_2 or a single subcutaneous injection of 0.2 ml of the antifoam. There was no increase in the incidence of malignant or benign tumours (Cutler et al., 1974). Diet containing 0.1% silicone fluid fed to three generations of male and female rats did not produce any significant change in health parameters including tumour incidence (FAO/WHO, 1975).

4.3.3 Silicon polyether copolymer fluids

These copolymers are mainly used in cosmetics. The results of their safety assessment, reviewed and tabulated by the Cosmetic Ingredient Review Expert Panel (1982), is summarised as follows.

Without exception the oral LD_{50} values of seven polyether copolymers were more than 10 g/kg in the rat. Exposure to 1% or 4% copolymers in the diet for 89 days had no deleterious effects in the same species. In rabbits at the dermal application of 200 mg/kg day for 28 days slight to moderate erythema (reddening of the skin) and oedema were observed, but without any other clinical or pathological abnormalities. In acute experiments undiluted samples caused only mild irritation. None of the 200 human subjects exposed dermally to undiluted polyether copolymers exhibited irritation and only one of 19 persons exhibited very mild irritation at the site of an occlusive patch test made with 40% copolymer emulsion.

4.3.4 Polymethylphenylsiloxane fluids

A handcream formulation which was taken off the market contained equilibrated methylphenylcyclotetrasiloxanes with oestrogenic properties resulting in testicular atrophy and alteration in spermatogenesis in rabbits and rats (Palazzalo et al., 1972). The most active constituent was 2,6-cis-diphenylhexamethyl- cyclotetrasiloxane (but not the 2,4-cis or the 2,6-trans isomers). Monophenyl heptamethylcyclotetrailoxane was somewhat less active. The linear diphenyltetramethyl- disiloxane and diphenylhexamethyltrisiloxane showed some activity but compared with the two cyclotetrasiloxanes their threshold doses were approximately a hundred times higher (Bennett et al., 1972). Compounds which were androgenic also affected the female reproductive system (Hayden and Barlow, 1972).

The high biological acitivity of 2,6-cis-diphenylhexamethylcyclotetrasiloxane is in contrast to its very low acute lethal toxicity. Thus the oral LD_{50} cannot be estimated in the mouse or in the rat because the stomach has too small a volume to take a lethal dose (Albanus et al., 1975). In the dog 40 days treatment with 250 mg/kg day was without any clinically observed effect, though at the end of one week treatment with 10 mg/kg day a significant decrease in ejaculate volume and increase in sperm tail abnormalities were observed (Albanus et al., 1975).In rabbits after two daily doses of 2.0 mg/kg there was some vacuolated cells with necrotic nuclei in the epididymal epithelium (Nicander, 1975). In the rhesus monkey (Macaca mulatta) 28 days treatment with 0.1 mg/kg, 1.0 mg/kg or 10.0 mg/kg resulted in pyknotic cells in the epididymis, disruption of spermatogenesis and gross

tubular atrophy respectively (LeVier et al., 1975). In castrated female rats 3 days treatment with 0.1 mg/kg increased uterine weight. In pregnant rats 0.33 mg/kg day given on days 1-5 gestation inhibited implantation. Treatment with 10 mg/kg day on 6-11 days of gestation, especially between 8-11 days, caused resorption. Pregnancy was unaffected by 2,6-cis given after day 11 of gestation (LeVier and Jankowiak, 1972).

Polymeric polymethylphenylsiloxanes are non-oestrogenic and expected to behave similarly to their PDMS counterparts (Firmin, 1982).

4.3.5 Silicone elastomers and resin

There are conflicting experimental reports on the effects of implanted silicone elastomers. Elastomers injected in large quantities in the fluid form may cause problems until the end of the curing process, as indicated by the observation that in a transsexual patient suffering from acute postinjection respiratory distress, bronchoalveolar washing contained silicone in the original fluid form (Editorial, 1983). Damage to blood vessels caused by large volumes of silicone injected subcutaneously for hip augmentation may have been responsible for the death of another transsexual patient who had received monthly 1 litre of silicone fluid and died of pneuminitis after the sixth injection (Durocher et al., 1983). The use of elastomer dressing, a non-adherent, non-allergic, slightly absorbent material which allows air to contact the wound, proved to be without adverse effects (Wood et al., 1977).

