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AN ASSESSMENT OF ORGANOSILICONS AS MARINE POLLUTANTS,  
WITH PARTICULAR REFERENCE TO THEIR STATUS IN THE  
MEDITERRANEAN DUMPING AND LAND-BASED SOURCES PROTOCOLS

# CONTENTS

	<u>Pages</u>
INTRODUCTION	1
EXECUTIVE SUMMARY	1 - 2
1. BACKGROUND	2 - 3
2. ASSESSMENT OF THE RATIONALE FOR THE LEGAL PROTECTION OF THE MARINE ENVIRONMENT	3 - 5
3. TOXICITY TO MARINE LIFE AND HUMANS	5 - 12
3.1 General comments	5
3.2 Bioconcentration and gastrointestinal absorption	5 - 6
3.3 Aquatic behaviour and toxicity	6 - 9
3.3.1 Silanes and silanols	6 - 7
3.3.2 Polydimethylsiloxane (PDMS) fluids	7 - 8
3.3.3 Silicone polyether copolymer fluids	8
3.3.4 Polymethylphenylsiloxane fluids	8
3.3.5 Organosilicone elastomers (rubbers) and resin	9
3.4 Mammalian toxicity including toxicity to humans	9 - 12
3.4.1 Silanes and silanols	9
3.4.2 Polydimethylsiloxane (PDMS) fluids	10 - 11
3.4.2.1 General toxicity	10
3.4.2.2 Reproduction, mutagenicity, carcinogenicity	11
3.4.3 Silicone polyether copolymer fluids	11
3.4.4 Polymethylphenylsiloxane fluids	11
3.4.5 Organosilicon elastomers (rubbers) and resin	11
3.4.6 Methylsiloxane derivatives	12
4. ASSESSMENT OF EFFECTS AND RISK TO MARINE BIOTA	12 - 15
4.1 Risk associated with silanes and silanols	12
4.2 Risk associated with siloxanes	12 - 13
4.3 Risk associated with production, transport and use	13 - 14
4.4 Risk associated with surface and sedimental layers	14
4.5 Conclusion on risk to marine biota	15
5. ASSESSMENT OF EFFECTS AND RISK TO HUMAN HEALTH	15
6. RATIONALE FOR CHANGING THE STATUS OF ORGANOSILICONS	16
7. PROPOSALS CONCERNING STATUS	17
8. MEASURES PROPOSED FOR ADOPTION BY THE CONTRACTING PARTIES	17 - 18
TABLE 1	19 - 20
9. REFERENCES	21 - 23

## INTRODUCTION

The protocol for the prevention of pollution of the Mediterranean Sea by dumping from ships and aircraft (UNEP, 1978) adopted by the Mediterranean coastal States in 1976, includes in annex I thereto "Organosilicon compounds and compounds which may form such substances in the marine environment, excluding those which are non-toxic or which are rapidly converted in the sea into substances which are biologically harmless, provided that they do not make edible marine organisms unpalatable". Under the terms of Article 4 of the protocol, the dumping into the Mediterranean Sea Area of wastes or other matter listed in annex I is prohibited.

In the protocol for the protection of the Mediterranean Sea against pollution from Land-based Sources (UNEP, 1980), adopted by Mediterranean States in 1980, "Organosilicon compounds and substances which may form such compounds in the marine environment, excluding those which are biologically harmless or are rapidly converted into biologically harmless substances", appear in annex II thereto, thereby, under the terms of Article 6 of the protocol, requiring an authorization from competent national authorities for inclusion in effluent discharges into the sea.

Recent information on the status of organosilicon compounds as marine pollutants has led to reviews of their position within the annexes of relevant global and regional marine pollution conventions, resulting in the adoption of less stringent statutory measures regarding these compounds.

In conformity with the principle of updating the annexes to protocols adopted under the terms of the 1976 Convention for the protection of the Mediterranean Sea against pollution as and when necessary, and at the request of one Contracting Party to the Convention and both protocols, the position regarding organosilicon in both the protocols mentioned above has been reviewed. The present document constitutes the scientific review carried out, and includes, on the basis of such review, appropriate proposed measures to the Contracting Parties with regard to each protocol.

## EXECUTIVE SUMMARY

Organosilicon compounds include two groups. one group consists of the silicon derivatives of organic compounds. This group is open ended because by silylation (the replacement of hydrogen atoms by organosilyl ( $R_3Si$ ) groups) or by sila substitution (the replacement of carbon by silicon) infinite number of compounds can be synthesised. Silylation and sila substitutions do not change the basic characteristics of the parent compound and therefore regulations on dumping, or discharge from land-based sources, must be based on the toxicity and behaviour of the parent compound.

The second group consists of siloxanes, and their precursors, silanes and silanols. Silanes and silanols are unstable. Their toxicity is inversely related to their stability, and is the consequence of hydrolysis to hydrochloric acid (chlorosilanes) or organic acids (alkoxysilanes). Dilution limits the effect of acids both in time and space. Dilution also prevents the condensation of the other hydrolytic product, silanol, to siloxane. When condensation is prevented, silanols are more stable than silanes, though slowly decompose to carbon dioxide and silicic acid.

As a consequence of their chemical inertness, siloxanes are persistent and have fairly low toxicity. Other characteristics are low water solubility, high viscosity and low bioconcentration and biomagnification potential. The volatility of oligomers prevents exposure to a steady concentration, while biological membranes are impermeable to polymers with a molecular weight of @ @600. Low water solubility, low bioaccumulation potential and low toxicity explain why observed concentrations in the aquatic environment are several orders below the toxic concentration for algae, the most sensitive species. Low toxicity to the marine biota is mirrored by low toxicity to man. The use of silicones in medicine, orthopedic and plastic surgery and cosmetics, and the use of PDMS as an antifoaming agent in the food industry testify to the low toxicity of siloxane polymers. Polyether copolymers, which are composed from hydrophilic polyalkylene groups or blocks and lipophilic siloxane blocks, can be water soluble, but their size prevents bioconcentration or gastrointestinal absorption.

The available data also indicate that in spite of the large scale use of organosilicon compounds over the last forty years, the presence of organosilicons is limited to very small areas of direct input. The highest levels were measured not in the water column, but in temporary surface films ( 40 ppb) or in sediments ( 3.0 ppm). Though sediment contained 40 ppm in the centre of the New York Bight sludge dumping site, near to Long Island no silicone pollution could be detected.

In summary, compounds characterised by the presence of Si-O- chain have very low toxicity and bioaccumulation potential. Their solubility is several orders below the toxic concentration and the same could be said about their concentration in surface films and the upper sedimental layer. Thus organosilicons built up from siloxane units and also their precursors do not pollute the marine environment to the extent which can endanger biota or amenities. Siloxanes form a well defined entity in the larger groups or organosilicone compounds. Silylated or sila substituted organic compounds do not share the characteristics of siloxanes, but the characteristics of the parent (organic) compounds. If and when such a compound becomes a marine pollutant, protocols covering synthetic organic compounds and pesticides will give adequate protection against their dumping and release into the marine environment.

## 1. BACKGROUND

Developments in organosilicon chemistry and increase in the commercial use of organosilicons, mainly polymers, and the possibility of parallel aquatic behaviour with organohalogen compounds, resulted in legal restrictions on the dumping of organosilicons into the marine environment. The absence of comprehensive knowledge on the behaviour and toxicity of these compounds was reflected by the non-uniformity of decisions. Thus the first two conventions which dealt with the problem, the Oslo (1972) and the London (1972) Dumping Conventions, though both held in the same year, recommended different restrictive practices. The Oslo Convention listed organosilicons in Annex I (the "black" list), thereby prohibiting their dumping (except for those compounds which are non-toxic, or which are rapidly converted in the sea into substances which are biologically harmless); while the London Convention (LDC, 1972) listed organosilicons in Annex II (the "grey" list), thereby permitting disposal under special licence). The Paris Convention (1974) followed the line of the London Convention, while the Barcelona Convention and its related protocols (UNEP, 1982) kept organosilicon compounds on the "black list" with

the exclusion of those which are non-toxic or rapidly converted into biologically harmless form and do not taint edible marine organism. In 1980, the Oslo Commission agreed that polydimethylsiloxanes (PDMS) could be entered on a register as being organosilicon compounds which are "non-toxic" and in 1985 removed all reference to organosilicon compounds from Annex I to the Convention and retained in Annex II only "persistent toxic organosilicon compounds". In the same year the Paris Commission decided that the listing of organosilicon compounds in the grey list should remain and that no change should be made to the terminology used in order to harmonize it with the Oslo Convention. Both Commissions acknowledged that no organosilicon compounds commercially produced at present are both persistent and toxic, and that polydimethylsiloxanes, which constitute about two-third of the organosilicon compounds "market", do not fall within the definition of a persistent, toxic organosilicon compounds. The latest London Convention (LDC, 1986) went one step further. Based on the view expressed by the Scientific Group on Dumping (LDC/SG.9, 1986) that "all available scientific evidence supported the removal", it removed organosilicons from the grey list. However, in the draft report, the delegations of Belgium, Denmark, Finland and the Netherlands expressed their opinion that the retention of certain organosilicon compounds in Annex II may be prudent, due to their synthetic nature, their extreme persistence and doubt about the quantities released in to the marine environment".

