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POLYCARBOXYLATE POLYMERS AS USED IN DETERGENTS

CONTENTS

SECTION 1. SUMMARY AND CONCLUSIONS

Polycarboxylates used in detergents are homopolymers of acrylic acid, P(AA), or copolymers of acrylic acid and maleic anhydride, P(AA-MA). They are water-soluble polymers of a molecular weight (MW) < 100,000 with dispersive properties and are predominantly used in low-phosphate and phosphate-free detergent formulations to inhibit the deposition of inorganic precipitates and to disperse dirt. The use of polycarboxylates as detergent adjuncts has initiated a broad range of investigations into their toxicological and ecotoxicological effects as well as environmental fate.

P(AA)s and P(AA-MA)s are of low acute toxicity to the rat and the mouse (LD_{50} > 5 g/kgbw/d). They are slightly irritating to the rabbit skin and eye, but have no sensitising potential; neither irritation nor sensitisation potential has been observed in human beings. Mild, reversible and probably non-specific pulmonary irritation was observed at concentrations of 1 and 5 mg/m^3 in a 91 day inhalation study in the rat. The responses seen were similar to those elicted by a number of different irritant materials and are not considered to be of particular significance. A No Observed Adverse Effect Level (NOAEL) of 0.2 mg/m^3 was obtained for P(AA-MA)70,000 and 1.0 mg/m^3 for P(AA)4,500. No other adverse findings were observed in this study. There was no evidence of mutagenic potential for P(AA)s and P(AA-MA)s using a variety of genetic endpoints, nor was there any teratogenic effect in the rat. Based on these data, it is concluded that exposure to polycarboxylates does not pose any particular hazard to human beings.

Comprehensive studies of the biodegradation behaviour of high-MW P(AA)s and P(AA-MA)s under relevant environmental conditions (sewage treatment, sludge digesters, soils, river waters) showed that these polycarboxylates are poorly degradable, both aerobically and anaerobically. However, P(AA)s with a MW ≤ 1,000 can be ultimately degraded to a considerable extent. High MW polycarboxylates used in detergents are largely removed during sewage treatment (> 90%) by adsorption onto sludge and precipitation of polycarboxylate calcium salts. Removal of more than 90% of all polycarboxylates is expected by precipitation with Fe or Al salts in plants where such chemical treatment is practised.

Disposal of digester sludge containing adsorbed polycarboxylates in landfills or its use on agricultural land as a fertiliser yields high-MW, non-degradable polycarboxylate species bound to the top layer of the soil, from which leaching does not occur. The mobile, low-MW species of polycarboxylates are accessible to ultimate degradation, as demonstrated in a number of tests, and usually removed before disposal of the sludge. Thus, contamination of ground-water by polycarboxylates is not anticipated.

Based on polycarboxylate usage and per capita water consumption, the estimated polycarboxylate concentrations in West Germany and Italy were calculated to be 4 mg/l in raw sewage, 0.3 mg/l in sewage treatment plant effluent, 30 μg/l in surface waters and < 3 μg/l in drinking water, the latter figures being a maximum level assuming worst-case conditions. For digested sewage sludge, a polycarboxylate level of 19 g/kg was calculated and for sludge-treated soil 6 mg/kg/y.

Using model systems, it has been determined that the estimated concentrations of the entire MW range of polycarboxylates in waste waters are far below the levels having adverse effect on the performance of sewage treatment plants and sludge treatment. The same is true with regard to the impact of polycarboxylates on the elimination of heavy metals in sewage treatment plants and their distribution in river waters.

Ecotoxicological tests of the entire MW range of polycarboxylates with microorganisms, aquatic and terrestrial organisms revealed that the no-observed effect concentrations (NOECs) are at least 1-2 orders of magnitude above the estimated environmental concentrations. The bioaccumulation potential of P(AA)s and P(AA-MA)s has not been tested, but bioaccumulation of these polymers is unlikely when considering their high MW and low solubility under environmental conditions.

The low toxicity and ecotoxicity of detergent P(AA)s and P(AA-MA)s, their effective removal from the water phase during sewage treatment and drinking water purification, and their almost complete immobilisation when released into the environment demonstrate that the use of these polycarboxylates in detergents poses no hazard to man and the environment.

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

2.1 IDENTITY

Polycarboxylates used in washing powders and detergents are homopolymers of acrylic acid or copolymers of acrylic acid and maleic anhydride, generally as sodium salts.

The various polycarboxylates are distinguished by the monomers used for their preparation, acrylic acid (AA)[1] and maleic anhydride (MA), and their mass-average molar mass or molecular weight (MW). The polymers are designated by codes consisting of the corresponding abbreviations, P(AA) for polyacrylic acid, and P(AA-MA) for the copolymer of acrylic acid and maleic anhydride, to which the numerical value of MW is suffixed. For example:

P(AA)4,500: a homopolymer of acrylic acid (or its sodium salt) with a MW of approximately 4,500

P(AA-MA)70,000: a copolymer of acrylic acid and maleic anhydride (or its sodium salt) with a MW of approximately 70,000

2.1.1 CAS Registry Numbers

Numerous polycarboxylic acids and their salts have been given Registry Numbers by the US Chemical Abstracts Service (CAS); the following list is confined to the acids and their sodium salts (Table 1 and 2).

Table 1: P(AA) Homopolymers and their Sodium Salts

CAS Registry No.	CAS Name
9003-01-4	2-Propenoic acid, homopolymer
9003-04-7	2-Propenoic acid, homopolymer, sodium salt
25549-84-2	2-Propenoic acid, sodium salt, homopolymer
28603-11-4	2-Propenoic acid, homopolymer, sodium salt, isotactic

[1] See Appendix A for abbreviations

Table 2: P(AA-MA) Copolymers their Sodium Salts

CAS Registry No.	CAS Name
29132-58-9	2-Butendioic acid (Z), polymer with 2-propenoic acid
51025-75-3	2-Butendioic acid (Z), monosodium salt, polymer with sodium 2-propenoate
51344-35-5	2-Butendioic acid (Z), sodium salt, polymer with sodium 2-propenoate
60449-78-7	2-Butendioic acid, disodium salt, polymer with sodium 2-propenoate
60474-42-6	2-Butenedioic acid (Z), polymer with 2-propenoic acid, sodium salt
61842-61-3	2-Butendioic acid (Z), disodium salt, polymer with 2-proprenoic acid
61842-65-7	2-Butendioic acid (Z), monosodium salt, polymer with 2-propenoic acid
63519-67-5	2-Butendioic acid (Z), sodium salt, polymer with 2-propenoic acid
112909-09-8	2-Butendioic acid (Z), disodium salt, polymer with sodium 2-propenoate
126595-54-8	2-Butendioic acid (Z), polymer with sodium 2-propenoate
52255-49-9	2-Propenoic acid, polymer with 2,5-furandione, sodium salt

2.1.2 EEC Numbers

None.

2.1.3 EINECS Numbers

Not applicable, because polycarboxylates are polymers.

2.1.4 Synonyms

Polycarboxylates, polycarboxylic acids (PCAs), polycarboxylic polymers, polyacrylates, acrylic resins. (The last 2 names are also common names for polymers of esters of acrylic acid.)

2.1.5 Structural Formulae (Figure 1 and 2)

Figure 1: Structure of P(AA) Homopolymers

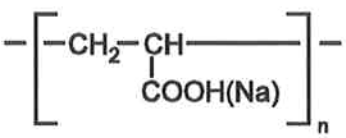
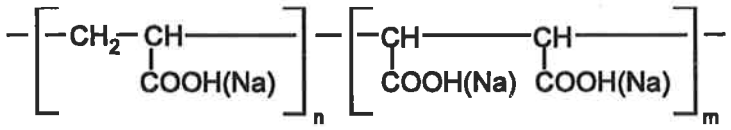


Figure 2: Structure of P(AA-MA) Copolymers



2.1.6 Molecular Weight

The MW of polycarboxylates used in washing powders and detergents normally lies between approximately 1,000 and 100,000. For other applications, polymers with a MW of up to 10^7 may be used (Section 3.3). For the determination of MW distributions the polymers can be fractionated by gel-permeation chromatography. Experience has shown that determinations of MW in different laboratories may yield divergent results. For example, one laboratory found MW = 60,000 and another found MW = 70,000 for the same polymer (Fachgruppe Wasserchemie, 1990).

2.1.7 Monomer Content

Depending on the reaction process, the residual content of monomeric AA in P(AA) can amount up to 0.5%; in most cases, the monomer content is < 0.1%, often much lower. The content of residual MA monomer in P(AA-MA) is generally < 1% (BASF, 1992a).

2.2 PHYSICAL AND CHEMICAL PROPERTIES

2.2.1 Physical Form

Polycarboxylates are available commercially as yellowish, highly viscous aqueous solutions containing up to 50% solids or as an almost white spray-dried powder or granular material. In many cases, fully neutralised (pH 6-8), partially neutralised (pH around 4) and acidic (pH around 2) products are on the market (pH measured in the liquid as delivered or in a 10% aqueous solution).

An unspecified 'polyacrylic acid' has been described as a hygroscopic, brittle, colourless solid with a glass-transition temperature of 106°C; at 200-250°C it loses water. Insoluble cross-linked polymeric anhydrides are formed which cannot be hydrolysed with water, but can be hydrolysed with sodium hydroxide (Jung *et al*, 1980).

2.2.2 Solubility

Polycarboxylic acids and their alkali metal salts are readily soluble in water, but the salts are insoluble in most organic solvents. The acids dissolve in dioxane, dimethylformamide and lower alcohols, but not in acetone, ether or hydrocarbons (Armstrong and Strauss, 1969).

In neutral or alkaline aqueous solution, higher MW polycarboxylates form salts with excess calcium ions that are poorly soluble. The solubility increases as the MW of the polymer decreases. Since the MW distribution of commercial polycarboxylates may be wide, their precipitation may be incomplete. The solubility of the high MW fraction (80-90%) of P(AA-MA)70,000 (Ca salt) is less than 0.01 mg/l (Opgenorth, 1987).

2.2.3 Adsorption

Because of the negative charge of the carboxyl groups, polycarboxylates have a strong tendency towards adsorption on solid surfaces. Substances with a positive zeta-potential, such as calcium carbonate or calcium sulphate, bind polycarboxylates solely through electrostatic forces (Nestler, 1968). In the presence of bivalent cations, adsorption onto solids with negative surface charge becomes possible (Opgenorth, 1987, 1992).