4.3.6 Some other organosilicons

Mercapto-functionalised silicone oil, a PDMS derivative release agent for xerographic toner, in acute toxicity tests produced only transient eye irritation and barely perceptible skin irritation. An oral dose of 34.6 g/kg caused temporary hypoactivity and laboured breathing, inflammation in the stomach and intestines, but no death (Parent, 1979a). Inhalation exposure of rats to 0.45 mg/l (6 h per day, 5 days per week) for a period of 90 days or dermal exposure of mice to 50 mg (three times weekly for 18 months) neither influenced weight gain nor produced clinical, haematological or pathological effects (Parent, 1979b,c).

DC FS-1265 fluid containing trifuoromethylpoly- siloxane (Hobbs et al., 1972) and trifluoropropylmethylcyclotrisiloxane (Siddiqui and Hobbs, 1982) did not affect the reproductive organs of rabbits. Daily dermal application of 40 mg/kg trisiloxane for 21 days did not cause adverse reaction, but 200 mg/kg.day affected weight gain and 400 mg/kg.day was lethal to five of 12 rabbits (Siddiqui and Hobbs, 1982).

Certain alkyl quarternary ammonium alkoxysilanes have been shown to confer antimicrobial properties to solid surfaces to which they adhere. 3-(Trimethoxysilyl)-propyldimethyl-octadecyl ammonium chloride is a representative of this group (Isquith et al., 1972) and used commercially to confer bacteriocidal and fungicidal properties to socks, hospital bed sheets, carpets, air filter etc. The compound was not removed from surfaces with repeated washing with water (Isquith et al., 1972) and there are no data indicating any adverse effect.

Other silylated organic compounds share the biological activity of the respective parent compound (Garson and Kirchner, 1971; Wannagat, 1977).

The most toxic organosilicon compounds are among the silatranes. Thus the LD_{50} of p-tolysilatrane is 0.2mg/kg in mice. Cold blooded animals, like frogs, are resistant to the toxic effects of silatranes (Garson and Kirchner, 1971). Their use as rodenticide was abandoned because of its rapid decomposition in damp baits (Rennison, 1974).

4.4 Total exposure to organosilicons

Man can be exposed to silicone from (a) the working environment, (b) the use of products, eg paint, waxes, cosmetics, (c) medical treatment, and (d) food.

There are no data on the degree of occupational exposure to silanes, silanols or siloxanes or intoxication of occupational origin (Stokinger, 1981) with the exception of lacrimation, running nose and cough in workers exposed to tetrachlorosilane vapour and hydrolysis products after an accidental spillage from a storage tank (Kizer et al., 1984).

Though burns caused by contact with chlorosilanes are a real possibility, poisoning by polymers is not, because a 70 kg worker would have to ingest 100 to 300 g polymer to be severely affected (Stokinger, 1981).

The use of products containing organosilicon polymers makes dermal exposure a frequent but so far not quantified event for the general population. The use of organosilicons in cosmetic surgery and other forms of medical treatments presents a less frequent but larger exposure. Breast and hip augmentation may require the subcutaneous injection of many litres of silicone elastomer. Against flatulence up to 2 g PDMS can be administered orally each day and less is given to decrease abdominal discomfort after hysterectomy and caesarian section or to improve the quality of ultrasonography. Elastomer dressing of granulating wounds, the use of silicone oil bath for the treatment of open wounds and the use of creams, lotions and ointments with 10 to 30% silicone content for the prevention of bedsores are the main sources of dermal exposure.

The most widespread exposure to organosilicons is with food. The use of PDMS in bottle washing (making use of their surface active properties), edible oil processing, in fermentation, in the manufacture of jam, jelly, marmalade, instant coffee, tea or cocoa, in soft drinks, meat extracts, frying oil, potato crisps and pickles makes dietary exposure to polyorganosiloxanes virtually unavoidable in many societies. The permitted concentration in food products can be as high as 10 ppm (Denmark, U.K., U.S.A.), though in the U.S.A. the limit is nil for milk, in Sweden 0.2 ppm for fruit juice and canned peas, in the F.R.G. 3.0 ppm for frying oil (Brinker et al., 1984). The actual concentration is usually lower than 10 ppm, thus in the U.K. 2.5 ppm was measured in marmalade (Brinker et al., 1980) and 0.15 to 0.2 ppm in beer (Baker and Boddy, 1977). According to a FAO/WHO Expert Committee (1975) the acceptable daily intake for man is 0 - 1.5 mg/kg.