The critical comments made by delegations representing four Contracting Parties to the London Dumping Convention, and the existing differences in the recommendations of various conventions, are important because they indicate that the debate about the level of ecological hazard presented by organosilicons has not ended. The reason for the preparation of the present document is to elucidate those characteristics of organosilicons which are pertinent to this debate.

## 2. ASSESSMENT OF THE RATIONALE FOR THE LEGAL PROTECTION OF THE MARINE ENVIRONMENT

Toxicity, persistence and bioaccumulation are the three main characteristics which determine the degree of hazard to an ecosystem. However none of these terms imply a self-explanatory and absolute quality. When referring to a single compound, the questions are how toxic, persistent or accumulative such a compound may be. These qualities can be quantitated and the possible ecological impact predicted from comparing these values with the toxicity, persistence and bioaccumulation of other compounds with known ecotoxicological effects. Judging from the 0.2 mg/kg LD 50 for mice (the dose killing 50% of experimental animals) of p-tolylsilatrane, silatranes can be extremely toxic (Garson and Kirchner, 1971). Silicone elastomers and resins are very persistent (Firmin, 1982) and when steady aquatic concentration was maintained, octamethylcyclotetrasiloxane had a bioconcentration factor of 1200 for the fathead minnow (*Pimephales promelas*) (Annelin, 1984). Thus, individual members of the organosilicon group of compounds show at least one of the three characteristics which justify legal restrictions on their dumping or on their input from land-based sources. Such considerations clearly influenced the recommendations of the Conventions to list organosilicons in one of the Annexes. The view that adverse effects to the ecosystem depend on the degree of exposure was also accepted as shown e.g. by the recommendation of the London Dumping Convention in 1972 when organosilicon concentrations from land-based sources were judged to be insignificant below 0.1%.

When some other qualities of silatranes, organosilicon elastomers or octamethyltetracyclosiloxane are considered, quite different conclusions can be drawn. Silatranes promised to be the ideal rodenticides, which kill the rat but because of rapid *in vivo* decomposition, do not cause secondary poisoning (e.g. in the cat which eats the dead rat). However, the use of silatranes as rodenticides had to be abandoned, partly because they also decomposed in dump baits (Rennison, 1974). Even if they were used and could reach the aquatic system, their rapid decomposition should render them innocuous.

Elastomers and resins are very persistent but also inoffensive, which explains their use in medicine. They are solid materials and only their use in the paint industry (as hardeners and accelerators) can contribute to pollution from land-based sources.

Though the bioconcentration potential of octamethylcyclotetrasiloxane is high (Annelin, 1984), its solubility in purified water is less than 0.6 ppm and more than 15 to 20 fold less in seawater (Firmin, 1984). Moreover, when 0.6 ppm was added to filtered water, concentration declined 6-fold within 1 day and 16-fold within 2 days (Annelin, 1984). When added to dry food, similarly to other cyclic and linear organosiloxanes with molecular weight below 400, volatilization made it impossible to carry out biomagnification studies in guppies (Bruggeman *et al.*, 1984). Octamethylcyclotetrasiloxane in a wastewater treatment plant could be detected only in two of the three WWTP-sludge cake samples (less than 0.5% of the total silicone) and there was none, or amounts below detection limits, in other samples (digester filter cake or final effluent). Only one of the six fresh water sediment samples had detectable amounts (0.07 mg/kg or 0.8% of total silicone) and none was found in 15 salt water sediment samples, though 9 of them had a measurable amount of silicone (Ann Arbor Technical Services, 1985).

One argument used for the introduction or retention of restrictions on marine pollution by organosilicons is based on the possibility of new uses for existing fluid silicones. Another argument is that new organosilicon compounds, which will exceed the presently used organosilicons in toxicity, persistence or bioaccumulation potential, or some other effects detrimental to the marine environment will be marketed. Thus, it is suggested that the replacement of polychlorinated biphenyls (PCBs) formulations in dielectric fluids by polydimethylsiloxane (PDMS) fluids has the potential to increase marine pollution by this polymer. In view of low water solubility, low surface tension, the retention with sewage particles in wastewater treatment plants and the economic interest to lose as little and recover as much as possible, this new use of PDMS may not increase land-based sources of organosilicon pollution significantly, and certainly not beyond sediments in the vicinity of input. The other consideration that the highly toxic PCBs will be replaced by inert PDMS is beyond the scope of this document.

As far as the possibility that so far unknown or at least unused compounds will be introduced into the market is concerned, one must consider that these would fall into one of the following two categories. Either they would retain the siloxane structure or will be the silicon analogues of organic compounds in which one or more hydrogen is replaced by trimethylsilyl group (silylation) or carbon is replaced by silicon (sila substitution). In the case of new siloxanes, the new oligomer or polymer would share the basic characteristics of one of the existing siloxane groups. Contrary to siloxanes, the introduction of silicon into an organic compound by silylation or sila substitution would modify but not change the basic biological characteristics of the parent compound (Vannagat, 1977). It may be that

silylation would increase the ability to penetrate through liquid membranes more easily, but rapid desilylation would cancel even this difference. Compounds obtained by sila substitution are usually metabolised faster than the parent compound. Whether the sila substituted compound is more or less active than the carbon parent compound depends on the relationship between structure, metabolism and biological action (Vannagat, 1977). In any case it seems reasonable to suggest that the protection of the marine environment against silylated or sila substituted products must depend on the characteristics of the parent organic compound and not on the presence of silicon.

### 3. TOXICITY TO MARINE LIFE AND HUMANS

#### 3.1 General comments

As an introduction to the toxicology of halogenated hydrocarbons, Irish (1963) made some remarks which are pertinent to the toxicology of organosilicons: "Not so many years ago, warning labels simply stated 'contains halogenated hydrocarbons' or 'contains chlorinated hydrocarbons'. The assumption appeared to be that they could all be considered in the same class. In examining the physiological response to different halogenated hydrocarbons, it becomes obvious that they cannot be lumped together in considering the hazard, either quantitatively or qualitatively".

This comment is even more valid for organosilicons than for halogenated hydrocarbon. The reason is that theoretically more organosilicons can be synthesised than halogenated hydrocarbons, and actually silylation and sila substitutions can increase the number of organosilicon compounds well above the number of organic compounds. However, based on the considerations mentioned in the previous paragraph, the present discussion is restricted to silanes, silanols and siloxanes.

Dimethyldichlorosilane, and a silanol, dimethylsilanediol, are intermediates of polydimethylsiloxane synthesis. In silanes organic radicals (alkyl, alkoxy, etc.) and hydrogen or/and halogen are attached to silicon, while in silanols, organic and hydroxyl radicals are so attached. When the compound has more than one silicon (e.g. disilane), the absence of an oxygen bridge between two silicons distinguishes these compounds from siloxanes. The characteristic of both linear and cyclic siloxanes is the alteration of Si-O- units. With the number of Si-O- units solubility in water decreases, while lipophilicity and viscosity increase. Polymers containing up to 2,000 Si-O- units remain fluid with increasing viscosity. Thus, kinematic viscosity (= viscosity/density), usually given in cSt (centiStoke), shows some degree of correlation with the number of Si-O- units (Howard *et al.*, 1974).

#### 3.2 Bioconcentration and gastrointestinal absorption

The tendency of a chemical to distribute between two separable phases, as between water and lipid or octanol, is measured by the equilibrium constant in the two phases. Both the lipid-water and octanol-water partition coefficients are indicators of the ability of an organic or organosilicon compound to penetrate cell membranes including the gastrointestinal tract. The bioconcentration factor (concentration in tissue, usually flesh, per concentration in water) can be predicted from the octanol-water partition coefficient ( $K_{ow}$ ) (Chiou, 1981). Though the bioconcentration factor increases with the octanol-water partition coefficient, the time to reach the

predicted steady state concentration in a marine organism is increased with decreasing water solubility. The predicted concentration cannot be reached at all when the aqueous concentration declines (Chiou, 1981) by hydrolysis (e.g. silanes), evaporation (e.g. siloxane oligomers) or sedimentation (e.g. PDMS). Even under ideal conditions, the correlation works only up to a certain molecular weight, which in the case of the uptake of chlorinated paraffins by salmon is about 600 (Zitko, 1974). The significance of molecular weight is shown by the fact that the gastrointestinal absorption of linear siloxanes decreases with molecular weight from the smallest hexamethyldisiloxane (m.w. 162) to dodecamethylpentosiloxane (m.w. 384) by 80%. Tetradecamehtylhexasiloxane (m.w. 458) is not absorbed at all. The absorption of cyclic pentasiloxane (m.w. 370) is 30% and that of hexasiloxane (m.w. 440) is 10% of the gastrointestinal absorption of octamethylcyclotetrasiloxane (m.w. 296) (LeVier *et al.*, 1977).