2.2.4 Stability

Polycarboxylates are very stable compounds as the carboxyl part of the molecule is the only functional group. The presence of multiple neighbouring carboxyl groups along the polymer chain adds further to their stability: for example, complete esterification cannot be achieved by standard methods of preparation. Strong oxidising agents, such as sodium hypochlorite, cause degradation of the polymer chain (BASF, 1992b).

2.3 ANALYTICAL DETERMINATION

2.3.1 In Applications

Polycarboxylates in cooling water from power stations and in waste water can be determined turbidimetrically as insoluble compounds with quaternary ammonium salts (Angenend and Schulte-Wieschen, 1979). Although the limit of detection is not given, the method seems to be applicable at concentrations ≥ 1 mg/l. Similar concentrations (≥ 1 mg/l) can be determined by adding excess iron(III), most of which will be bound by the polycarboxylates, and colorimetric analysis of excess

iron as iron thiocyanate; water-soluble interfering substances can be separated by adsorption of the polycarboxylate on a special column (Hach, 1984).

2.3.2 Environmental Media

Methods are being developed for the analysis of polycarboxylates in environmental samples, e.g. treated effluent, surface water or drinking water. The main problem with environmental samples is caused by the simultaneous occurrence of large amounts of natural polyanions such as humic acids.

In the (unlikely) absence of interfering substances, mass concentrations of polycarboxylates (≥ 0.01 mg/l) can be determined by polyelectrolyte titration. This method is based on titration of polyanions with polycations in the presence of an anionic metachromic indicator (Schroeder *et al*, 1991).

Polycarboxylates in drinking water containing high levels (> 1 mg/l) of organic substances (predominantly humic acids) can be determined if the interfering substances are first destroyed by oxidation with potassium permanganate. Since some polycarboxylate is not recovered, the limit of detection is effectively increased (Wassmer *et al*, 1991).

In general, reliable results have not been obtained from analysis of samples of treated effluent or surface water (Wassmer *et al*, 1991).

No methods are available for the analysis of polycarboxylates in soil, sediment and in biological media; radiolabelling techniques can be used to examine the fate of polycarboxylates in these systems.

SECTION 3. PRODUCTION, STORAGE, TRANSPORT AND USE

3.1 PRODUCTION

Polycarboxylates used in washing powders and detergents are generally prepared by free-radical polymerisation of AA, or AA and MA, in aqueous solution. The MW is influenced by the reaction conditions such as temperature and concentration, but the most important factors are the proportion and nature of initiators and chain-transfer agents used. For initiation, peroxides, azo compounds, and redox systems such as iron(II) and hydrogen peroxide or sulphite and peroxydisulphate are employed; the most important chain-transfer agents include alcohols, amines and mercaptans (Jung *et al*, 1980).

3.2 STORAGE AND TRANSPORT

Polycarboxylates are handled and transported as aqueous solutions, powders or granules; as such they are stable over long periods. Transport of polycarboxylates does not present any special risks and they are not classified as dangerous goods for transportation.

3.3 USE

3.3.1 General

The properties of polycarboxylates can be modified to meet many applications, e.g. by variation of the MW, addition of co-monomers or cross-linking (Jung *et al*, 1980).

Polyacrylates of very high MW (1-10 million) are used as flocculants in water treatment and paper manufacture, as thickeners in paste pigments, cosmetics, and pharmaceuticals and to bind water in superabsorbent products such as disposable baby-napkins. They can also be used to increase the viscosity of water injected during petroleum fractionation, a process used in tertiary oil refining.

Polycarboxylates of MW 1,000-100,000 are primarily dispersing agents, used in pigment dispersions for paper coating, to prevent furring of water-cooling systems, and in textile sizes. In phosphate-free or low-phosphate washing powders they serve as anti-ash and dirt redeposition inhibitors.

3.3.2 Role in Detergents

Polycarboxylates in low-phosphate or phosphate-free detergent formulations inhibit the formation of inorganic crystals and disperse dirt (McGrew, 1986).

As a consequence of the reduction of phosphate content in detergents, the concentrations of free calcium and magnesium rise in the washing water. The metal ions tend to form precipitates with hard water and some detergent components. Polycarboxylates inhibit the crystal growth of inorganic precipitates at sub-stoichiometric levels (threshold effect), so that these salts remain in suspension and do not precipitate onto the textile fabrics. By virtue of their dispersive properties, polycarboxylates play an important role in laundering, where they prevent redeposition of dirt removed from fabrics.

The fact that polycarboxylates can form insoluble salts does not counteract the functions just described. Whether or not precipitation takes place depends on the alkalinity of the solution and above all on the ratio of the calcium ion concentration to the carboxyl group concentration. In detergent formulations designed to achieve a pH > 9 the concentration of free calcium ions is too low to cause precipitation. When the pH falls to 7-8 and calcium ions are present in excess (e.g. in sewage), precipitation of calcium salts of polycarboxylates will occur.

3.3.3 Consumption Data

The consumption of polycarboxylates in household detergents is estimated at 19 kt/y in West Germany in 1989 (Fachgruppe Wasserchemie, 1990) and 15 kt/y in Italy (Chiaudani and Poltronieri, 1990). In both countries almost exclusive use is made of phosphate-free household washing powders formulated with polycarboxylates (mass fraction of 2-5%). Thus, an estimated per capita consumption of 0.3 kg/y is obtained.

The total consumption of polycarboxylates in Italy was estimated to be 18 kt/y; this figure includes applications other than detergents (Section 3.3.1) (Chiaudani and Poltronieri, 1990).

SECTION 4. ENVIRONMENTAL DISTRIBUTION AND TRANSFORMATION

Over the past 20 years, a great deal of data has been generated on the environmental distribution and transformation of polycarboxylates used in detergents. In some cases, the test method was insufficiently specified and/or the exact nature (e.g. MW) of the tested polycarboxylates not given (Lehmann, 1973; Schefer, 1982; Jakobi, 1984; Schefer and Romanin, 1988). Recently, four reviews on detergent polycarboxylates and their environmental impact have been published (Hunter *et al*, 1987; Fachgruppe Wasserchemie, 1990; Chiaudani and Poltronieri, 1990; UK Department of the Environment, 1991). Hereafter, only those references that provided supplementary, specific data or additional information to the original publications and company reports are taken into account. In general, data from the available literature are in agreement concerning the environmental behaviour of polycarboxylates.

Due to their major use in detergents, the main pathway of polycarboxylates into the environment is via domestic waste water and sewage treatment to surface waters receiving treated effluents. Once in the sewerage system, polycarboxylates are removed from water by physico-chemical processes such as adsorption on to particulate matter and precipitation. The same processes of adsorption and precipitation are responsible for the elimination of polycarboxylates in a 2-stage (mechanical-biological) sewage treatment plant (STP), where a major part will be removed with the primary and secondary sludges. In the STP effluent, only minute amounts of soluble, non-absorbed polycarboxylates are expected. The sewage sludges are normally stabilised by anaerobic digestion and are subsequently used in agriculture as fertilisers, or disposed of by incineration or land-filling. Therefore, with respect to the environmental fate of polycarboxylates, degradation and elimination processes in STPs, surface waters and soils are of main interest.

4.1 DEGRADABILITY

4.1.1 Aerobic Biodegradation in Discontinuous Test Systems

Discontinuous biodegradation tests with P(AA) and P(AA-MA) were carried out under various bacterial inoculation conditions.

Respirometric Tests

No evidence for short-term biodegradation was obtained when P(AA)3,000-4,000 (test concentration: 5-200 mg/l) was evaluated for BOD_5, BOD_{10} (Biological Oxygen Demand after 5 and 10 d) and DOC (Dissolved Organic Carbon) removal after inoculation with effluent of a municipal STP (Metzner and Naegerl, 1982).

Similar tests with P(AA)920-15,700 showed a BOD_5/ThOD (Theoretical Oxygen Demand) ratio of < 13% (Abe *et al*, 1984).

A respirometric closed-bottle test with P(AA-MA)70,000 resulted in < 14% biodegradation (Jakobi, 1984).

River Water Die-away Tests

A number of ^{14}C-labelled P(AA)s (MW 1,000, 2,000 and 10,000 labelled backbone; MW 4,500 labelled backbone and at the COO group) and P(AA-MA)s (MW 12,000 and 70,000 labelled backbone and at the COO group) were tested in flasks fitted with CO_2 absorbers to trap the $^{14}CO_2$ evolved during biodegradation of the polycarboxylates. The polycarboxylates (test concentration: 0.1 and 1 mg/l) were incubated for up to 19 wk in river water, pre-adapted river water or a mixture of river water and sediment. Mineralisation in river water was < 20% for all polymers tested. The P(AA)s were mineralised to a higher degree in pre-adapted river water and river water plus sediments than in river water alone, the extent of degradation being 63% and 58% for P(AA)1,000, and 15% and 12% for P(AA)10,000 in the first 2 media. The results for P(AA-MA)s were not significantly different in these 3 test waters and show that their degradation is very slow under discontinuous test conditions (Hennes, 1991).

Tests with Activated Sludge Inoculum

Several batch degradation tests were conducted employing activated sludge as a bacterial inoculum.

Partial biodegradability of polycarboxylates (MW 1,000-70,000) was shown in long-term incubations (≤ 90 d) of ^{14}C-labelled P(AA) and P(AA-MA). The polycarboxylates (1, 10, 100 mg/l) were added to activated sludge (2-3 g Dry Suspended Solids [DSS]/l) from a municipal STP fed with a synthetic nutrition medium during the test period. P(AA)1,000 was mineralised to an average extent of 43%.

The results for the remaining polycarboxylates showed a decrease in mineralisation with increasing MW, from 19% for P(AA)2,000 to around 15% for the copolymers (Hennes, 1991).

The partitioning of ^{14}C-labelled P(AA-MA) 70,000 was investigated in an activated sludge batch system (2-3 g DSS/l). After addition of the ^{14}C-polymer (1-5 mg/l), the mixture was aerated for 4 h and allowed to settle for 2 h in order to simulate realistic STP retention times. The $^{14}CO_2$ evolution was ≤ 4% when non-acclimated or acclimated sludges from a municipal STP or a laboratory simulation plant were used. In most cases > 80% of the radiolabel was associated with the sludge solids; very little remained in the supernatants (Yeoman *et al*, 1990).