At present it is impossible to calculate total exposure to organosilicons or intake from food. Because of the low to nil absorbability of polymers some variation in intake cannot cause meaningful variation in uptake.

4.5 Contribution of organosilicons from marine food

There is no data on organosilicon concentrations in marine food products. Watanabe et al. (1984b) in the Nagara River area, where industrial effluents and sludge were sometimes heavily contaminated with silicone found measurable concentrations (2.0, 2.0, 2.8, 7.9 and 54.2 ppm) in five of the nine water samples. Mean and maximum silicone concentrations in four fish species were below 1.0 ppm, though in 6 deep bodied crucian carp (Carassius cuvieri) the maximum concentration was 4.47 ppm with 0.69 ppm mean. The low bioconcentration and biomagnification factors (Bruggeman et al., 1984; Aubert et al., 1985 and the review of Vonk et al., 1984), and the limited spread of contamination from rivers and estuaries to sea due to the low mobility of sedimented organosilicons (Pellen, 1979b; CEFIC, 983; Eales and Taylor, 1983), makes it unlikely that organosilicons in marine food can have a significant impact on total exposure to organosilicons.

4.6 Evaluation of potential health effects

It is very unlikely that organosilicons in marine food products present any hazard to human health. However it must be pointed out that in the absence of comprehensive analytical data on silicone concentrations in unprocessed marine food products, this view is based on (a) experimental evidence on bioaccumulation or biomagnification, (b) the dependence of gastrointestinal absorption on molecular size and on practical experience obtained from the use of organosilicons in medicine.

5. SUMMARY AND CONCLUSIONS

The theoretical number of organosilicon compounds is extremely large because most organic compounds can be converted to organosilicon by replacement of one or more carbon atoms by silicon or by silylation. The presence of silicon does not change substantially the toxic characteristics of the parent compound, therefore organosilicons do not form a distinct group from the toxicological point of view. Consequently it is impossible to evaluate the organosilicons as one single group with regard to their hazard rating in "black" and "grey" lists of international treaties, i.e. with regard to their toxicity, persistence and bio-

accumulation. The specific properties that an organic compound obtains upon the inclusion of silicon relate to:

- increased tendency for polymerization;
- changes in surface activity;
- changes in adsorbability.

Also when the organosilicons are subdivided into more uniform chemical subgroups the assessment of toxicity and environmental fate of organosilicons is impaired by the lack of comprehensive analytical data on concentrations in fresh marine products. Data are also missing on toxicological and environmental properties of individual organosilicon compounds.

5.1 Potential harm to living resources

Organosilicon input into the marine environment is completely anthropogenic and it is derived mainly from the use of organosilicon products and not from processes associated with their production or transport. Wastewater contaminated with silicone washed off from surfaces and accidentally or intentionally released, eg with break fluids, may be further enriched in sewage disposal plants with silicone antifoam. In spite of filtering of the sludge, some organosilicon is released with the effluent, but more may be dumped with sludge into rivers and estuaries. Organosilicons attached to solid particles are likely to be removed by sedimentation from the water column, while fluid can form a microlayer on the water surface. However their low surface tension promotes adsorption by solid particles and therefore sedimentation. The mobility of sedimented organosilicons is low and associated with the movement of fine-grained bottom sediments (Pellenbarg, 1979). Small molecular weight polymers, like octamethylcyclotetrasiloxane are lost from water mainly by evaporation. Volatility may explain why in sediments less than 1.0% of the total organosilicon concentration was in the form of octamethylcyclotetrasiloxane (Ann Arbor Technical Services, 1985).

The practical absence of octamethylcyclotetra- siloxane in sedimented organosilicons near to wastewater treatment plants is important, compared to other organosilicons, because this compound has an outstandingly high bioconcentration factor when the effect of volatization on exposure is cancelled by maintaining water concentration at a constant level. In this case the bioconcentration factor was 1200 for the fathead minnow (Pimephales promales) (Annelin, 1984). In feeding experiments no measurable concentration could be achieved in guppies, because the same compound rapidly escaped from the supplemented food (Bruggeman et al., 1984). For linear siloxanes with 6 to 12 silicon atoms and cyclosiloxanes with 6 and 9 silicon atoms the biomagnification factor was 0.16 or less (Bruggeman et al., 1984). A foodchain experiment also indicated that exposure to 47 cs PDMS resulted in similarly low bioaccumulation factor, expressed as a concentration ratio between water and molluscs (Mytilus edulis) or fish (Carassius auratus) though their respective food, a phytoplankton (Tatraselmis sp) and a plankton (Artemia) concentrated PDMS by a factor of 2 (Aubert et al., 1985).