The influence of molecular weight on bioconcentration (and also on biomagnification) = concentration in tissue per concentration in food) explains why the high bioconcentration factor of octamethylcyclotetrasiloxane (Annelin, 1984) is not shared by PDMSs. Bluegill sunfish exposed for 30 days to 1 or 10 ppm PDMS fluid of 300 cSt showed no accumulation in the flesh (Hobbs *et al.*, 1975). A similar conclusion was drawn from experiments in which black bluueheads (*Ictalurus melas*) were fed with 50 cSt PDMS fluid (Annelin, 1979). Worms exposed to 200 mg/1.47 cSt PDMS in the presence of bacteria and plankton, or fish and crustacea fed on exposed annelid worms, had a bioconcentration factor of 0.05. Both phytoplankton and plankton had a bioconcentration factor of 2.0, but molluscs (*Mytilus edulis*) and fish (*Crassius auratus*) fed on plankton had 0.24 and 0.1 bioconcentration factors respectively (Aubert *et al.*, 1985). Contrary to these observations Watanabe *et al.* (1984a) found significantly higher bioconcentration factors in silver carps exposed for 3 days to one of four PDMSs. Molecular weights ranged from 1,200 to 56,000. The bioconcentration factor increased with molecular weight from 2.9 to 1,250 and tissue concentration from 4.1 to 75.3 ppm. Such large molecules could not pass through biological membranes, but the possibility of surface contamination increases with viscosity. Thus, tissue residues estimated by the authors most likely gave concentrations in whole fish and not in flesh and consequently were unsuitable for the calculation of the bioconcentration factor.

From the point of view of bioaccumulation and gastrointestinal absorption, polyether copolymers and polymethylphenylsiloxane fluids behave like PDMS. The molecular weight of polyether copolymer fluids is too high to permit absorption, while low molecular weight phenylmethylcyclosiloxanes are easily absorbed through the gastrointestinal tract.

### 3.3 Aquatic behaviour and toxicity

#### 3.3.1 Silanes and silanols

Silanes undergo rapid hydrolysis in water. Degradation of chlorosilanes also produces HCl which is responsible for their prompt toxic effects. The 1 hr LC 50 of chlorosilanes was between 180 and 300 ppb (ug/l) in the brown shrimp (*Crangon crangon*) and the armed bullhead (*Agonus cataphractus*). The extension of exposure time did not increase mortality (Franklin, 1981). Different methoxysilanes in the 100 to 300 ppm concentration range caused 50% inhibition in algal growth (Vonk *et al.*, 1984). Alkoxy silanes, including vinyltriacetoxysilane, tested up to 100 ppm caused no mortality in crustaceans (Vonk *et al.*, 1984). In the rainbow trout (*Salmo gairdneri*) and bluegill

sunfish (*Leponis macrochirus*) the 96 hr LC 50 values were 237 ppm and 275 ppm for glycidoxypropyltrimethoxysilane. Rainbow trout was sensitive to vinyltrimethoxysilane (LC 50 = 191 ppm) while bluegill sunfish tolerated 1,000 ppm without any toxic effect. Decomposition to acetic acid is most likely responsible for the relatively low (68 ppm) 96 hr LC 50 of vinyltriacetoxy silane in bluegill sunfish (Firmin, 1984).

Under natural sunlight, or when irradiated with ultraviolet light, methylsilanols break down in water to carbon dioxide and silicic acid (Frye, 1980). Fathead minnows (*Pimephales promales*) exposed to a maximum of 10 ppm dimethylsilanediol for 60 to 90 days did not show any signs of bioaccumulation (Annelin and Buch, 1978). Exposure to 1,000 to 2,000 ppm trimethylsilanol, dimethylsilandiol or methylsilanetriol did not affect algal growth (Vonk et al., 1984), while the 96 hr LC 50 of dimethylsilanediol was 271 ppm in shore crab (*Pachygrapsus crassipes*), and 604 ppm in marsh shrimp (*Palaemonetes vulgaris*) (Firmin, 1984). In the rainbow trout, bluegill sunfish and killifish (*Fundulus heteroclitus*) 96 hr exposure to 1,000 ppm dimethylsilanediol caused only 10% death in the first species and non in the other two (Firmin, 1984).

### 3.3.2 Polydimethylsiloxane (PDMS) fluids

There is no evidence of biodegradation, but volatile methylsiloxanes decompose under the influence of UV light. PDMS undergoes hydrolysis and rearrangement in contact with the clay components of soil when the water content is not more than 3% (Frye, 1980). Thus, surface membranes or typical sedimental layers do not have the condition for this form of degradation.

As the densities are below 1, PDMS fluids have the ability to form surface films, but they are rapidly adsorbed onto particles and sink to the sedimental layer where mobility is low (Pellenbarg, 1979a, b; Gettings and Lane, 1982). As oxygen is more soluble in PDMS than in water (Clark and Gollan, 1966), PDMS layers cannot asphyxiate the biota.

The solubility of methylsiloxanes is very poor. In seawater the smaller molecular weight compounds have solubilities around the 50 ppb range, and the solubility of larger polymers is below 20 ppb (Firmin, 1984, Vonk et al., 1984). As most of the experiments were done at concentrations several orders above solubility, a substantial difference may exist between the concentration calculated from the weight of siloxane added to the known volume of water in the aquarium and the actual concentration.

Exposure to cyclic methylsiloxanes, at least up to 100 ppm concentration for 96 hr, did not affect algal growth or the mortality of marsh shrimp (*Palaemonetes vulgaris*). There was 10% mortality in brine shrimp (*Artemia salina*) exposed to 500 ppm for 24 hr (Meurice, 1981a). Zebra fish (*Brachydanio rerio*) tolerated 96 hr exposure to the same concentration (Bessemans, 1981) or 105 days exposure to 10 ppm (Meurice, 1981b).

True solutions of different PDMSs (100, 350 and 12,000 cSt) exerted no adverse effects during a 96 hr exposure period on a wide variety of marine organisms ranging from plankton to fish (Maggi and Alzieu, 1977). The community structure of a microcosm, including bacteria, algae and protozoa was not affected by 24 weeks exposure to 144 ppb (median) 55 cSt hydroxy endblocked PDMS (Gettings and Lane, 1982). In this experiment the concentration ranged from 17 to 260 ppb, but an even larger fluctuation would be expected with higher

concentrations because of the formation of surface film, sedimentation, adsorption onto the surface of the aquarium, and generally because of unequal distribution within the water column. Hobbs *et al.* (1975) found the 48 hr LC 50 of an antifoam with 30% PDMS emulsion (350 cSt) to be 244 ppm (73 ppm PDMS) in water flea (*Daphnia magna*). The authors observed that many water fleas became entrapped in the surface film and died there. However, as table 1 shows, the LC 50 values for many other species were more than 1,000 ppm, and in some cases, more than 10,000 ppm.

PDMS (50 cSt) mixed with bottom sediment in a flow-through test system did not affect the survival of the marine polychaete worm *Nereis diversicolor* up to 1,000 mg/kg concentration in 29 days experiments. Both 100 and 1,000 ppm delayed the burrowing activity of the worms by about 17 hours (Craig *et al.*, 1984). The effects of PDMS on other parameters (growth and body burden) could not be judged because of the laxity of presentation.

PDMS formulations can contain other compounds, e.g. emulsifiers. Mussels seemed to be more sensitive to the emulsifier than to PDMS (Aubert *et al.*, 1985). In another experiment sheepshead minnow (*Cyprinodon variegatus*) embryos and larvae were exposed to a PDMS formulation containing 60% water, 35% PDMS of 50 cSt and 5% emulsifiers. Besides the control group there were six exposure groups, five groups were exposed to the formulation at 91, 200, 293, 606 and 671 ppm and one group only to the emulsifier present in the water of the second highest exposure group. Hatchability and length were significantly decreased in the highest exposure group, but length was also decreased by the emulsifier. Survival was affected by the second and fourth exposure levels and by the emulsifier, while weight only by the emulsifier (Hill *et al.*, 1984).