Additional evidence of the substantial biodegradability of low MW polycarboxylates was obtained when the non-adsorbed fraction (7%) remaining in solution was tested following incubation of ^{14}C-P(AA-MA)70,000 in a sludge batch system. This fraction was mineralised to 77-89% in a soil-bacteria inoculated screening test within 32 days (Opgenorth, 1989).

In conclusion, the experimental results show that only partial biodegradation associated with the low MW fraction of polycarboxylates can be expected under discontinuous screening test conditions.

4.1.2 Sewage-Treatment-Plant Model Systems

P(AA-MA)70,000 was investigated in a model STP using pre-adapted (4-5 wk) sewage sludge. The ^{14}C-labelled copolymer (5-20 mg/l) was added either continuously for 4-5 d or by pulse loading (1 single addition of 5 mg/l). The sludge loading was 0.3 g BOD_5/g DSS/d, the hydraulic retention time was 17 h and the sludge age 10 d. In both cases, > 90% of the radiolabel was recovered in the sludge, whilst 2-3% remained in the supernatant. Under continuous dosing conditions, 5% of the ^{14}C was mineralised to $^{14}CO_2$; pulse loading yielded almost 2% $^{14}CO_2$. The authors concluded that in real STPs the low MW fraction of P(AA-MA) can probably be ultimately biodegraded (Schumann, 1990).

4.1.3 Soil Systems

^{14}C-labelled P(AA) of MW ≤ 10,000 and P(AA-MA)12,000 and P(AA-MA)70,000 were tested (10-10,000 mg/kg soil) in a batch system containing sludge-treated soil. After 5 months incubation, the $^{14}CO_2$ evolution ranged from ≤ 12% for P(AA)s and P(AA-MA)s with MW ≥ 2,000 to 35% for P(AA)1,000 (Hennes, 1991).

The $^{14}CO_2$ production from added P(AA-MA)70,000 was followed for 1 year after incubation in standard soil (loamy sand, 1% organic C). The total amount of $^{14}CO_2$ evolved was 4-7%, mainly within the first month (Opgenorth, 1989).

These results suggest poor biodegradation of polycarboxylates in soils. The degradable fraction is assumed to arise from the low MW P(AA) species.

4.1.4 Anaerobic Biodegradability

Based on studies simulating the digestion of sewage sludge no evidence exists for anaerobic biodegradability of high MW polycarboxylates.

^{14}C-P(AA-MA)70,000 (20 mg/l) was incubated anaerobically (258 d at 35°C) in digester sludge with added nutrients. After purging of volatile products with nitrogen, 11-16% of ^{14}C was transformed into unidentified gaseous products (Opgenorth, 1989). Anaerobic incubation of ^{14}C-P(AA-MA)70,000-loaded activated sludge in a model digester did not result in degradation (Opgenorth, 1989). Most (94-95%) P(AA-MA) remained adsorbed onto the digester sludge. A small non-adsorbed quantity (5-6%) of P(AA-MA) was partly biodegraded and partly re-adsorbed onto the activated sludge when the water was released back into the STP. The authors concluded that renewed entry of adsorbed polymer materials into the aquatic phase after sludge digestion can be excluded (BASF, 1992c).

4.2 ELIMINATION IN SEWAGE TREATMENT PLANTS

4.2.1 Primary Clarification

The removal of polycarboxylates during primary clarification of raw waste water in STPs depends on their MW, but is low compared to the removal of Total Suspended Solids (TSS).

A dynamic settling test with ^{14}C-labelled P(AA)4,500, P(AA-MA)12,000 and P(AA-MA)70,000 (5-6 mg/l) was carried out to simulate the primary clarification process, using raw municipal sewage sampled after elimination of coarse particles by a comminuter. TSS removal in the test unit (2 h retention time) was 70-84%, comparing favourably to normal TSS removal (50-70%) by an effectively operated primary clarifier (Metcalf and Eddy, 1979). The degree of removal was 13% for P(AA)4,500 , 8% for P(AA-MA)12,000 and 29% for P(AA-MA)70,000 (Hennes, 1991).

Results obtained with P(AA-MA)70,000 added to raw sewage filled into batch test units confirmed the slow settling of polycarboxylates: 12-44% settled after 2 h and 81-88% after 96 h (BASF, 1992d).

4.2.2 Activated Sludge Treatment

Screening Tests

In a screening test to predict full-scale activated sludge treatment, removal of polycarboxylates was found to be a function of their MW. In semi-continuous activated sludge (SCAS) batch tests, relatively high polymer concentrations (e.g. 20 mg/l) were added to municipal activated sludge suspensions. The test systems were aerated for 23 h and renewed daily for 7 consecutive days. The results showed that elimination of polycarboxylates in activated sludge tests generally increased with increasing MW (Table 3).

Table 3: Elimination in Activated Sludge Tests

Polycarboxylate	Elimination (%)	Reference
P(AA)1,000	45	Hennes, 1991
P(AA)2,000	21	Hennes, 1991
P(AA)4,500	40	Hennes, 1991
P(AA)10,000	58	Hennes, 1991
P(AA)60,000	93	Hennes, 1991
P(AA-MA)12,000	83	Hennes, 1991
P(AA)9,400	40	Unilever, 1989
P(AA)23,000	48	Unilever, 1989
P(AA)111,000	81	Unilever, 1989
P(AA)152,000	95	Unilever, 1989
P(AA)215,000	95	Unilever, 1989
P(AA-MA)70,000	94-99	Opgenorth, 1987; Hennes, 1991; Unilever, 1989; Ziegler, 1985

These figures represent removal of P(AA)s and P(AA-MA)s by a combination of adsorption-precipitation and biodegradation. A comparison with the results of pure biodegradation tests with activated sludge inoculum (Section 4.1.1.) demonstrates that the removal of P(AA)1,000-2,000 is mainly due to biodegradation. Adsorption/precipitation accounts for the overall removal of the higher MW polycarboxylates.

The same conclusion can be drawn from results obtained in the Zahn-Wellens test, another screening test system with activated sludge (1 g DSS/l). After 3 h, the elimination of P(AA-MA)70,000 (50-400 mg/l at start) was 86%; at completion of the test (28 d), the C removal was about 98% (Chiaudani and Poltronieri, 1990).

The sorptive-precipitative nature of polycarboxylates was shown in sorption flask tests with activated sludge (water hardness 2-17°d; 1°d = 10 mg/l CaO) when biodegradation was excluded by the test design. The elimination was 92-94% for radiolabelled P(AA-MA)70,000 (0.5-10 mg/l) (Opgenorth, 1989) and 45-60% for P(AA)3,000-4,000 (5-200 mg/l) in the pre-sence of washed phosphorus-free activated sludge (water hardness not specified) (Metzner and Naegerl, 1982).

Model Plants for Activated Sludge Treatment

Studies simulating full-scale activated sludge treatment also demonstrate that the removal of polycarboxylates generally increases with increasing MW.

Several polycarboxylates (concentration 1-3 mg/l for ^{14}C-labelled; 10-30 mg/l for unlabelled materials) were tested in model STPs. The studies were conducted according to the OECD confirmatory and coupled units test protocols. The units were filled with municipal activated sludge and continuously fed with raw or synthetic sewage. The operating conditions were similar to a full-scale system, including sludge loading (0.3 BOD_5/g TSS/d), sludge retention time (approximately 10 d) and TSS content. The hydraulic retention time varied from 3 h in the Coupled Units Test (Henkel Laboratory, 1987) to 6-7 h (Hennes, 1991; Opgenorth, 1987) and 17 h (Schumann, 1990) in various OECD confirmatory tests.

From these tests data on overall removal are obtained (cf. degradability, Section 4.1.) The results show that the elimination of polycarboxylates by activated sludge treatment increases with their MW (Table 4).

The differences in the results for P(AA)4,500 are assumed to be due to differences in the initial test concentrations (1 mg/l: 75% [Rohm and Haas, 1991d]; 3 mg/l: 27% and 30 mg/l: 16% [Hennes, 1991]).

The elimination of polycarboxylates of MW > 2,000 by activated sludge treatment is mainly by adsorption/precipitation of their calcium salts on the sludge. This requires calcium to be present in molar excess with respect to polycarboxylate. According to the data obtained in a number of tests,

Table 4: Elimination by Activated Sludge Treatment

Polycarboxylate	Elimination (%)	Reference
P(AA)1,000	9 - 24	Hennes, 1991
2,000	13 - 18	Hennes, 1991
4,500	16 - 27	Hennes, 1991
	75	Rohm and Haas, 1991d
P(AA-MA)12,000	70 - 80	Hennes, 1991
70,000	82 - 93	Hennes, 1991
	>94	Opgenorth, 1987
	97 - 98*	Schuman, 1990
P(AA)78,000	78	Henkel Laboratory, 1987

* Continuous dosing and pulse loading

an average elimination rate of at least 90% can be anticipated for P(AA-MA) 70,000 in the biological stage of a STP.

Tertiary Treatment (Simultaneous Phosphate Precipitation)

P(AA)4,500 and P(AA-MA)12,000 were tested in a model STP with added ferric chloride (100 mg $FeCl_3$/l), to simulate simultaneous phosphate precipitation. Under these conditions the removal increased from 22 and 74%, respectively, to > 90% for both polymers. Since the removal efficiency is a function of MW, the figure will be even higher for P(AA-MA)70,000 (Hennes, 1991).

In conclusion, the results from screening and simulation tests with activated sludge give evidence that the removal of polycarboxylates is mainly due to adsorption/precipitation of the polymers. Non-adsorbed low MW polycarboxylates are significantly removed by biodegradation processes.

4.3 MOBILITY IN SOILS

Since a major part of polycarboxylates in STPs is eliminated by adsorption/precipitation, polycarboxylates can be expected to reach the soil environment via disposal of sewage sludge. Their potential to migrate with rain or irrigation water can be assumed to be very low. Evidence for this behaviour was found in lysimeter studies with ^{14}C-labelled polycarboxylates, described below.