These data indicate that those low molecular weight polymers, which are absorbed from the gastrointestinal tract of mammals (LeVier et al., 1977) have the potential to bioconcentrate, and larger compounds, which are not absorbed through the gastrointestinal tract of mammals do not bioconcentrate and have no biomagnification potential.

Low water solubility restricts concentration for both groups to below 5 ppm and mostly to the ppb range. They are removed from the water body or water surface by adherence to sedimenting particles. In the case of low molecular weight siloxanes evaporation accelerates clearance and acts against bioaccumulation.

Toxicological data indicate that the sensitivity of marine organisms to silicones is very low. The experiments of Maggi and Alzieu (1977) demonstrated that 96 h exposure to saturated solutions of 100, 300 or 12,500 cSt PDMSs caused no mortality in a variety of marine species. Table 1. shows that every species so far tested has LC_{50} values for various organosilicons above and frequently substantially above the solubility limit.

Mammalian experiments indicated that siloxanes with more than 6 silicon atoms are not absorbed from the gastrointestinal tract and this observation gives weight to the few bioconcentration and magnification experiments which showed that the bioaccumulation factor in marine organisms is less than one. Thus low bioaccumulation, low toxicity, low water solubility and the volatility of low molecular weight polymer argue against the possiblity of a significant environmental impact.

5.2 Potential hazards to human health

In the absence of occupational exposure or medical treatment with fluids or elastomers, organosilicons are acquired through the ingestion of food. Organosilicons are intentionally added to food and drink products to prevent foaming during their industrial processing. There is experimental evidence which indicate that the gastrointestinal absorption of siloxanes is limited to small molecular weight compounds which are not present in food additive silicones.

There are no data on organosilicon concentrations in human tissues, but the rapid clearance of small molecular weight compounds and the non-absorbeability of large molecular weight polymers argue against the possibility that oral intake could increase organosilicon concentration in the body, outside of the gastrointestinal content, above detection limit.

There is a wide variation in the toxicity of organosilicons but, as a result of change in the synthetic pathway, polymethylphenyl polymers no longer contain oestrogenic derivatives and the production of toxic silatranes is extremely low, mainly to satisfy research. Apart from these two groups and chlorosilanes, which act through the hydrolytic release of HCl, the toxicity of organosilicons is very low as shown by tolerance to implanted elastomers. Dietary intake probably shows wide variation, but it is unlikely that exposure exceeds the upper limit of acceptable daily intake of 1.5 mg/kg set by a FAO/WHO Expert Committee (1984).

The contribution of marine fish or other seafood to the daily organosilicon intake has not been investigated. Low water concentration of silicones in the effluents of wastewater treatment plants (Pellenbarg, 1979a), the practical absence of octamethylcyclotetrasiloxane (with a substantial bioconcentration potency) in organosilicon contaminated sediments (Ann Arbor Technical Services, 1985), the low mobility of sedimented silicone (Pellenbarg, 1979b) and the lack of bioconcentration or biomagnification (factors below 1.0) in molluscs and fish (Aubert et al., 1985; Bruggeman et al., 1984) suggest that organosilicons in fresh marine products cannot contribute significantly to total intake and cannot increase organosilicon intake to a hazardous level.

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SECOND SESSION OF THE GESAMP WORKING GROUP
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PUBLICATIONS IN THE UNEP REGIONAL SEAS REPORTS AND STUDIES SERIES

No. 1 UNEP: Achievements and planned development of UNEP's Regional Seas Programme and comparable programmes sponsored by other bodies. (1982)

No. 2 UNIDO/UNEP: Survey of marine pollutants from industrial sources in the West and Central African region. (1982)

No. 3 UNESCO/UNEP: River inputs to the West and Central African marine environment. (1982)

No. 4 IMCO/UNEP: The status of oil pollution and oil pollution control in the West and Central African region. (1982)

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No. 7 UNIDO/UNEP: Industrial sources of marine and coastal pollution in the East African region. (1982)

No. 8 FAO/UNEP: Marine pollution in the East African region. (1982)

No. 9 WHO/UNEP: Public health problems in the coastal zone of the East African region. (1982)