### 3.3.3 Silicone polyether copolymer fluids

As polyether copolymers (also called silicone glycols) are polyalkylene (mostly polyoxyethylene or polyoxypropylene) blocks attached to blocks of siloxane polymers or polyoxyalkylene side chains grafted on a polymethylsiloxane backbone. The characteristics of these copolymers depend on both the polyether and polysiloxane constituents. Thus, some of them are water-soluble, others miscible or insoluble in water. Unlike PDMS, polyether copolymers are surfactants. Both water and solubility and surfactant property vary with the proportion of hydrophilic and lipophilic parts of the molecule (CIR Expert Panel, 1982).

There are no data on biodegradability, but photodegradation may be possible. As table 1 shows, green algae and rainbow trout were more sensitive to silicone polyether copolymer than to PDMS. Table 1 also shows the 48 LD 50 for *Daphnia magna* as 311 ppm, though other reported values for 48 h exposure are 486, 816 and 1,000 ppm. In a static test no effect was recorded after 21 days of exposure to 10 ppm (Firmin *et al.*, 1984).

### 3.3.4 Polymethylphenylsiloxane fluids

Polymethylphenylsiloxane fluids are expected to behave like PDMS. Low molecular weight compounds, mainly cyclic ones, are volatile and can pass through biological membranes. The molecular weight and viscosity of polymers can be as high as those of PDMSs, but their density is not below, but equal or above 1 and their water solubility is low (Howard *et al.*, 1974). Table 1 shows that the toxicity of PMPhS fluids to marine organisms does not exceed the toxicity of PDMS.

### 3.3.5 Organosilicon elastomers (rubbers) and resin

The cross linking of linear polymers through reactive (e.g. H, OH or vinyl) radicals results in the formation of solid materials insoluble in water and non-biodegradable. It has been suggested that *Streptomyces* may utilize acetate catalysator residues (Firmin, 1984).

## 3.4 Mammalian toxicity including toxicity to humans

### 3.4.1 Silanes and silanols

Silanes which contain only silicon and hydrogen are oily substances which very slowly decompose in water. Hydrolysis is increased with the replacement of hydrogen by alkoxy radicals and becomes vehement when the substituent is chloride. Chlorosilanes are also hydrolysed in contact with the humidity of mucous membranes or skin and act as local irritants. The other hydrolytic product of chloroalkylsilanes is alkylsilanol, which may undergo condensation to siloxane (LeVier *et al.*, 1977). However, the formation of hydrochloric acid constitutes the hazard to health. In the largest accidental spill of silanes, 1,200 gallons silicon tetrachloride leaked from a tank in a chemical plant within several hours. The substance promptly hydrolysed on the moist ground and with the evaporated silicon tetrachloride, formed a large gray-white cloud of 150-200 m height. Six workers caught in the area developed nausea, runny eyes and nose, coughing and mild wheezing. All these symptoms can be explained by the effect of hydrochloric acid (Kizer *et al.*, 1984). The toxic effects of alkylchlorosilanes is also due to the formation of HCl. The relatively milder corrosive effect of organic acids explains why alkoxy silanes are less toxic than chlorosilanes. In the rat the oral LD 50 of chlorosilanes is about 1 g/kg or more, while the LD 50 of tetraethoxysilane is 6.3 g/kg (Smyth *et al.*, 1949, 1954) and that of  $\gamma$ -glycidoxypropyltrimethoxysilane is 8.5 g/kg (Siddiqui and Hobbs, 1984). The latter compound given to pregnant rats by gavage in daily doses of 1.0 g/kg on days 6 through 15 of gestation did not cause adverse effects in the mother or in foetuses (Siddiqui and Hobbs, 1984).

Trimethylsilanol and dimethylsilandiol are nearly completely absorbed from the gastrointestinal tract and rapidly excreted. The more polar dimethylsilandiol was almost exclusively excreted in urine, while exhalatory loss was responsible for about 10-30% of the total excretion of trimethylsilanol dose in monkeys (Bennett and Statt, 1973). Male and female rats tolerated daily doses of 100 mg/kg dimethylsilandiol or trimethylsilanol for 31 days without adverse effects, but two weeks treatment, 5 days a week, with 500 mg/kg trimethylsilanol caused signs of neurotoxicity and reduction in weight gain (Firmin, 1984). Diphenylsilandiol is excreted in the rat with a half life of 7.2 hr and has an oral LD 50 of 2.15 g/kg in the same species (Firmin, 1984). This compound, a plasticizer in silicon elastomers, has an anticonvulsant effect and in 50% of mice and rats the LD 50 (effective dose) was 25 mg/kg against maximal electroshock-induced seizures or convulsions provoked by strychnine (LeVier *et al.*, 1977).

### 3.4.2 Polydimethylsiloxane (PDMS) fluids

#### 3.4.2.1 General toxicity

The absorption and route of excretion depends on molecular size and excretion also depends on volatility. Within 49 hr of the oral administration of  $^{14}\text{C}$  labelled hexamethyldisiloxane primates exhaled 20% of the radioactivity, excreted 78% in urine and 1% in faeces (Bennett and Statt, 1974). After the administration of octamethylcyclotetrasiloxane, the corresponding numbers were 20% , 63% and 5% (LeBeau and Gorzinski, 1973). The urinary excretion of silicone by human volunteers given PDMS orally was noticeable only when the PDMS contained low molecular weight silicones, otherwise it was less than 0.2% (FAO/WHO, 1974; LeVier *et al.*, 1977). After the oral administration of non-absorbable PDMS, the only route of excretion is the fecal one (LeVier *et al.*, 1977). Twenty-five days after the intraperitoneal administration of PDMS, 96.5% of the dose was recovered in rats without any trace of demethylation. The bulk of the dose was deposited in the fat, and none was found in heart or blood (FAO/WHO, 1974). From the peritoneal cavity (and probably from subcutaneous injection sites) large molecular weight polymers may be transported by phagocytizing cells (Rees *et al.*, 1967) and through the lymphatic circulation.

The acute toxicity of small molecular weight alkylsiloxanes is low. Rats or guinea pigs were not affected by a single dose of 30 ml/kg hexamethyl- disiloxane and the same dose of dodecamethylpentasiloxane has only a laxative effect. Only hexamethyldisiloxane, but not the longer chains, irritated the mucous membrane of peritoneum or gastrointestinal tract (Rowe *et al.*, 1948).

Short-term and long-term studies have also indicated that polyorgano- siloxanes have an extremely low toxicity. Mice given from weaning for 76 weeks a silicone antifoam (94% PDMS and 6% finely divided silicon dioxide) in the diet at levels of 0.25 and 2.5% showed neither detectable adverse effects nor tissue levels of silicone (Cutler *et al.*, 1974). Neither the daily administration of 20 doses of 20 g/kg silicone fluid (350 cSt) over 28 days (Rowe *et al.*, 1984) nor 50, 350, 1,000, 10,000 or 60,000 cSt silicone fluids fed for 90 days at a dietary level of 1% (McDonald *et al.*, 1960) caused any deleterious effect in rats. The outcome was similar when the 50 or 350 cSt fluids were fed at the same dietary level for one year (Carson *et al.*, 1966) or an emulsion containing 50% antifoam A (350 cSt) at 2% level for 260 days (FAO/WHO, 1974). Only one study reported a slight depression of body weight in rats by 1% dietary level (FAO/WHO, 1974). In long-term studies lasting two years 0.3% silicone fluid produced no biochemical or morphological adverse effects, and 0.1% fed to male and female rats for the same period did not affect the first or second generation (FAO/WHO, 1974).

An unexplained and so far not confirmed observation is that dogs given 0, 300, 1,000 or 3,000 mg/kg DC antifoam A (which besides 350 cSt PDMS contains 12% low molecular weight cyclic PDMS and 4% silica aerogel) five days each week for six months developed a dose-dependent increase of brown-black iron free bile deposits in livers (Child *et al.*, 1951).

No adverse effects were noted in four human volunteers fed 7.1 g PDMS daily for ten days (Howard *et al.*, 1974) and 48 ml PDMS fluid given daily in divided doses for 3-13 months caused nothing more than occasional nausea (FAO/WHO, 1974). PDMS with and without 6% free silica has antifatulent properties and can protect the gastric mucosa from the irritant effect of aspirin (Birtley, 1973).

#### 3.4.2.2 Reproduction, mutagenicity and carcinogenicity

A survey of the relevant literature did indicate that PDMS has no teratogenic, mutagenic or carcinogenic effects (GESAMP, 1986).

#### 3.4.3 Silicone polyether copolymer fluids

The molecular weight of commercial polyether copolymers is too high to permit gastrointestinal absorption and there is no data on decomposition during their passage through the stomach or intestines. Polyether copolymers are not irritant to eyes or skin (CIR, 1982). Toxicity studies are restricted to acute tests. Most of the polyether copolymers have oral LD 50 values above 10 ml or 10 g/kg in rats and some above 35 and 65 ml/kg (CIR, 1982).