When 50 µg ^{14}C-labelled P(AA)4,500, P(AA-MA)12,000 and -70,000 were spiked on to medium grained sandy soil (96% sand, 2% silt, 2% clay and 0.02% organic C) in a lysimeter percolated with

simulated groundwater for 10 wk, the mobile fraction, analysed as the activity in the column effluent, consisted of 10% of P(AA)4,500, 16% of P(AA-MA)12,000 and 7% of P(AA-MA)70,000. The major part of this mobile fraction was eluted with the percolated water and was assumed to be of low MW. Similar elutable polycarboxylate fractions would not be found in a soil treated with sewage sludge because of their tendency to remain with the aqueous phase and their biodegradation potential in activated sludge (Section 4.2.2). Most of the polycarboxylate fraction was non-mobile and remained within the first 10-15 mm of the soil column, as demonstrated by the combustion of soil segments and recovery of $^{14}CO_2$ at the end of the experiments (Hennes, 1991).

In another lysimeter, digested sewage sludge with added radio-labelled P(AA-MA)70,000 was applied to a humus-rich, peaty soil. The soil was percolated with distilled water (equivalent to the average rainfall over 6-7 y) and, during another test run, with water of pH 4.8 and 3.0 to simulate acid rain. In all experiments, no free P(AA-MA)70,000 could be detected in the eluate. Activity analysis of different soil segments demonstrated that the polycarboxylate had been retained by the upper soil layer (Opgenorth, 1987).

4.4 ELIMINATION IN DRINKING WATER PREPARATION PROCESSES

Polycarboxylates are removed from raw drinking water to a large extent by coagulation- flocculation with aluminium chloride ($AlCl_3$) or ferric chloride ($FeCl_3$). This purification process is applied typically to surface water of high turbidity or TSS content when used as a source of raw drinking water. In some cases, the water intake may contain traces of polycarboxylates.

In an experiment similar to the jar test, ^{14}C-labeled P(AA)4,500, P(AA-MA)12,000 and P(AA-MA)70,000 were added at concentrations of 5-600 µg/l. The jar test is normally conducted at drinking water treatment plants to determine the optimum coagulant dose for TSS removal. At optimal coagulant doses (10 - 50 mg/l $AlCl_3$ or $FeCl_3$), removal of the polymers was > 90% in river water of acceptable quality and > 60% in river water of low quality for drinking water production. The removal was not found to be a function of MW (Hennes, 1991).

When high concentrations of P(AA)3,000-4,000 (100 mg/l) and coagulant doses (50-500 mg/l $AlCl_3$, $FeCl_3$ and lime slurry) were applied, the polycarboxylate removal was lower: 30-70% (Metzner and Naegerl, 1982). However, this study was designed to test the polymer for use as a conditioning agent in drinking water preparation and the low removal may not be representative in the context of trace concentrations of polycarboxylate in raw drinking water. A similar study with P(AA)15,000 (30 mg/l) showed > 90% removal with $AlCl_3$ and $FeCl_3$ (Jekel and Sontheimer, 1981).

SECTION 5. ENVIRONMENTAL LEVELS AND HUMAN EXPOSURE

5.1 ENVIRONMENTAL LEVELS

No data are available on polycarboxylate levels measured in the environment (Section 2.3.2). The only valid measurement results refer to drinking water, where polycarboxylate levels were below the limit of analytical detection of 10 μg/l (Schroeder *et al*, 1991).

Levels of polycarboxylates in the environment were estimated from the data on their removal in different environmental compartments (Appendix B). Calculations were carried out for P(AA-MA)70,000 which is predominantly used in phosphate-free laundry detergents (Section 3.2). The levels of P(AA-MA)70,000 in different environmental compartments were estimated for West Germany and Italy as follows (Table 5):

Table 5: Estimated Levels of P(AA-MA)70,000

Environmental Compartment	Level	Unit
Raw sewage	4.1	mg/l
Sewage treatment effluent (mechanical/biological)	0.29	mg/l
Surface water (dilution of treated effluent)	0.03	mg/l
(dilution of untreated effluent)	0.41	mg/l
Drinking water	<0.003	mg/l
Digested sewage sludge	19	g/kg
Sludge-treated soil	6	mg/kg/y

The extremely low concentrations of polycarboxylates in drinking water are supported by the above-mentioned measurements of Schroeder *et al* (1991).

As P(AA) and P(AA-MA) are poorly degradable, elevated concentrations are to be expected in agricultural soils treated with sewage sludge. It should be noted that the polycarboxylates are deposited in the soil as inert and insoluble calcium compounds.

5.2 HUMAN EXPOSURE LIMITS

No data exist on human exposure levels and no occupational exposure limits have been fixed for polycarboxylates used in industrial processes. Toxicological results in the laboratory and practical experience during production and use have shown that detergent polycarboxylates exhibit a low toxicity profile which substantiates the lack of need to define specific exposure limits.

In view of their high affinity for moisture, there is a potential for polycarboxylates to cause discomfort by drying and adherence to mucous membranes. Therefore it is advisable to keep exposure levels as low as resonably practicable and plant target limits of 1 mg/m^3 for total airborne dust have been operational in detergent manufacturing plants without apparent detrimental effect on the workers (see company safety datasheets).

SECTION 6. EFFECTS ON THE ENVIRONMENT

6.1 WASTE-WATER TREATMENT PROCESSES

6.1.1 Sludge Sedimentation during Primary Clarification

The influence of polycarboxylates on sludge TSS during primary clarification (the mechanical stage of STPs) was determined in the influent raw sewage and the effluent of a continuous test system (hydraulic retention time 2 h) simulating the primary settler of an STP. In the presence of P(AA)1,000, P(AA)2,000, P(AA)4,500 and P(AA-MA)12,000 (30 mg/l, maximum concentration tested), no effects on TSS removal were obtained; P(AA-MA)70,000 had no deleterious effect at levels < 22 mg/l. With P(AA)10,000, a small effect (< 10% TSS removal) was noted at 1, 10 and 30 mg/l, but not at 0.3 and 3 mg/l (Hennes, 1991). Hence, no influence on the sludge sedimentation behaviour in primary classifiers is to be expected at realistic polycarboxylate concentrations in raw sewage.

6.1.2 Activated-Sludge Waste-Water Treatment

Addition of P(AA)3,000-4,000 (up to 150 mg/l) to municipal raw sewage in a discontinuous Sapromat test did not inhibit the degradation of peptone within the 5-d test period. There were no significant effects on biodegradation kinetics and cumulative BOD (Metzner and Naegerl, 1982). The performance of a continuous activated sludge model plant was not significantly affected, in terms of COD (Chemical Oxygen Demand), TSS removal and SVI (Sludge Volume Index), by the addition of P(AA)4,500, P(AA-MA)12,000 and P(AA-MA)70,000 (up to 30 mg/l, the highest concentration tested) (Hennes, 1991).

When P(AA)78,000 (up to 50 mg/l, i.e. 20 mg/l organic C) was tested in a Coupled Units Test, representing a continuous STP model system, the highest concentration tested had no significant effect on the removal of organic C, COD and MBAS (Methylene-Blue Active Substances) (Henkel Laboratory, 1987). Thus, no adverse effects on the performance of an STP are anticipated.

P(AA-MA)70,000 (10 mg/l) was added alternately to each of 2 bench-scale model STPs (operating conditions, see Section 4.2.2, model plants) for several weeks to compare polymer-dosed and undosed model STPs. Daily determination of DOC-, COD- and BOD_5-removal, effluent concentrations of settleable solids and the SVIs showed no differences between the 2 test plants. There were also no significant differences in quality of the excess sludges, measured by their dry

matter, volatile solids and TOC contents. The same was true for the microscopic structure of the sludges' flocs and the presence of filamentous bacteria and protozoa (Opgenorth, 1989).

6.1.3 Settling Behaviour of Activated Sludge

In addition to the model STP investigations (Section 6.1.2), several tests were conducted on the settling behaviour of activated sludge loaded with polycarboxylates.

In batch tests with P(AA)2,000, P(AA)4,500, P(AA)10,000 and P(AA-MA)12,000 up to 100 mg/l, the highest concentration tested, there was no effect on the settling rate of activated sludge. In the presence of P(AA)1,000 at 30 and 100 mg/l, a small increase in sedimentation was seen, whereas there was a gradual decrease with P(AA-MA)70,000 at 30 and 100 mg/l (i.e. the slope of the regression line was significantly different from 0 at a 95% confidence level). Due to the varying settling velocities in a real sludge clarifier, where sludge is allowed to settle and thicken, this effect has no practical significance (Hennes, 1991).

Concentrations of up to 100 mg/l P(AA)9,400, P(AA)23,000, P(AA)111,000, P(AA)152,000, P(AA)215,000 and P(AA-MA)70,000 had no significant effect on the SVI (Unilever, 1989).

6.1.4 Anaerobic Digestion

No effects on the kinetics and amount of gas formed were observed when a batch of activated sludge loaded with P(AA)78,000 was incubated in a laboratory digester for 7 wk at 36°C, up to 500 mg/l (the highest concentration tested; corresponding to a sludge load of 25 mg/g of dry matter) (Henkel Laboratory, 1987). A similar anaerobic incubation of P(AA-MA)70,000-loaded sludge obtained from a model STP (concentration not given) produced qualitative data suggesting no disturbance of the digestion process by the polymer (Opgenorth, 1987).

6.1.5 Phosphate Precipitation

To simulate simultaneous precipitation of phosphates by polycarboxylates in STPs, 100-150 mg/l of $FeCl_3$ or $Al_2(SO_4)_3$ (corresponding to molar ratios of 1.3-2.0:1 for Fe/Al:P in the influent) were added in the presence of P(AA)4,500, P(AA-MA)12,000, a mixture of these 2 polymers, or P(AA-MA)70,000. The phosphorus concentration in the STP model effluents was not affected by any polycarboxylates up to 30 mg/l, the highest concentration tested (Hennes, 1991).

6.1.6 Dewatering of Digested Sludge

A comparison of capillary suction times during dewatering of digested sludge, with optimum dosage of $FeCl_3$ for sludge conditioning, showed that the presence of 10 mg/l of P(AA)1,000, P(AA)4,500 and P(AA-MA)70,000 was without any effect (Hennes, 1991).

The same conclusion may be drawn from results of a STP model with P(AA-MA)70,000 dosed for several weeks (Section 6.1.2). The produced activated sludge did not reveal any differences in sludge dewatering properties and the demand of flocculation additives (Opgenorth, 1989).

6.1.7 Coagulation of Raw Sewage by $FeCl_3$

Coagulation of raw sewage by Al or Fe salts is often used in STPs to reduce the organic load of the subsequent biological treatment step.