No. 10 IMO/UNEP: Oil pollution control in the East African region. (1982)

No. 11 IUCN/UNEP:Conservation of coastal and marine ecosystems and living resources of the East African region. (1982)

No. 12 UNEP: Environmental problems of the East African region. (1982)

No. 13 UNEP: Pollution and the marine environment in the Indian Ocean. (1982)

No. 14 UNEP/CEPAL: Development and environment in the Wider Caribbean region: A Synthesis. (1982)

No. 15 UNEP: Guidelines and principles for the preparation and implementation of comprehensive action plans for the protection and development of marine and coastal areas of regional seas. (1982)

No. 16 GESAMP: The health of the oceans. (1982)

No. 17 UNEP: Regional Seas Programme: Legislative authority. (1985)

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No. 25 UNEP: Marine pollution. (1983)

No. 26 UNEP: Action Plan for the Caribbean environment programme. (1983)

No. 27 UNEP: Action Plan for the protection and development of the marine environment and coastal areas of the West and Central African region. (1983)

No. 28 UNEP: Long-term programme for pollution monitoring and research in the Mediterranean (MED POL) - Phase II. (1983)

No. 29 SPC/SPEC/ESCAP/UNEP: Action Plan for managing the natural resources and environment of the South Pacific region. (1983)

No. 30 UNDIESA/UNEP: Ocean energy potential of the West and Central African region. (1983)

No. 31 A. L. DAHL and I. L. BAUMGART: The state of the environment in the South Pacific. (1983)

No. 32 UNEP/ECE/UNIDO/FAO/UNESCO/WHO/IAEA: Pollutants from land-based sources in the Mediterranean. (1984)

No. 33 UNDIESA/UNEP: Onshore impact of offshore oil and natural gas development in the West and Central African region. (1984)

No. 34 UNEP: Action Plan for the protection of the Mediterranean. (1984)

No. 35 UNEP: Action Plan for the protection of the marine environment and the coastal areas of Bahrain, Iran, Iraq, Kuwait, Oman, Qatar, Saudi Arabia and the United Arab Emirates. (1983)

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No. 38 FAO/UNEP: Legal aspects of protecting and managing the marine and coastal environment of the East African region. (1983)

No. 39 IUCN/UNEP: Marine and coastal conservation in the East African region. (1984)

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No. 41 UNEP: Socio-economic activities that may have an impact on the marine and coastal environment of the East African region. (1984)

No. 42 GESAMP: Principles for developing coastal water quality criteria. (1984)

No. 43 CPPS/UNEP: Contingency plan to combat oil pollution in the South-East Pacific in cases of emergency. (1984)

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No. 53 UNEP: UNEP Regional Seas Programme: the Eastern African Experience. (1984)

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No. 59 UNEP: Environmental problems of the marine and coastal area of India: National Report. (1985)

No. 60 IUCN/UNEP: Management and conservation of renewable marine resources in the Indian Ocean region: Overview. (1985)

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No. 64 IUCN/UNEP: Management and conservation of renewable marine resources in the Red Sea and Gulf of Aden region. (1985)

No. 65 IUCN/UNEP: Management and conservation of renewable marine resources in the East Asian Seas region. (1985)

No. 66 IUCN/UNEP: Management and conservation of renewable marine resources in the Eastern African region. (1985)

No. 67 UN/UNEP: Coastal erosion in West and Central Africa. (1985)

No. 68 GESAMP: Atmospheric transport of contaminants into the Mediterranean region. (1985)

No. 69 UNEP: Environment and resources in the Pacific. (1985)

No. 70 UNESCO/ROPME/UPM/UNEP: Proceedings of the Symposium/Workshop on oceanographic modelling of the Kuwait Action Plan (KAP) region. (1985)

No. 71 IUCN/ROPME/UNEP: An ecological study of the rocky shores on the southern coast of Oman. (1985)

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No. 74 UNEP: Environmental problems of the marine and coastal area of Sri Lanka: National Report (1986)

No. 75 UNEP: Environmental problems of the marine and coastal area of Bangladesh: National Report (1986)

No. 76 UNEP: Environmental problems of the marine and coastal area of Maldives: National Report (1986)

No. 77 UNEP: Environmental problems of the marine and coastal area of Pakistan: National Report (1986)

No. 78 GESAMP: Organosilicons in the marine environment. (1986)

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