#### 3.4.4 Polymethylphenylsiloxane fluids

The gastrointestinal absorption of methylphenylsiloxanes is similar to dimethylsiloxanes. Within 48 hr of the administration of  $^{14}\text{C}$  labelled 2,6-cis-diphenylhexamethylcyclotetrasiloxane to monkeys, about 90% of the dose was recovered in excreta, 3% in exhaled air, 24% in faeces and 63% in urine (Lebeau and Gorzinski, 1974). The clearance half-life of this copolymer was 12 hr in monkeys, and 18 hr in human volunteers (Pilbrant and Strindberg, 1975). Even low molecular weight cyclosiloxanes are not absorbed dermally (Palazzolo *et al.*, 1972).

Methylphenylsiloxanes have attracted widespread attention because some of them have an oestrogenic effect. They increase the weight of the uterus and accelerate the passage of the ovum, but induce its destruction, and therefore interfere with female reproduction. In males they cause testicular atrophy and disrupt spermatogenesis (LeVier *et al.*, 1977). The most prominent organosilicon oestrogen is 2,4-cis-diphenylhexamethyltetrasiloxane (but not the trans isomer), monophenylheptamethyltetrasiloxane is less active, while the linear diphenyltetramethyldisiloxane and diphenylhexamethyldisiloxane are a hundred times less active (Benet *et al.*, 1972). With the exception of this very specific oestrogenic effect, even the most active cyclotetrasiloxane lacks toxicity. Its LD 50 value could not be estimated in the mouse and the rat, because the stomach is too small to take a lethal dose (Albanus *et al.*, 1975; LeVier *et al.*, 1975).

Polymeric methylphenylsiloxanes share the biological and toxicological inertness of PDMSs (Firmin, 1982).

#### 3.4.5 Organosilicon elastomers (rubbers) and resins

Both elastomers and resins are solid, but elastomers can be injected in the fluid form (e.g. to increase breast or hip) and cured *in situ* within the body. As large amounts can be injected, e.g. 1 litre in one sitting, damage to local tissue and blood vessels may promote migration to other tissues before solidification (Editorial, 1983). Thus, a transsexual patient died of pneumonitis after the sixth monthly injection of 1 litre silicone fluid into his hip (Durocher *et al.*, 1983). However, such a lethal outcome cannot be described as toxic damage. Organosilicon resins have found application in arthroplastic surgery.

### 3.4.6 Methylsiloxane derivatives

The replacement of a methyl group by a  $\gamma$ -mercaptopropyl group on 5% of the Si-O- units in PDMS gives a release agent for the fusing of xerographic toner. A battery of acute animal toxicity tests, consisting of 90 days inhalation exposure, and long-term dermal exposure revealed no significant response, except for transient eye irritation (GESAMP, 1986).

Tris(trifluoropropyl)trimethylcyclotrisiloxane is used as an intermediate for polymers when PDMS does not satisfy the solvent/chemical resistance needed. The daily application of 400 mg/kg for 21 days was associated with the death of 5 of 12 rabbits, 200 mg/kg reduced weight gained and 40 mg/kg had no adverse effect (Siddiqui and Hobbs, 1982).

## 4. ASSESSMENT OF EFFECTS AND RISKS TO MARINE BIOTA

### 4.1 Risk associated with silanes and silanols

Silicon compounds discussed in the present document can be divided into two groups. The first group of silanes and silanols, the precursors of siloxanes. The most toxic silanes are not organosilicons at all and the health hazard presented by inorganic silanes actually decreases when alkyl groups are substituted for halogens. The environmental impact of silanes depends on the hydrolytic product, hydrochloric acid in the case of chlorosilanes or organic acid in the case of alkoxy silanes. They are almost exclusively used for the synthesis of siloxanes, but smaller quantities are used as coupling agents in reinforced plastics, in cross-linking polyolefins, in the treatment of surfaces to achieve bound antimicrobial activity and in the synthesis of organic compounds. These uses are not associated with release into the marine environment and make dumping a highly uneconomical and unlikely exercise. Therefore, marine pollution cannot be other than accidental. In case of aquatic pollution, dilution of the acid limits the environmental effect both in space and time. While dilution of chlorosilanes in water favours hydrolysis and silanol formation, it antagonises the condensation of silanols to siloxanes. Silanols are not persistent, as they undergo photooxidation to silicic acid and carbon dioxide. The toxicity of silanols (see data for dimethylsilanediol in table 1) is low. Considering both the possibility of pollution and toxicity, the risk that marine biota will be affected by silanols is infinitesimal.

### 4.2 Risk associated with siloxanes

Silanes and silanols are discussed under the heading of organosilicon compounds only because they are precursors of oligomeric and polymeric siloxanes. The difference between precursors and siloxanes is that condensation significantly decreases water solubility, volatility and reactivity, and increases lipophilicity, viscosity and resistance to degradation. Some of these characteristics would have very significant ecotoxicological consequences if (a) passage through biological membranes was not limited by increasing molecular weight, (b) monomers and oligomers up to 5 cSt were not volatile, and (c) commercial siloxane compounds had specific toxicity or biological effects. The only siloxanes with a specific biological effect, the oestrogenic phenylmethyltetracyclosiloxanes have been eliminated from phenylmethyl intermediates. Another group of organosilicons which have some compounds

with remarkable toxicity are silatranes. From the point of view of marine pollution they are insignificant for the following reasons. Firstly, though a few members of this group are toxic to mammals, they are not toxic to cold blooded animals. Secondly, silatranes are rapidly detoxified in water (Garson and Kirchner, 1971) and thirdly, the use of silatranes is restricted to small-scale experiments (Vonk *et al.*, 1984).

All the other siloxanes have very low toxicity, as examples in table 1 demonstrate, and with the exception of low molecular weight siloxanes, have low bioconcentration and biomagnification potential. However, even the solubility of oligomers is fairly low and stable organic compounds that have low water solubility usually require several weeks to reach maximum concentration in the organism (Chiou, 1981). Moreover, volatility does not allow prolonged exposure to a steady concentration of the dissolved compound, while uptake of non-reactive compounds is followed by a rapid clearance. From fathead minnow 75% of the body burden of octamethylcyclotetrasiloxane cleared with a half-life of 17 hr (Annelin *et al.*, 1984). Thus, in spite of favourable molecular weight and lipophilicity, the bioconcentration potential of oligomers is suppressed in the natural marine environment by other physical and chemical properties. Therefore, the chance to reach a toxic body burden is low. Though there is no data on the input of octamethylcyclotetrasiloxane in the marine environment, it is relevant to point out again that in upper layer marine sediment samples, collected in a zone of high anthropogenic pollution, no octamethylcyclotetrasiloxane was found, though 60% of the samples had measurable amount of silicone (Ann Arbor Technical Services, 1985).

Decrease in solubility with molecular weight and the impermeability of biological membranes to large molecules (600) are two factors which act against the uptake of PDMS by marine organisms. Though some of the polyether copolymers have fairly good water solubility, their molecular weight prevents bioconcentration. Nevertheless, intake is not restricted to diffusion, but can involve incorporation of particulate matter at the lower end of the food chain. The consequences of such a bioaccumulation process is limited as species fed on the lower organism cannot absorb PDMS from the gastrointestinal tract.

#### 4.3 Risk associated with production, transport and use

The degree of marine pollution is mainly dependent on the physical state and the use of organosilicons. Solids are either landfilled or incinerated and therefore do not count as potential marine pollutants. About 50 to 66% of the yearly production of 500,000 tons (metric) of organosilicons are fluids (Vonk *et al.*, 1984; Howard *et al.*, 1974). Silicone fluids, as listed by Howard *et al.* (1974), are used as additives to waxes and polishes, as greases, lubricants, paintable (PDMS) and non-paintable (polyether copolymers) release (abherent) agents, water repellents on textiles, glass and leather, as antifoams (PDMS), as foaming agents in polyurethane production (polyether copolymers), dielectric coolants, for impregnating electric appliances (e.g. transformers, capacitors, etc.), in shock absorbers, in vacuum pumps, and in cosmetics and toiletries.