In a batch test of raw sewage loaded with polycarboxylates, the effect of different polycarboxylate concentrations on TSS concentration and turbidity of the supernatant were determined following $FeCl_3$ addition, subsequent stirring and sedimentation for 30 min. The NOECs (No Observed Effect Concentrations) were in the range of 1-3 mg/l of P(AA)1,000, P(AA)4,500, P(AA)10,000; 10 mg/l of P(AA)2,000 and 30 mg/l of P(AA-MA)12,000 and P(AA-MA)70,000 (Hennes, 1991). These NOECs are higher than the predicted polycarboxylate concentrations in sewage.

6.2 ECOTOXICITY

6.2.1 Micro-organisms

Polycarboxylates proved to be harmless to bacteria at concentrations of at least 100 times above the environmentally relevant range (Section 5.1).

In tests examining effects of polycarboxylates on physiological reactions, the EC_{50} (O_2-consumption) for P(AA)1,000-4,500 and P(AA-MA)12,000-70,000 was > 100 mg/l; the EC_{50} (glucose consumption) for P(AA)4,500 and P(AA)10,000 was > 1,000 mg/l (Hennes, 1991). Additional data on bacterial oxygen consumption are available for P(AA)78,000, where the EC_0 was 36 mg/l in a test with *Pseudomonas putida* (Henkel Laboratory, 1987); for P(AA-MA)70,000 the EC_{10} was ≥ 200 mg/l and the EC_0 400 mg/l with sludge bacteria (BASF, 1992e). In the Microtox test with luminescent bacteria, P(AA-MA)70,000 showed an EC_{20} > 200 mg/l (BASF, 1992f).

Chronic bacterial toxicity tests determining the growth inhibition concentration underlined the low bacterial toxicity of high MW homo- and heteropolymers: the EC_0 of P(AA)78,000 was 300 mg/l (Henkel Laboratory, 1987), the EC_{10} of P(AA-MA)70,000 was 180 mg/l (Opgenorth, 1987).

6.2.2 Aquatic Organisms

Acute Toxicity (Tables 6 and 7)

Acute fish and *Daphnia* toxicity data are available for a number of polycarboxylates. A consistently low toxicity was observed (Tables 6 and 7). It should be pointed out that in most cases the highest concentration tested was below the LC_{50} so that different "greater than" values reflect the highest concentrations tested, but do not necessarily refer to differences in toxicity.

Table 6: Acute Toxicity to Fish

Polymer tested	Zebra fish (*Brachydanio rerio*) 96h LC_{50} (mg/l)	Golden orfe (*Leuciscus idus melanotus*) 96h LC_{50} (mg/l)	Bluegill (*Lepomis macrochirus*) 96h LC_{50} (mg/l)	Trout (*Salmo gairdneri, Oncorhynchus mykiss*) 96h LC_{50} (mg/l)
P(AA)1,000	> 200[a]		> 1,000[e]	> 1,000[g]
P(AA)2,000	> 200[a]			
P(AA)4,500	> 200[a]		> 1,000[a]	700[h]
			> 1,000[i]	
P(AA)9,400	> 1,000[f]			
P(AA)10,000			> 1,000[a]	
P(AA)23,000	> 1,000[f]			
P(AA)78,000	> 1,000[c]	1,590[d]		
P(AA)111,000	> 1,000[f]			
P(AA)152,000	> 1,000[f]			
P(AA)215,000	> 1,000[f]			
P(AA-MA)12,000	> 200[a]			
P(AA-MA)70,000	> 100[a]	> 200[b]		
	> 1,000[f]			

References:
a = Hennes, 1991
b = Opgenorth, 1987
c = Henkel Laboratory, 1987
d = Degussa, 1985
e = Rohm and Haas, 1983a
f = Unilever, 1989
g = Rohm and Haas, 1983a
h = Rohm and Haas, 1983c
i = Rohm and Haas, 1983d

Table 7: Acute Toxicity to the Freshwater Flea (*Daphnia magna*)

Polymer	48h EC_{50} (mobility) (mg/l)	Reference
P(AA)1,000	> 200	Hennes, 1991
	≥ 1,000	Rohm and Haas, 1983e; Chiaudani and Poltronieri, 1990
P(AA)2,000	> 200	Hennes, 1991
P(AA)4,500	> 200	Hennes, 1991
	> 1,000	Rohm and Haas, 1983f; Chiaudani and Poltronieri, 1990
P(AA)78,000	750 (24h)	Henkel Laboratory, 1987
P(AA-MA)12,000	> 200	Hennes, 1991
P(AA-MA)70,000	> 100	Hennes, 1991
	> 500	Chiaudani and Poltronieri, 1990
	> 200	Opgenorth, 1987
	> 908	Schuman, 1990

The acute toxicity of P(AA)4,500 to chironomid larvae was tested in a sediment batch system. After 96 h, no effect was observed at the highest concentration tested (4,500 mg/kg dry matter) (Hennes, 1991).

Subchronic and Chronic Toxicity

Inhibitory effects on algal growth were observed with *Scenedesmus subspicatus*, the 96-h EC_{10} being 180 mg/l for P(AA)4,500 (Hennes, 1991); different values were obtained for P(AA-MA) 70,000 with 96-h EC_{10} values of 32 mg/l (Schumann, 1990) and ≥ 200 mg/l (Opgenorth, 1987). The EC_{10} (algal growth, 4-14 d) for P(AA)78,000 was 82 mg/l with *Scenedesmus* and 30 - > 1,000 mg/l with *Chlorella kessleri.* The toxicity decreased with the test period, indicating some adaptation (Henkel Laboratory, 1987).

In 21-d reproduction (life-cycle) tests using P(AA)4,500 with *Daphnia magna* divergent results were obtained, with NOEC values of 12 mg/l (Rohm and Haas, 1991c) and 450 mg/l (Hennes, 1991). For P(AA)78,000, the NOEC was 400 mg/l (Henkel Laboratory, 1987) and for P(AA-MA)70,000, 350 mg/l (Hennes, 1991). The NOEC for P(AA-MA)70,000 was much lower under test conditions where precipitation of the polymers by formation of their calcium salt took place, viz. 6.2 mg/l (Opgenorth, 1987) or 1.3 mg/l (Schumann, 1990). Opgenorth (1992) pointed out that polycarboxylates are less toxic in solution (NOEC 350 mg/l) than when precipitated due to water hardness at lower concentrations. He assumed that physical - rather than toxic - effects must be

held responsible, depending on the state of coagulation of the polycarboxylate salt. The author concluded that the environmental relevance of these findings is limited because in practice polycarboxylates are preferentially adsorbed on solids and the tested form will not be present in surface waters. It should be noted that the lowest NOEC is much higher than the estimated concentrations in surface water (Section 5.1).

The 14-d EC_{10} for inhibition of colony growth of *Hydra littoralis* was 40 mg/l for P(AA-MA)70,000 (Opgenorth, 1987). A 14-d sublethal toxicity test with zebra fish (*Brachydanio rerio*) resulted in a NOEC of 1,000 mg/l (highest concentration tested) for P(AA)78,000 (Henkel Laboratory, 1987), and 40 mg/l (highest concentration tested) for P(AA-MA)70,000 (Opgenorth, 1987).

In a subchronic (4 wk) early life-stage test with zebra fish (*Brachydanio rerio*), the NOEC was 450 mg/l (highest concentration tested) for P(AA)4,500 (Hennes, 1991), and, in a 6-wk test, 40 mg/l (highest concentration tested) for P(AA-MA)70,000 (Opgenorth, 1987). An early life-stage test of P(AA)4,500 with Fathead minnow (*Pimephales promelas*) resulted in a NOEC of 124 mg/l (Rohm and Haas, 1991a).

6.2.3 Terrestrial Organisms

The acute toxicity of polycarboxylates to earth worms (*Eisenia foetida foetida*) is low. For P(AA)4,500, the LC_{50} was > 1,000 mg/kg soil (Rohm and Haas, 1991b). LC_0 values were reported for P(AA)78,000: 1,000 mg/kg soil (Henkel Laboratory, 1987) and for P(AA-MA)70,000: 1,600 mg/kg soil (Opgenorth, 1987).

P(AA)4,500 did not inhibit the growth of corn, soybean, wheat and grass seeds up to 225 mg/kg soil, the highest concentration tested (Hennes, 1991). P(AA)78,000 showed a NOEC of 1,000 mg/kg soil for growth of turnip seed (Henkel Laboratory, 1987). In a growth inhibition test of oats seeds with P(AA-MA)70,000, a NOEC of 400 mg/kg soil was established (Opgenorth, 1987).

6.2.4 Bioaccumulation

Experimental data on the bioaccumulation potential of polycarboxylates are not available.

The estimation of the bioconcentration potential by means of the *n*-octanol/water partition coefficient (P_{ow}) is only applicable to substances with an MW < 600 (Veith and Kosian, 1988) and non-ionisable compounds (OECD, 1981). Bioaccumulation of polycarboxylates is unlikely because absorption through biological membranes is only assumed to occur for substances with a MW < 600

(Zitko, 1981). In addition, the high water solubility of the parent compound together with its propensity to form insoluble calcium salts in natural waters suggests that bioaccumulation is unlikely.

6.3 HEAVY METAL MOBILISATION

The mobility of heavy metals in activated sewage sludge, river sediments and soils is not affected by the presence of polycarboxylates at realistic environmental concentrations (estimated in Section 5.1).

6.3.1 Activated Sludge

The distribution of P(AA)s and P(AA-MA)s of different MW was tested in a batch test with activated sewage sludge (Hennes, 1991) and, for P(AA-MA)70,000 only, in a model STP (Opgenorth, 1987). The batch tests were carried out in centrifuge bottles with polycarboxylate concentrations of 10, 30 and 100 mg/l added to sludge suspensions which were stirred and aerated for 24 h, allowed to settle and centrifuged. Analysis of dissolved Cd, Cu, Ni, Pb, and Zn showed that P(AA-MA)70,000 did not cause any effect, compared to the control, within the concentration range tested. Addition of 10 mg/l P(AA)1,000 and P(AA)2,000 resulted in an increase of up to 30% in Cu-concentrations; 100 mg/l of these polymers and P(AA)4,500 caused an increase in the concentrations of Zn (up to 100%) and Cu (up to 80%); 100 mg/l P(AA-MA)12,000 resulted in a 46% increase of Cu. It should be noted that these concentrations will never occur in municipal activated sludge. The distribution of the other heavy metals remained unaffected at all polycarboxylate concentrations tested.