The contribution of manufacturing operations to environmental pollution is not significant (Howard *et al.*, 1974) and any contamination associated with transport is accidental spillage. Thus, regular environmental pollution must be associated with the use of organosilicons. Heat exchange and dielectric fluids may be leaked accidentally or intentionally into the environment, though economic interests call for recycling. Treatment bath for coating textiles,

glass and leather may be the source of environmental contamination. Other uses are too dispersed, and in many cases the silicone is attached to solid material, e.g. when used as a foaming agent in the polyurethane industry or used as water repellent or release agent. One regular source of marine pollution is the use of silicone antifoam in wastewater treatment plants. The source of marine pollution is not the final effluent, but the disposal of sludge (Ann Arbor Technical Services, 1985; Pellenbarg, 1979a). In the New York Bight where until 1975 some 17 millions metric tons of sewage sludge was dumped, sediments with the highest observed silicone concentration (40 ppm; dry weight) were found at the site of dumping, while silicone could not be detected in sediment near to Long Island (Pellenbarg, 1984b).

It is expected that heavily contaminated rivers have higher silicone concentrations than seawater and may indicate the upper limit of pollution in heavily contaminated marine areas. Data tabulated by Vonk *et al.* (1984) indicate that the concentration of oligomers both in Rhine and the river Lee in G.B. was below 1.0 ppb, and mostly below 0.01 ppb. In a heavily industrialised area in Japan four of nine river water samples had silicone concentrations below the 0.1 ppb detection limit, four samples had 2 to 8 ppb and one sample 54 ppb (Watanabe *et al.*, 1984b).

#### 4.4 Risk associated with surface and sedimental layers

The two layers where the concentration of siloxane polymers can be the highest are the surface and the sedimental layers. The surface film of PDMS is transitory, while the PDMS in the sedimental layer moves with the sediment (Pellenbarg, 1979b). Marinas, which concentrate small boat activity, can serve as sources of silicone surface film. Thus, the surface layer in the Chesapeake Beach and Delaware Bay contained 24-44 ppb silicone, while surface sediments in the Delaware Bay contained an average of 0.61 ppm organic silicone on the dry weight basis. Compared with the Delaware Bay, the average sedimental concentration of silicone was twice as much, with a maximum of 3.07 ppm in the Potomac River near a waste water treatment plant (Pellenbarg, 1979a). In the New York Bight, significantly higher concentrations, up to 40 ppm, were found at and near to the sludge dumping site (Pellenbarg, 1979b). In a Japanese river with heavy exposure to industrial effluents, only two of the nine sediment samples had measurable amount, (0.3 and 5.8 ppm dry weight) of silicone (Watanabe *et al.*, 1984b).

Experimental studies indicate that the desorption of PDMS from the sediment is negligible (Eales and Taylor, 1984). Unfortunately the lack of long-term monitoring of silicone concentrations in the sedimental layer does not permit the drawing of any conclusion on the existence or absence of a trend. At present there is no known mechanism for the degradation of PDMS in sediments, and therefore one expects a continuous increase in the amount of sedimental silicone, though not necessarily with a parallel increase in sedimental silicone concentration. Horizontal and downward movements of siliconised particles may maintain a steady state concentration in the upper layer. Moreover the catalytic decomposition of PDMS by contact with slightly wet clay (Frye, 1980) suggests that PDMS is not fully resistant to degradation.

#### 4.5 Conclusion on risk to marine biota

Based on the above considerations, it seems unlikely that even a substantial increase in the production of siloxane based organosilicons will endanger the marine environment and biota. The very low level of toxicity of both oligomers and polymers, the uses and applications of siloxanes and their physicochemical properties are the main points on which this conclusion is based. In this context, it is pertinent to refer to the ecotoxicological conclusions in the review of Firmin (1984). According to him, in the large collection of data on the effects of organosilicons, adverse effects are restricted to the liberation of trace acids from chlorosilanes, the entrapment of *Daphnia magna* by surface silicone layers and the delayed burrowing activity of *Nereis diversicolor* into PDMS-polluted sediment. In the absence of contradictory data, these conclusions are based on firm grounds.

### 5. ASSESSMENT OF EFFECTS AND RISK TO HUMAN HEALTH

GESAMP (1986) expressed the view that "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 silicon 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 (c) on practical experience obtained from the use of organosilicons in medicine".

The medicinal use of organosilicons includes elastomer dressing of granulating wounds, silicone baths for the treatment of open wounds, lotions and ointments with 10 to 30% silicone content for the prevention of bedsores, the injection of large amount of fluid elastomer mixed with curing agent for breast and hip augmentation, the oral administration of up to 2 g PDMS against flatulence and less against abdominal discomfort after hysterectomy or caesarian section (GESAMP, 1986). Every medicinal use indicates very low toxicity, but from the viewpoint of human exposure to organosilicons in marine food, the oral administration of PDMS is the relevant one. To ingest 2 g PDMS with a meal prepared from 200 g fish, the flesh has to contain 10,000 ppm (wet weight) silicone. In a river area where industrial effluent and sludge was sometimes heavily contaminated with organosilicons, the average organosilicon concentration in the flesh of 22 fish was 0.61 ppm and the highest value was 4.47 ppm (Watanabe *et al.*, 1984b). However, according to a FAO/WHO Expert Committee (1975) the acceptable daily intake for man is 0-1.5 mg/kg. As silicone concentrations in marine fish, if any, are unlikely to be higher than values given by Watanabe *et al.* (1984b) for fish caught in a highly polluted river, it would appear impossible for man to reach the upper limit of the acceptable daily intake through eating unprocessed marine food products.

The presence of organosilicons in unprocessed marine food is accidental, but many foods are deliberately supplemented with organosilicons in order to avoid foaming during processing. The permitted concentration in food 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). Considering the presence of organosilicons in everyday food products, the possibility that marine food sold unprocessed can contribute significantly to the daily silicone intake is negligible.

## 6. THE RATIONALE FOR CHANGING THE STATUS OF ORGANOSILICONS

The rationale for changing the status of organosilicons built from siloxane (Si-O-) units is based on their behaviour. Both the toxicity and bioconcentration of oligomer and polymer siloxanes are low to allow interference with the marine biota. Thus, neither the toxicity nor the bioconcentration of PDMS fluids justifies the inclusion of PDMS (or other siloxanes) in grey and black lists. The only argument against this move is that though PDMS is not persistent in soil, and volatile methylsiloxanes undergo photochemical degradation in the atmosphere (Frye, 1980), there is no known mechanism for the degradation of methylsiloxanes in water. This persistency immediately invokes comparison with the persistent and toxic polychlorinated biphenyls (PCBs). However, while PCBs are distributed globally and occur in fish products from environments as dissimilar as the Antarctic Ocean, North Sea and Alpine lakes (Eisenrich and Johnson, 1983), the environmental distribution of PDMS does not include atmospheric vapour transport, and thus intake by aquatic systems is restricted to direct input. Low water solubility promotes surface film formation and sedimentation, and therefore limits the pollution of the bulk of the water column. As PDMS is a better solvent for oxygen than water, PDMS surface films will not interfere with the oxygenation of water and, after sedimentation, will not asphyxiate sedimental biota.

Pollution of the marine environment, and particularly seawater by organosilicon compounds is very far from the toxic level, in spite of their large scale production over the last forty years. Even in polluted rivers, marinas, estuaries, or even near to wastewater treatment plants, the water concentration of organosilicons is around 1 ppb, or below detection limit (Pellenberg, 1979a; Vonk *et al.*, 1984; Watanabe *et al.*, 1984b). There is about a thousand-fold difference between these concentrations and the "no effect" concentration of polyether copolymer in algae, i.e. in the most sensitive species. Based on a Dow Coming report, Vonk *et al.* (1984) deduced that the no effect concentration is about 1.0 ppm for *Selenastrum capricornutum*. Unlike the water-soluble polyether copolymer, PDMS at a concentration of 2,000 ppm was practically atoxic to the same species (Firmin, 1984).

The human toxicity of siloxanes is also extremely low, and the intake of organosilicon compounds cannot reach the upper limit of acceptable daily intake recommended by FAO/WHO (1974) through the consumption of unprocessed marine food products.

Though the argument for deleting siloxanes and their precursors from the black and grey lists is strong, this argument naturally becomes weaker, when under the heading of organosilicon compounds all the possible sila substituted and silylated products are included. It is true that presently no known sila substituted or silylated product is a potential marine pollutant and silicone derivatives of organic compounds are usually less stable than the parent compound. However, while the behaviour of siloxanes is determined by Si-O- bonds, the biological activity of sila substituted and silylated compounds is dominated by the characteristics of the organic parent compound.

## 7. PROPOSALS CONCERNING STATUS

Data accumulated on the toxicity and environmental behaviour of siloxane precursors, like chlorosilanes and of oligomeric or polymeric organosilicons, indicate that silicon compounds belonging to this category do not share toxicity and persistency jointly. Thus, toxic chlorosilanes in contact with water are immediately hydrolysed and diluted. Persistent siloxanes have a high degree of chemical inertness and silicone layers do not form a physical barrier against the diffusion of oxygen. Based on these considerations, it is proposed that siloxanes and their precursors should be deleted from the black and grey lists.

At present, solid organosilicon wastes are either disposed of in landfills, or are incinerated. Moreover, the item covering persistent plastic and other synthetic materials which is included in annex I (the "black list") to the Protocol for the prevention of pollution of the Mediterranean Sea by dumping from ships and aircraft (UNEP, 1978), provides satisfactory protection against possible dumping.

Though there is no guarantee against the future production of toxic silylated or sila substituted organic compounds (e.g. silicone derivatives of pesticides), the present restrictions on pesticides and synthetic organic compounds are adequate to deal with any such eventually. Consequently there is no need to include a new heading for silylated or sila substituted products in Annex I or Annex II.

## 8. MEASURES PROPOSED FOR ADOPTION BY THE CONTRACTING PARTIES

In the light of the information contained in the present document, it is considered that no valid reason remains for retaining organosilicon compounds as such within annex I or annex II of either the dumping or the Land-based Sources Protocol and the following recommendations are submitted for the consideration of the Working Group with a view to their transmission by the secretariat to the Contracting Parties:

- (a) Measures concerning the status of organosilicon compounds within the Protocol for the prevention of pollution of the Mediterranean Sea by dumping from ships and aircraft
- considering recent scientific evidence regarding the toxicity and persistence of organosilicon compounds, and their status as actual or potential marine pollutants;
  - further considering that any future control measures becoming necessary can be adequately covered by the provisions of Annex I, item 5 and annex II, item 1(iv) to the above-mentioned protocol;
  - amend annex I to the protocol for the prevention of pollution of the Mediterranean Sea by dumping from ships and aircraft, by deleting item 2 thereof - "Organosilicon compounds and compounds which may form such substances in the marine environment, excluding those which are non-toxic or which are rapidly converted in the sea into substances which are biologically harmless, provided that they do not make edible marine organisms unpalatable".

- (b) Measures concerning the status of organosilicon compounds within the protocol for the protection of the Mediterranean Sea against pollution from Land-based Sources
- considering recent scientific evidence regarding the toxicity, persistence and bioaccumulation of organosilicon compounds, and their status as actual or potential marine pollutants;
  - further considering that any future control measures becoming necessary can be adequately covered by annex I, item 7, annex II, item 10 and annex II, item 13 to the above-mentioned protocol;
  - amend annex II to the protocol for the protection of the Mediterranean Sea against pollution from Land-based Sources by deleting item 3 thereon - "Organosilicon compounds and substances which may form such compounds in the marine environment, excluding those which are biologically harmless or are rapidly converted into biologically harmless substances".

Table 1 - The comparative aquatic toxicology of dimethyldisilanediol, cyclic siloxanes, PDMS, polyether copolymers and polymethylphenyl (PMPhS) fluids. Adapted from GESAMP (1986) and compiled from reviews by Firmin (1984), Firmin, Frye and Raum (1984) and Vonk *et al.* (1984)

	LC 50 in ppm for (X) hour exposure			Polyether copolymers	PMPhS fluids
	dimethyl-silanediol	cyclic methyl-siloxanes	PDMS a= 50 cSt b=350 cSt c=30% 50 cSt d=30% 350 cSt		
<u>Selenastrum capricornutum</u> (green algae)	> 2,000	> 100 (96)	> 2,000 ?	16.8	> 10,000
<u>Anabaena flos-aquae</u> (blue-green algae)	> 2,000	> 100 (96)	> 2,000 c	753	> 10,000
<u>Daphnia magna</u> (water flea)	> 1,000 (72)	> 100 (96)	244 (48) d	311 (48)	500 (24)
<u>Artemia salina</u> (brine shrimp)		> 500 (96)	> 20,000 (24) a	> 500 (96)	> 500 (96)
<u>Pachygrapsus crassipes</u> (shore crab)	471 (96)	> 1,000 (96)	> 1,000 (48) a		
<u>Palaemonetes vulgaris</u> (marsh shrimp)	604(96)				

Cont'd

Table 1 - The comparative aquatic toxicology of dimethyldisilanediol, cyclic siloxanes, PDMS, polyether copolymers and polymethylphenyl (PMPhS) fluids. Adapted from GESAMP (1986) and compiled from reviews by Firmin (1984), Firmin, Frye and Raum (1984) and Vonk et al. (1984) (cont'd)

	LC 50 in ppm for (X) hour exposure			Polyether copolymers	PMPhS fluids
	dimethyl-silanediol	cyclic methyl-siloxanes	PDMS a= 50 cSt b=350 cSt c=30% 50 cSt d=30% 350 cSt		
<u>Panaeus octecus</u> (brown shrimp)			> 1,000 (48) d		
<u>Prothaca spaminea</u> (cockle)			> 1,000 (48) d		
<u>Mytilus edulis</u> (mussel)			> 10,000 (96) a		
<u>Salmo gairdneri</u> (rainbow trout)	> 1,000 (96)	> 1,000 (96)	> 10,000 (96) d	> 245 (96)	> 1,000 (96)
<u>Lepomis macrochirus</u> (bluegill sunfish)	> 1,000 (96)	> 1,000 (96)	> 10,000 (96) d		
<u>Fundulus heteroclitus</u> (killifish)	> 1,000 (96)	> 1,000 (96)	> 1,000 (48) d		
<u>Brachidanio regio</u> (zebra fish)		> 500 (96)		> 500 (96)	> 500 (96)
<u>Pleuronectus platessa</u> (plaice)		> 10,000 (96) a			

(For algae the numbers are IC50 (median inhibitory concentration) = IL<sub>M</sub>(median inhibitory limit) = concentration which decreases exponential growth by 50%.

## 9. REFERENCES

- Ann Arbor Technical Services (1985), Organosilicons in fresh water and salt water sediments. Final report for the Silicones Health Council. Ann Arbor, Michigan.
- Annelin, R.B. (1979), Bioaccumulation of DC 561 transfer fluid in bullheads (oral ingestion). DC Rep. I-0030-5721.
- Annelin, R.B. (1984), Bioconcentration of octamethylcyclotetrasiloxane in fish. DC Rep. I-0030-5721.
- Annelin R.B. and R.R. Buch (1978), Bioconcentration study of dimethylsilanediol in fathead minnows under dynamic conditions. DC Rep. I-0005-0560.
- Aubert M., J. Aubert, H. Augier and C. Guillemaut (1985), Study of the toxicity of some silicon compounds in relation to marine biological chains. Chemosphere, 14:127-138.
- Birtley, R.N.D., J.S. Burton, D.N. Kellett, B.J. Oswald and J.C. Pennington (1973), The effect of free silica on the mucosal protective and anti- flatulent properties of polydimethylsiloxane. J. Pharm. Pharmacol., 25:859-863.
- Bennet, D.R. and W.H. Statt (1973), Primate absorption and elimination balance studies including pulmonary, urinary, biliary and fecal excretion of t-butanol, trimethylsilanol, dimethylsilanediol and hexamethyldisiloxane. Toxicol. Appl. Pharmacol., 25:445.
- Bessamans, J. (1981), Essais de toxicité aigüe vis-à-vis Brachydanio Rerio (DC 556, DC 190, DC 345, DC 193). Rep. C.E.R.I.O. Bruxelles.
- Brinker, N., R. Firmin and A. Jenkins (1980), Silicone antifoams in the food industry. DC Rep. (unpublished).
- Bruggeman, W.A., D. Weber-Fung, A. Opperhuizen, J. Van der Steen, A. Wijnbenga and O. Hutzinger (1984), Absorption and retention of polydimethyl- siloxanes (silicones) in fish: preliminary experiments. Tox. Environ. Chem., 7:287-296.
- Carson, S., M.S. Weinberg and B.L. Oser (1966), Safety evaluation of Dow Coming 360 fluid and Antifoam A. Proc. Sci. Section of the Toilet Goods Assoc., 45:8-19.
- Child, G.P., H.Jr. Osmond and W.B. Deichman, (1951), Chronic toxicity of the methylpolysiloxane "Dc Antifoam A" in dogs. Arch. Ind. Hyg. Occup. Med., 3:479-482.
- Chiou, T. (1981), Partition coefficient and water solubility in environmental chemistry. In: J. Saxena and F. Fisher (eds) Hazard Assessment of Chemicals. Current developments, Academic Press, New York, 1:117-153.
- Clark, L.C. and F. Gollan (1966), Survival of mammals breathing organic liquids equilibrated with oxygen at atmospheric pressure. Science, 152:1755-1756.
- CIR (Cosmetic Ingredient Review) Expert Panel (1982), Final report on the safety assessment of dimethicone copolyol. J. Am. Coll. Toxicol., 1:33-54.
- Craig, N.C.D., J.E. Caunter and G.J. Eales (1984), DC 561: an investigation of long-term toxicity to polychaete worm Nereis diversicolor. DC Rep. I-9039-7.
- Cutler, M.G., A.J. Collings, I.S. Kiss and M. Sharatt (1974), A life span study of polymethylsiloxane in the mouse. Food Cosmet Toxicol., 12:443-450.
- Durocher, A., F. Salunier, D. Dubois, F. Fourier, C. Chopin and F. Watter (1983), Adult respiratory distress syndrome and silicone injection. Toxicol. Europ. Research, 5:171-174.
- Eales, G.J. and D. Taylor (1983), A study of the movement of polydimethylsiloxane fluid (DC 561) in sediment columns - Phase 2. DC Rep. I-9039-6.
- Editorial (1983), Silicone pneumonitis. Lancet, 2:283.
- Eisenreich, S.J. and T.c. Johnson (1983), PCBs in the Great Lakes. In: F.M. D'itri and M.A. Kammin (eds). PCBs: Human and Environmental Hazards. Butterworth Publ., Boston, pp. 49-75.
- FAO/WHO Expert committee on food additives (1974), Dimethylpolysiloxane. In: Toxicological Evaluation of some Food Colours, Enzymes, Flavour Enhancers, Thickening Agents and Certain Food Additives. WHO Food Additives Series. 6:168-174.
- Firmin, R (1982), Organosilicon compounds and the marine environment. Summary Report for the Barcelona Convention.
- Firmin, R. (1984), Les composés organosilicés et l'environnement aquatique. Thèse, Sciences Environnement, Université Libre Bruxelles.