P(AA-MA)70,000 (10 mg/l) was dosed alternately for several weeks to 2 model STPs operated in parallel (operating conditions, see Section 4.2.2, model plants). Concentrations of Cr, Cu, Ni, Pb, Zn, Cd and Hg were analysed in the effluent and compared with the control. No differences in the extent of elimination of Cr, Cu, Ni, Pb, and Zn were observed. The concentrations of Cd and Hg were at the limit of detection and the degree of elimination could not be calculated, but the effluent concentrations were not increased (Opgenorth, 1987, 1989).

6.3.2 Sediments

Experiments with batch sediment suspensions were conducted in the way described above (Section 6.3.1). The sediment was taken from the top 1-2 cm of river sediment, wet-sieved to remove coarse particles and suspended in river water from the same location. Following the addition of polycarboxylates, no mobilisation of Zn, Ni, Pb, Cd or Cu into the dissolved phase was observed up

to a concentration of 10 mg/l P(AA)1,000, P(AA)2,000 and P(AA)4,500, and 30 mg/l P(AA-MA)12,000 and P(AA-MA)70,000, the highest concentration tested. Only at 30 mg/l of P(AA)2,000 and P(AA)4,500, a concentration far beyond the level expected in real surface waters, was there an increase in the concentration of Zn (up to 45%) (Hennes, 1991).

6.3.3 Soils

In a batch test using a suspension of soil loaded with heavy metal salts of Cd, Cr, Cu, Hg, Ni and Pb (250 mg/kg), P(AA-MA)70,000 (10 and 100 mg/l) were added and stirred for 1 h to test the possible leaching of heavy metals. Addition of 10 mg/l P(AA-MA)70,000 did not cause any increase in the concentration of heavy metals in the eluate, compared to the control run. Only 100 mg/l P(AA-MA), a level that is not expected to occur in real soils, resulted in slightly increased effluent concentrations of Cu and Cr (Opgenorth, 1989).

SECTION 7. KINETICS AND METABOLISM

7.1 HUMAN

No data are available on the toxicokinetics and metabolism of any P(AA)s or P(AA-MA)s in man.

7.2 EXPERIMENTAL

Some limited metabolism studies have been undertaken on a phosphinated P(AA), P(AA-P)2,500 (50% aqueous solution) containing < 2% phosphinate (Unilever, 1990). The results are summarised below because they may give some insight into the toxicokinetics and metabolism of P(AA) and P(AA-MA).

7.2.1 Gavage

^{14}C-labelled P(AA-P)2,500, prepared from ^{14}C-labelled AA (3.6 μCi/mg), was administered by gavage at 25 mg P(AA-P)/kgbw to Colworth Wistar rats. Urine, faeces and expired air were assayed for radioactivity over 4 d and tissues and carcass remains were also assayed. Only 0.35% of the administered dose was recovered as expired air, and 0.47% in the urine. Tissue levels and carcass levels after 4 d were extremely low, 0.03% and 0.3% respectively. Most of the ^{14}C dose (82-94%) was recovered in the faeces, indicating there was very little absorption from the intestinal tract (Unilever, 1990).

7.2.2 Skin

Guy and Hadgraft (1987) have shown that compounds with a MW > 1,000 are unlikely to penetrate the skin readily. The presence of polar groups in a molecule also tends to reduce its permeability through the skin. Thus it would be anticipated that skin penetration by P(AA)s and P(AA-MA)s would be low.

^{14}C-P(AA-P)2,500 as described above was also applied topically to the clipped skin of Colworth Wistar rats as a 21.4% aqueous solution providing a dose of 43 mg/animal. The area was covered by an occlusive patch to prevent evaporation of water from the skin and to optimise conditions for penetration. Excreta, carcass, skin and protective patch were assayed for ^{14}C after 2 d and penetration of sample occurring over 10 cm^2 of skin was estimated by summation of the ^{14}C levels in expired air, urine and faeces. Most of the applied dose remained on the skin at 48 h, with some remaining on the occluded patch. Penetration was low since only 0.3% was recovered in expired air, urine and faeces (Unilever, 1990).

SECTION 8. EFFECTS ON EXPERIMENTAL ANIMALS AND *IN VITRO* TEST SYSTEMS

There are very few published data on the toxicology of polycarboxylate polymers, the major exceptions being some genotoxicity and teratogenicity testing reported recently (Thompson *et al*, 1989; Nolen *et al*, 1989) and mucous membrane irritancy and repeated dose testing undertaken mainly in the 1950s (e.g. Finnegan and Dienna, 1953). However, much of the toxicological data in company files on P(AA) and P(AA-MA) copolymers has been made available to aid the compilation of this chapter.

A summary of the findings for P(AA) over a wide range of MW and for P(AA-MA)12,000 and P(AA-MA)70,000 is provided in Table 8. Essentially, negative findings have been obtained (with the exception of some skin and eye irritancy data at high test concentrations). In general, the polymers were supplied as an aqueous solution containing 40-50% of the polymer, and tested either as supplied or diluted. Substances were normally neutralised and frequently tested as the salts. Monomer content was not normally stated. Unless stated otherwise, doses are expressed in this chapter as a % or weight of the received solutions. Where adjustments are made for the water content, doses are expressed as a % or weight of the active P(AA) or P(AA-MA) ingredient.

8.1 ACUTE TOXICITY (Table 8)

P(AA)s and P(AA-MA)s are of an extremely low acute toxicity to rat or mouse, oral LD_{50} values being generally > 5 g/kgbw.

8.1.1 Oral

Neutralised P(AA)1,000 was neither toxic nor lethal following its oral administration to groups of 3 rats at a dose level of 5 g/kgbw; the LD_{50} was > 5 g/kgbw (Rohm and Haas, 1982a).

In a rat acute oral study undertaken on P(AA)4,500 using groups of 3 rats, the LD_{50} was > 5 g/kgbw (Rohm and Haas, 1982b). Clinical observations included increased salivation and staining around the nose at 5 g/kgbw, but not at 0.5 g/kgbw. When P(AA)1,200, P(AA)2,500, P(AA)8,000 and P(AA-MA)70,000 were tested to standard OECD LD_{50} protocols, the LD_{50} was > 5 g/kgbw in each case. Older investigations with P(AA)15,000 and P(AA)70,000 revealed LD_{50} values > 10 g/kgbw (BASF, 1992g). When P(AA)78,000 was tested using groups of 5 male and 5 female animals, the LD_{50} was > 10 g/kgbw (Degussa, 1983a,d).

Table 8: Summary of Acute Toxicity in *In Vitro* Test Systems and Experimental Animals (Section 7 and 8)

	← P(AA) →											← P(AA-MA) →	
MW:	1,000	1,200	2,000	2,500	4,500	8,000	15,000	37,000	70,000	78,000	90,000	12,000	70,000
LD_{50} (mg/kgbw)													
oral (rat)	> 5	> 5		> 5	> 5	> 5	> 10		> 10	> 10			> 5
dermal (rabbit)	> 5				> 5								
Irritation													
skin (rabbit)	NI	NI		NI		NI			SL/NI	NI			NI
eye (rabbit)	SL	SL[m]		SL	SL	NI			SL/NI	SL			SL
Sensitisation													
M&K/BU (guinea pig)					-ve			-ve		-ve			-ve
Subchronic toxicity													
28 d (rat)				a									a,c
91 d (rat)					b								a,b
Ames test			-ve		-ve							-ve	-ve
In vitro cytogenetics					-ve							-ve	
UDS assay			-ve		-ve							-ve	-ve
Gene mutation			-ve		-ve							-ve	-ve
In vivo chromosome			-ve										-ve
ADME studies				-ve									
Teratogeniticy (rat)					-ve						-ve	-ve	

SL	Slight effects observed; not classified under EEC regulations (m, marginal score 1 h after application)
NI	Not irritant
-ve	Test done, negative response obtained
a	See text, oral
b	See text, inhalation
c	See text, dermal

8.1.2 Dermal

In a rabbit dermal study on P(AA)4,500 with 2 rabbits the LD_{50} was > 5 g/kgbw using an occluded patch protocol. No deaths occurred. Toxic signs included well defined erythema with no oedema on day 1 with recovery by day 2. The slight skin irritation observed was insufficient to warrant classification (Rohm and Haas, 1982b).

P(AA)1,000 was applied dermally to 2 rabbits at the maximum dose of 5 g/kgbw for 24 h before being wiped off. No toxic signs were observed and no gross organ changes recorded. Erythema was noted on day 1 which had cleared by day 5 and skin desiccation observed on day 5 which had cleared by day 8. The LD_{50} was > 5 g/kgbw (Rohm and Haas, 1982a).

8.2 SKIN AND EYE IRRITATION, SENSITISATION (Table 8)

P(AA)s and P(AA-MA)s are not normally classified under EEC regulations as hazardous with respect to their skin and eye irritation and sensitising properties. Nevertheless, there are some observations described below which indicate that these substances may be slightly irritating to both skin and eye under certain conditions of exposure not related to detergent use. The term SL as applied in Table 8 indicates that the hazard is insufficient to attract the R and S phrases as described in EEC directive 67/548 and its amendments. None of the polymers and copolymers tested have been reported to be sensitisers.

8.2.1 Skin Irritation

When P(AA)1,000 (Rohm and Haas, 1982a), P(AA)1,200, P(AA)2,500 or P(AA)8,000 (BASF, 1992g) was applied dermally to 3 rabbits for 4 h as an occluded patch, no signs of erythema or oedema were detected.

Evidence of slight skin irritation was recorded for P(AA)70,000 when tested on 6 rabbits as a 1-1.5 times dilution in aqueous solution. The Primary Irritation Index (PII) was < 1 (Rohm and Haas, 1974). However, a 40% active solution of P(AA)70,000 was not irritant to the skin of 3 rabbits following a non-OECD protocol (BASF, 1992g). When P(AA)78,000 was tested on the intact skin of 3 rabbits for 4 h as an occluded patch, no signs of irritation were observed (Degussa, 1983b,e).

P(AA-MA)70,000 was not irritant to the skin of 3 rabbits (BASF, 1992g) or 6 rabbits (Rohm and Haas, 1991).

8.2.2 Eye Irritation

When P(AA)1,000 (Rohm and Haas, 1982a) or P(AA)1,200 (BASF, 1992g) was applied to the eyes of 3 rabbits, no damage to the cornea or iris was detected. Slight conjunctival irritation was observed but this had cleared 24 h after administration.

Similarly, evidence of slight eye irritation was observed following administration of P(AA)2,500 to 3 rabbits (BASF, 1992g). Slight eye irritancy has also been observed for P(AA)4,500 (Rohm and Haas, 1982b). P(AA)8,000 was non-irritant when tested as a 45% active solution in water (BASF, 1992g).

P(AA)70,000 was also slightly irritant to the eyes of 6 rabbits, causing conjunctival effects which cleared by 72 h. No damage to the cornea or iris was noted (Rohm and Haas, 1974). However, P(AA)70,000 was not irritant following a non-OECD protocol (BASF, 1992g). P(AA)78,000 was slightly irritant when tested on 3 rabbits, with recovery by 24 h (Degussa, 1983c,f).

P(AA-MA)70,000 was only slightly irritating to the eye when tested in 3 rabbits, with full recovery by 48 h (BASF, 1992g).

8.2.3 Sensitisation

P(AA)4,500 tested in a M&K assay was found to be a non-sensitiser. Induction and challenge doses of 0.4% active ingredient were given (Rohm and Haas, 1988).

P(AA)37,000 has been tested in a modified Draize sensitisation test and found to be a non-sensitiser. Induction doses of 0.75% active ingredient were used, followed by challenge concentrations of 0.3% active (i.d.) and 5% active in saline (topical). None of the 10 animals per test group became sensitised (Unilever, 1990).

P(AA)78,000 has been tested in a Magnusson and Kligman Guinea pig maximisation test (M&K assay). The animals were given 0.1 ml of an 0.1% aqueous solution i.d. as one of the induction doses and 0.2 ml of a 20% aqueous solution as the occluded patch induction dose. This was applied for 48 h. After the appropriate period all animals received a challenge dose of 0.2 ml of a 2.5% dilution of the test compound as a single occluded patch administration for 24 h. No skin reactions were observed in the test group or in the control group (Henkel, 1990).

P(AA-MA)70,000 was tested in a standard M&K assay. After i.d. induction of 0.1 ml of the test substance formulation, distinct erythema and oedema was observed at all injection sites of the test animals. Two separate challenge doses of 80% of the test substance formulaton were applied and no sensitisation was observed. The challenges were given at day 19 and 26 following the induction phase. It was concluded that P(AA-MA)70,000 did not have a sensitising effect on guinea pigs (Rohm and Haas, 1988b; BASF, 1992h).

8.3 SUBCHRONIC TOXICITY

A number of subchronic studies have been undertaken, none of which indicated any serious adverse effects.

8.3.1 Inhalation

P(AA)4,500 and P(AA-MA)70,000 have been tested separately in a 91-d inhalation study using groups of 25 male and 25 female rats. They were exposed to 0.2, 1.0 or 5.0 mg/m^3 of each polymer for 6 h/d, 5 d/wk for 13 wk. The polymers were administered as aerosols, delivering measured respirable doses near the target concentrations. Ten animals from each group were allowed a recovery period of a further 91 d. Microscopic examination of lung tissues from the animals killed immediately after the last exposure found signs of mild pulmonary irritation based on at least 1 of the following: increase in polymorphonuclear granulocytes or alveolar macrophages, pneumocyte hyperplasia, alveolar wall thickening and focal alveolitis in the animals exposed to 1 and 5 mg/m^3 of P(AA-MA)70,000 and to 5 mg/m^3 of P(AA)4,500. Microscopic examination of those animals allowed the recovery period showed no lasting or residual microscopic lesions which could be considered to be treatment-related. All other parameters including body and organ weights, food and water consumption, clinical observations and blood chemistry were within the normal range. From these studies it was concluded that the NEL (No Effect Level) is 0.2 mg/m^3 for P(AA-MA)70,000 and 1.0 mg/m^3 for P(AA)4,500 (Procter and Gamble, 1991).

8.3.2 Oral

Groups of 6 male Wistar rats were exposed for 28 d to 2.5% P(AA)2,500 (active ingredient of a 50% neutralised solution) in the diet to examine the effect upon body mineral status. Growth, weight and appearance of the animals were normal throughout this study. At week 4, a small but significant decrease in the total weight of minerals in the bones was observed, which was confirmed by radiographic and histological examination, and the concentration of magnesium in the bones and plasma was significantly decreased; calcium loss was slight but not statistically significant.

Urinary excretion of sodium and phosphorus was markedly increased and excretion of calcium was slightly increased. It was considered that these effects observed were probably caused by a metabolic or nutritional mechanism rather than a toxic one which may be connected with the large amount of sodium fed to the animals as a result of neutralisation of the P(AA)2,500 (Unilever, 1990).

P(AA-MA)70,000 was administered to 10 male and 10 females Wistar rats for 90 d in drinking water at dose levels of 1,000, 4,000 or 16,000 ppm of test substance, the top dose being equivalent to 1,000 mg/kgbw/d for males and 2,216 mg/kgbw/d for females. Prior to administration and towards the end of the study ophthalmoscopy on the control and high dose groups was undertaken. In week 6 and towards the end of the study clinical chemistry and urine estimations were made. Macroscopic and histopathological examinations were made. In the high dose group receiving 16,000 ppm increased water consumption was observed in both sexes, this being more pronounced in females. No other test substance related changes were observed. The NEL in this study was 16,000 ppm equivalent to > 1,000 mg/kgbw/d (BASF, 1992h).

8.3.3 Dermal

P(AA-MA)70,000 has been examined in a 28-d rabbit dermal study. Groups of 15 male and 15 female rabbits received 10, 25 or 50% solutions of the test substance on to abraded skin. In the high dose group, slight erythema was seen commencing after day 4 persisting until the end of the study. In the middle dose group slight erythema was observed but this occurred in only 3 animals commencing in the third week and persisting until the end of the study. No evidence of skin irritation was observed in the control or low dose groups. No changes in body weight gain were observed in any of the treatment groups when compared with the concurrent control group and none of the animals showed abnormal clinical signs or adverse changes when subjected to haematological, pathological or histopathological examinations. The NOEL was a 10% solution of P(AA-MA)70,000 (BASF, 1992h).

8.4 GENOTOXICITY (Table 8)

None of the P(AA)s or P(AA-MA)s has shown any evidence of mutagenic potential in studies using a variety of genetic end points. Evidence of cell damage was noted in a number of the experiments involving mammalian cells and this may have interfered with the interpretation of results.

8.4.1 Gene Mutation *In Vitro*

Gene Mutation in Bacteria: Ames Salmonella Test

Thompson *et al* (1989) have tested neutralised samples of aqueous solutions containing 45-54% P(AA)2,000, P(AA)4,500 and P(AA-MA)12,000 in a plate incorporation protocol using *Salmonella typhimurium* strains TA1535, TA1537, TA1538, TA98 and TA100 with and without rat liver S9 mix. No evidence of toxicity or of mutation was observed at test substance concentrations up to 10 mg/plate, this being higher than the maximum dose recommended by the OECD.

P(AA-MA)70,000 has also been examined in a standard 5-strain plate incorporation assay in a dose range 20-5,000 μg/plate. No evidence of mutagenic potential was observed (BASF, 1992h).

Gene Mutation in Mammalian Cells

Mouse Lymphoma

Thompson *et al* (1989) have tested neutralised samples of aqueous solutions containing 45-54% P(AA)2,000, P(AA)4,500 and P(AA-MA)12,000 in a mammalian cell gene mutation assay using mouse lymphoma L5178YTK+/- cells. The assay was performed according to standard procedures of Clive and Spector (1975) and Clive *et al* (1979). Each substance was tested in the presence and absence of S9 mix on 1 occasion only. When tested in the absence of S9, cell growth was reduced to 34, 76 and 17% at concentrations of 37, 75 and 50 μl/ml respectively with P(AA)2,000, P(AA)4,500 and P(AA-MA)12,000. No increases in mutation frequency were observed. In the presence of S9, cell growth was reduced to 18, 37 and 12% at concentrations of 28, 32 and 32 μl/ml for the same 3 samples described above. Again no increases in mutation frequency were observed.

Chinese Hamster Ovary Cells

P(AA-MA)70,000 has been examined in a mammalian cell gene mutation assay using CHO cells (BASF, 1992h). The test was conducted in the presence and absence of S9 mix, using dose levels ranging from 0.01 μg/ml to 10 mg/ml. Although some increases in the number of mutant colonies were observed these were not clearly dose related and were considered to be due to other effects such as calcium chelation, cytotoxicity and precipitation out of solution of the test substance. It was concluded that P(AA-MA)70,000 was not mutagenic in this assay (BASF, 1992h).

Chromosome Aberrations in Cultured Mammalian Cells

Neutralised aqueous solutions containing 45-54% P(AA)4,500 and P(AA-MA)12,000 have been tested for clastogenic activity using CHO cells. Cells were treated for 4 hours in the presence and absence of S9 mix followed by 16 hours in compound-free medium. Both compounds were tested at concentrations up to 77 μl/ml in the presence and absence of S9 mix. Single cultures were used. No increases in chromosome aberrations were detected with either substance. More toxicity was observed at the higher concentrations with the copolymer than with P(AA)4,500 (Thompson *et al*, 1989).

Unscheduled DNA Synthesis: Primary Rat Hepatocytes

Neutralised aqueous solutions containing 45-54% P(AA)2,000, P(AA)4,500 and P(AA-MA)12,000 have been tested for induction of UDS (Unscheduled DNA Synthesis) in primary rat hepatocytes following the methods described by Williams *et al* (1977). P(AA)2,000 was tested to a maximum concentration of 5 μl/ml, P(AA)4,500 to a maximum of 20 μl/ml and P(AA-MA)12,000 to a maximum of 4 μl/ml. All 3 test substances showed appreciable toxicity at the highest concentrations tested. No evidence of UDS was observed (Thompson *et al*, 1989).

P(AA-MA)70,000 was also tested in an UDS assay using primary rat hepatocytes with the highest concentration being 10 μl/ml. This caused appreciable and erratic toxicity at concentrations down to 1 μl/ml. No evidence of UDS activity was obtained in this experiment (BASF, 1992h).