- Firmin, R., C.L. Frye and A.L.J. Raum (1984), The environmental impact of organosilicon compounds on the aquatic biosphere. In: G. Persoone, E. Jaspers and C. Claus (eds), Ecotoxicological Testing for the Marine Environment, State university of Ghent, 1:591-623.
- Franklin, F.L. (1981), The acute toxicity of three chlorosilanes to shrimp and fish. MAFF Fish Lab., Rep. No. ST38.
- Frye, C.L. (1980), The environmental chemistry of liquid polydimethylsiloxanes: an overview. J. Organomet. Chem. Rev., 9:253-260.
- Garson, L.R. and L.K. Kirchner (1971), Organosilicon entities as prophylactic and therapeutic agents. J. Pharm. Sci., 60:1113-1127.
- GESAMP (1986), Review of potentially harmful substances: Organosilicon compounds (silanes and siloxanes). Rep. No. 29.
- Gettings, R.L. and T.H. Lane (1982), The use of microsystems in determining the environmental fate of polymethylsiloxanes. DC Rep. 1005-10957.
- Hill, R.W., J.E. Caunter and G.J. Eales (1983), Effect of an organosilicon formulation on embryos and larvae of the sheepshead minnow (Cyprinodon variegatus). IXI Brixham Rep. No. BL/B/2392.
- Hobbs, E.J., M.L. Keplinger and J.C. Calandra (1975), Toxicity of polydimethylsiloxanes in certain environmental systems. Environ. Res., 10:397-406.
- Howard, P.H., O.R. Durkin and A. Hanchett (1975), Assessment of liquid siloxanes (silicones). Final Report EPA-560/2-75-004, Washington.
- Irish, D.D. (1963), Hologenated hydrocarbons: I. Aliphatic. In: F.A. Patty (ed.). Industrial Hygiene and Toxicology. 2nd rev. ed., Interscience Publ., New York, 2:1241-1242.
- Kizer, K.W., L.G. Garb and C.H. Hine (1984), Health effects of silicon tetrachloride. Report of an urban accident. J. Occup. Med., 26:33-36.
- LDC (London Dumping Convention)(1972), Convention on the prevention of marine pollution by dumping of wastes and other matter, London.
- LDC (London Dumping Convention)(1986), Convention on the prevention of marine pollution by dumping wastes and other matter, London.
- LDC/SG.9. (London Dumping Convention)(1986), Draft report on the Scientific group on dumping. Agenda item 13. London.
- Lebeau, J.E. and S.J. Gorzinski (1973), Primate absorption and elimination balance studies including pulmonary, urinary, biliary and faecal excretion of octamethylcyclotetrasiloxane and 2,6-cis-diphenylhexamethylcyclotetrasiloxane. Toxicol. Appl. Pharmacol., 25:445-446.
- LeVier, R.R., M.L. Chandler and S.R. Wendel (1977), The pharmacology of silanes and siloxanes. In: G. Bendz and I. Lindquist (eds.). Biochemistry of silicon and related problems. Plenum Press, New York, 473-513.
- Maggi, P. and C. Alzieu (1977), Etude de la nocivité d'huiles PDMS à l'égard d'organismes. Sci et Pêches, 269:1-4.
- Meurice, A. (1981), Essais de toxicité à court terme vis-à-vis de Artemia salina (DC 556, DC 345, DC 193). Rep. C.E.R.I.A., Bruxelles.
- Meurice, A. (1981), Essais de toxicité à long terme (3 mois, DC 556, DC 190, DC 345). Rep. C.E.R.I.A., Bruxelles.
- Oslo Convention (1972), Convention for the prevention of marine pollution by dumping from ships and aircraft. Oslo.
- Oslo Commission (1980), Fifth Annual Report.
- Oslo Commission (1985), Tenth Annual Report.
- Paris Convention (1974), Convention for the prevention of marine pollution from Land-based Sources. Paris.
- Paris Commission (1985), Seventh Annual Report.
- Pellenbarg, R. (1979a), Environmental poly(organosiloxanes)silicones. Environ. Sci. Technol., 13:565-569.
- Pellenbarg, R. (1979b), Silicones as tracers for anthropogenic additions to sediments. Marine Poll. Bull., 10:267-269.
- Rees, T.D., D.L. Ballantyne, I. Jr, Seidman and G.A. Hawthorne (1967), Visceral response to subcutaneous and intraperitoneal injections of silicone to mice. Plastic. Reconstruct. Surg., 34:402-410.
- Rennison, B.D. (1974), Field trials of rodenticide 5-p-chlorophenyl silatrane against wild rats (Rattus norvegicus Berk.) J. Hyg. Camb., 73:45-48.
- Rowe, V.K., H.C. SPencer and S.L. Bass (1948), Toxicological studies on some commercial silicones and hydrolyzable silane intermediates. J. Ind. Hyg. Toxicol., 30:332-352.

- Siddiqui, W.H. and E.J. Hobbs (1982), Subchronic dermal toxicity to tritri-fluorofluoropropylmethylcyclotrisiloxane. Drug Chem. Toxicol., 5:415-426.
- Siddiqui, W.H. and E.J. Hobbs, (1984), Teratological evaluation of -glycidopropyltrimethoxysilane in rats. Toxicology, 31:1-8.
- Smyth, H.J. Jr, C.P. Carpenter and C.S. Weil (1949), Range-finding toxicity data, list III. J. Ind. Hyg. Toxicol., 31:60-62.
- Smyth, H.J. Jr, C.P. Carpenter, C.S. Weil and U.C. Pozzani (1954), Range-finding toxicity data, list V. Arch. Ind. Hyg. Occup. Med., 10:61-67.
- UNEP (1978), Mediterranean Action Plan and the Final Act of the Conference of Plenipotentiaries of the Coastal States of the Mediterranean Region for the Protection of the Mediterranean Sea. United Nations, New York.
- UNEP (1980), Conference of Plenipotentiaries of the Coastal States of the Mediterranean Region for the Protection of the Mediterranean Sea against pollution from Land-based Sources, May 1980. Final Act and Protocol. United Nations, New York.
- Vonk, J.W., T.G. Meerbeek and H.A. Meinema (1984), Evaluation of the impact of organosilicon compounds on the aquatic environment. Final Report to EEC, U/83/208(605), TNO, The Hague.
- Wannagat, U. (1977), Sila-pharmaca. In: G. Benda and I. Lindquist (eds). Biochemistry of silicon and related problems. Plenum Press, New York, 447-472.
- Watanabe, N., Y. Nakamura, E. Watanabe, E. Sato and Y. Ose (1984a), Bioconcentration potential of polymethylsiloxane (PDMS) fluids in fish. Sci. Total. Environ., 38:167-172.
- Watanabe, N., Y. Nakamura, E. Watanabe, E. Sato and Y. Ose (1984b), Distribution of organosiloxanes (silicones) in water, sediments and fish from the Nagara river watershed, Japan. Sci. Total. Environ., 35:91-97.
- Zitko, V. (1974), Uptake of chlorinated paraffins and PCB from suspended solids and food by juvenile Atlantic salmon. Bull. Environ. Contam. Toxicol., 12:406-412.