8.4.2 Gene Mutation *In Vivo*

Micronucleus Test

P(AA)2,000 has been tested in a mouse micronucleus assay using groups of 5 male and 5 females. Animals were dosed by gavage with the maximum tolerated dose (13.85 g/kgbw) and observed over a 3 d period. Animals were killed at 24, 48 or 72 h after dosing and 1,000 cells per animal examined for micronuclei in polychromatic erythrocytes and also for the ratio for polychromatic to normochromatic erythrocytes. During the experiment 3 females died, 1 at each of the harvest times. No increase in micronucleus induction was observed, neither was there any marked reduction in the ratio of polychromatic to normochromatic erythrocytes (Thompson *et al*, 1989).

Chromosome Aberrations

P(AA-MA)70,000 has been tested for chromosome aberrations in the bone marrow of male and female Chinese hamsters following a single i.p. injection of 200, 600 and 1,780 mg/kgbw. Animals from the high dose group were killed and bone marrow examined at 6, 24 or 48 h after dosing. Animals from the other dose groups were killed only at 24 h. No increases in chromosomal aberrations were observed (BASF, 1992h).

8.5 CHRONIC TOXICITY AND CARCINOGENICITY

No data are available for evaluation.

8.6 REPRODUCTION, EMBRYOTOXICITY, TERATOGENICITY

None of the P(AA)s or P(AA-MA)s tested had any detrimental effects on reproductive performance of the rat.

P(AA)4,500 was tested in a rat teratogenicity study in which the compound was administered by gavage on days 6-15 of pregnancy at dose levels of 500, 1,000 and 3,000 mg/kgbw/d. No treatment related effects on foetal development or on pregnancy were noted. The NEL was 3,000 mg/kgbw/d (Nolen *et al*, 1989).

Using a similar protocol, P(AA)90,000 a was administered at dose levels of 125, 375 and 1,125 mg/kgbw/d. In the high dose group 3 treatment-related deaths occurred but there were no adverse effects on developmental toxicity or pregnancy rate. The foetuses from the treated groups were slightly larger than the controls but this was considered to be of no special biological significance. No treatment-related differences in either soft tissue or skeletal abnormalities were seen (Nolen *et al*, 1989).

P(AA-MA)12,000 was administered to rats by gavage at dose levels of 67, 667 and 6,670 mg/kgbw/d during days 6-15 of gestation. There were no deaths in the high-dose group but in the low dose group there were 8 malformed foetuses all from 1 litter and all with short thickened bodies with numerous malformations. Animals from the other 23 litters in this test group were perfectly normal and showed no irregularities whatsoever. This singular finding was therefore not considered to be treatment-related (Nolen *et al*, 1989).

SECTION 9. EFFECTS ON MAN

There is very little information on the effects of polycarboxylates in man.

9.1 IRRITATION AND SENSITISATION

A group of 50 volunteers were subjected to a 48 h occluded patch test with a 15% aqueous solution of sodium P(AA) (MW not stated). No evidence of irritation was observed in any of these subjects. Two weeks after the initial 48 h patch test, the same group of volunteers was challenged with the same material. No evidence of sensitisation (erythema or oedema) was observed (Finnegan and Dienna, 1953).

A group of 25 human volunteers wore nylon squares, washed with polycarboxylate containing detergent, as occluded patches for 48 h. No evidence of irritation was present at the end of this period or following rechallenge for a further 48 h period 12 days later (Rohm and Haas, 1951).

SECTION 10. FIRST AID AND SAFE HANDLING ADVICE

10.1 FIRST AID AND SAFE HANDLING

Polycarboxylates of the type used in detergents are of low toxicity and do not pose any risk to human health under normal conditions of handling and use. General measures used in industrial practice and personel hygiene for non-dangerous materials are appropriate for the safe handling of polycarboxylates. In cases of exceptional exposure these measures may include skin protection and dust respirators.

In the case of contact with eyes, irrigate with water for 10 min, and seek medical advice if there are presistent symptoms.

Following skin contact, wash the affected area with water and launder contaminated clothing.

10.2 SPILLAGE AND WASTE DISPOSAL

10.2.1 Spillage

Keep dust to a minimum. Wear respirator for dust encountered. Any spilled dry material or solutions should be diked and contained with inert material such as sand or earth. Scoop or shovel solid material into a separate container for recovery or disposal. Keep spilled material out of municipal sewers and open bodies of water.

Thoroughly launder clothing before re-use; do not take contaminated clothing home.

10.2.2 Waste Disposal

Waste containing polycarboxylates should be disposed of in accordance with local, regional, national and EEC regulations.

APPENDIX A. SPECIAL ABBREVIATIONS

AA	-	Acrylic Acid
ADME	-	Absorption, Distribution and Metabolism
BOD	-	Biological Oxygen Demand, e.g. after 5 d: BOD_5.
BU assay	-	Buehler assay (sensitisation)
C	-	Carbon
CAS	-	US Chemical Abstracts Service
COD	-	Chemical Oxygen Demand
DOC	-	Dissolved Organic Carbon
DSS	-	Dry Suspended Solids
EC	-	Effect Concentration, e.g 48h-EC_{50}: median EC at which 50% of organisms is affected following 48 h exposure; with *Daphnia*, the effect is mobility)
EINECS	-	European Inventory of Existing Commercial Chemical Substances
LC	-	Lethal Concentration, e.g. 96h LC_{50}: median LC at which 50% of organisms die following exposure for 96 h
LD	-	Lethal Dose, e.g. LD_{50}: similar to LC
MA	-	Maleic Anhydride
MBAS	-	Methylene-Blue Active Substances
M&K assay	-	Magnusson and Kligman guinea pig maximisation test (sensitisation)
MW	-	Molar mass (Molecular Weight)
NEL	-	No Effect Level
NOAEL	-	No Observed Adverse Effect Level
NOEC	-	No Observed Effect Concentration
P(AA)	-	Polyacrylic Acid, with suffix indicating MW
P(AA-MA)	-	CoPolymer of Acrylic Acid and Maleic Anhydride, with MW suffix
P(AA-P)	-	Phosphinated PolyAcrylic Acid, with MW suffix
PCAs	-	PolyCarboxylic Acids
P_{ow}	-	*n*-Octanol/water Partition coefficient
SCAS	-	Semi-Continuous Activated Sludge
STP	-	Sewage Treatment Plant
SVI	-	Sludge Volume Index
ThOD	-	Theoretical Oxygen Demand
TLV	-	Threshold Limit Value (standard for occupational exposure to airborne concentrations of a substance)
TSS	-	Total Suspended Solids
UDS	-	Unscheduled DNA Synthesis

APPENDIX B. CALCULATION METHOD FOR ENVIRONMENTAL LEVELS

The polycarboxylate levels in different environmental compartments mentioned in Section 5.1. were calculated according to the following procedure. It is assumed that polycarboxylate containing detergents are equally distributed in the considered area and completely discharged into waste water. This assumption is valid to a great extent in West Germany, for which a calculation example was carried out previously (Fachgruppe Wasserchemie, 1990).

Concentrations in raw waste water (C_{rww}) were derived from the following equation:

$$C_{rww}\ [mg/l] = \frac{\text{Polycarboxylate consumption } [g/inh/y] \times 10^3}{\text{Sewage flow } [l/inh/d] \times 365}$$

For a conservative calculation of P(AA-MA)70,000 concentrations in raw sewage, a per capita consumption of 300 g PCA/y and a sewage flow of 200 l/inh/d is assumed.

Effluent waste water concentrations (C_{eww}) can be calculated according to the following equations, depending on the different types of waste water treatment:

$$C_{eww/mech-biol}\ [mg/l] = C_{rww} \times (1-R_{mech-biol})$$

$$C_{eww/sept}\ [mg/l] = C_{rww} \times (1-R_{sept})$$

$R_{mech,\ biol,\ sept}$: fraction of polycarboxylates removed in mechanical, or mechanical-biological waste water treatment, or in septic tanks. The respective figures are given in Table B.1.

In this context, physico-chemical waste water treatment (mainly for phosphate elimination) is not taken into account because it increases the removal of P(AA-MA)70,000 only marginally. The removal figures are mentioned in Chapter 4; mechanical treatment: result of dynamic settling test, on average 30% (Section 4.2.1.), biological treatment: result of mass-balance study, on average 93% (Section 4.2.2), septic tank removal: sedimentation after 96 h (Section 4.2.1.).

Table B.1: Removal of P(AA-MA)70,000 In Waste-Water Treatment Processes

Process	Average extent of removal (R x 100%)
Mechanical/biological	93
Mechanical	30
Septic tank	84

Further downstream, effluent waste water is increasingly diluted with river water. The dilution factors vary with seasonal fluctuations and depend on the conditions of a specific discharge site. For the estimation of polycarboxylate levels in surface waters, a standard dilution factor of 1:10 is used; elimination in the river, e.g. by adsorption of settled sediments, is not considered.

The elimination of polycarboxylates during drinking water preparation from river water is estimated by assuming 90% removal. This was measured as a minimum removal in flocculation experiments of raw drinking water with $AlCl_3$ and $FeCl_3$ and in lysimeter studies with sand and an artificial groundwater when considering this as a simulation for bank filtration (Section 4.3).

The amount of polycarboxylates adsorbed onto digested sewage sludge (C_{dsl}) is estimated by the overall removal in activated sludge treatment.

$$C_{dsl}\ [g/kg] = \frac{C_{rww}\ [g/m^3] \times R_{biol}}{F\ [kg/m^3]}$$

with F: ratio of the amount of sewage sludge/sewage flow; 1 m^3 raw waste water after biological treatment and digestion produces 0.2 kg sewage sludge (dry matter): 0.2 kg/m^3.

Maximum possible sludge-treated soil concentrations (C_{soil}) are estimated with the following equation.

$$C_{soil}\ [g/t/y] = \frac{C_{dsl} \times F_1 \times 10^3\ [kg/t]}{F_2 \times F_3 \times 10^4\ [m^2/ha]}$$

Two calculations were made with different assumptions:

a. Fachgruppe Wasserchemie (1990)

F_1: Sludge disposal factor (t/ha/y); 5/3 = 1.7 (t/ha/y); according to the German Sludge Disposal Decree of 25.06.1982 a maximum of 5 t digested sewage sludge may be disposed onto 1 ha of agricultural soil within 3 y

F_2: Soil density; 0.88 - 1.85 t/m^3

F_3: Agricultural soil depth; 0.3 m

b. Chiaudani and Poltronieri (1990):

F_1: Sludge disposal factor, 0.2 (t/ha/y)

F_2: Soil density, 0.88-1.85 t/m^3

F_3: Agricultural soil depth, 0.1 m

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