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A Review of Polyelectrolytes to Identify Priorities for EQS Development

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A REVIEW OF POLYELECTROLYTES TO IDENTIFY PRIORITIES FOR EQS DEVELOPMENT

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Statement of Use
This review is designed to evaluate the nature and range of applications for this diverse group of chemicals in addition to giving an indication of the likely risk of causing environmental damage. It will assist Agency staff in assessing the potential effects of these substances on water quality.

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SUMMARY

Polyelectrolytes are finding increasing use in the treatment of wastewater and water intended for potable supply. They are used as aids in the removal of solids (as coagulants or flocculants), the dewatering of sludges or, occasionally, as dispersants to stabilize suspensions. They comprise a number of different chemical types within which different charge classes (cationic, anionic, non-ionic) exist. These charge characteristics largely determine the use to which a product is put.

These applications of polyelectrolytes inevitably mean they will be used in proximity to surface waters which raises concerns about possible risks to aquatic life. This review is designed to evaluate the nature and range of applications for this diverse group of chemicals in addition to giving an indication of the likely risk of causing environmental damage. It will assist Agency staff in assessing the potential effects of these substances on water quality.

Cationic polyelectrolytes (principally polyacrylamides, polyamines and poly(DADMAC)s) are the most extensively used product type, especially in wastewater treatment, and they are more acutely toxic to aquatic organisms than anionic polyelectrolytes which, in turn, appear to be more toxic than non-ionic polyelectrolytes. All are characterised by a wide range of toxicities, with considerable overlap in toxicities between product types. As far as the cationic polyelectrolytes are concerned, aquatic toxicity is predominantly a function of cationic charge density.

Although they are clearly intrinsically hazardous to aquatic organisms, possible impacts are reduced by a number of factors affecting their bioavailability, especially for the more hazardous cationic products. These factors include strong and irreversible sorption to suspended and dissolved organic matter, losses due to hydrolysis and biodegradation, and a low potential to bioaccumulate. By contrast, there is comparatively little information on the environmental fate of anionic and non-ionic products.

Polyelectrolytes may contain low concentrations of residual monomers such as epichlorohydrin, acrylic acid and acrylamide. The indications from laboratory studies are that these are less toxic to aquatic organisms than cationic polyelectrolytes. However, adverse effects of acrylamide at very low concentrations in the field have been reported but there is little data on concentrations of acrylamide occurring in surface waters as a result of polyelectrolyte usage.

An assessment of the likely risks posed by polyelectrolytes to aquatic life has been undertaken. This considered the amounts of different types of polyelectrolyte used, their toxicity to aquatic life, bioaccumulation potential and persistence. The relatively high toxicities of the cationic polyelectrolytes is strongly ameliorated by losses due to sorption and degradation. The non-ionic and anionic products are much less hazardous by comparison and are also used in smaller quantities than the cationic polyelectrolytes. As a result, all polyelectrolyte types (anionic, non-ionic polyacrylamides, cationic polyacrylamides, polyamines and poly(DADMAC)s) are judged not to be a priority for EQS development.

KEY WORDS

Polyelectrolyte, cationic, anionic, non-ionic, EQS, hazard, risk, toxicity, acrylamide, acrylic acid, epichlorohydrin.

1. INTRODUCTION

This report reviews the polyelectrolytes used in the UK and, where necessary, prioritises substances for EQS development. It is designed to evaluate the nature and range of applications for this diverse group of chemicals in addition to giving an indication of the likely risk of causing environmental damage. It will assist Agency staff in assessing the potential effects of these substances on water quality.

Polyelectrolytes are water soluble, high molecular-weight polymers which are based on either synthetic or naturally-occurring chemicals. Synthetic polyelectrolytes include polyacrylamides (which are available in anionic, cationic and non-ionic forms), and various cationic products, mainly polyDADMACs and polyamines. Natural polyelectrolytes are alginates (anionic), tannins (anionic) and chemically modified starches which can have anionic, cationic or non-ionic characteristics.

Synthetic polyelectrolytes are manufactured by the polymerisation of monomer compounds; the monomer types and their proportions in the reaction mixture influence the charge characteristics of the resulting polyelectrolyte, and the degree of polymerisation can be varied to influence the molecular weight; thus a wide variety of anionic, cationic and non-ionic polyelectrolytes of various molecular weights are commercially available.

Polyelectrolytes are used in water, sewage and sludge treatment to control and enhance the coagulation and flocculation of suspended particulate matter. Use of synthetic polyelectrolytes in the UK for the treatment of raw water for potable supply and for the treatment of wastewaters and sludges prior to disposal appears to be increasing. Their intended use, often in close proximity to watercourses, has raised concerns about possible effects on aquatic life. Possible risks due to residual monomers entering surface waters also warrant consideration.

In this review, we consider the chemistry and uses of different types of polyelectrolytes (Section 2), the evidence for their occurrence in effluents and surface waters (Section 3), their fate and behaviour on entering surface waters (Section 4) and the available data concerning the hazards posed by polyelectrolytes and impurities to aquatic life (Sections 5 and 6). Finally, in Section 7, we undertake an assessment of the likely risk of environmental damage resulting from the use of polyelectrolytes, and thereby indicate whether or not development of EQSs is warranted.

2. CHEMISTRY AND USE OF POLYELECTROLYTES

In the UK polyelectrolytes are used by the Water Utilities for water clarification, waterworks sludge treatment and sewage sludge thickening. Polyelectrolytes may also be used in sewage treatment to assist in primary settlement, often in combination with iron or aluminium salts. They are also used in other industries such as the mining and paper industries, e.g. to aid in the removal of fine particles from wash waters and to improve the efficiency of the separation of paper fibres from water.

2.1 Types and uses of polyelectrolytes

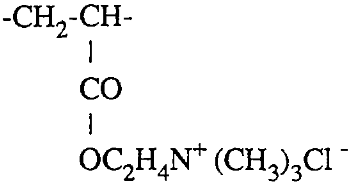
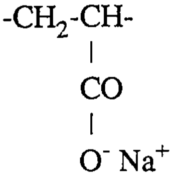
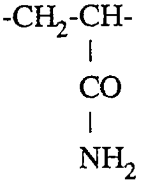
With respect to their usage and reaction mechanisms, polyelectrolytes can be divided into two major types; primary coagulants and flocculant aids.

Polyelectrolyte coagulants are usually comparatively low molecular weight cationic substances, and are used in drinking water treatment as total (when they would be regarded as primary coagulants) or partial replacements for conventional inorganic coagulants such as aluminium or iron salts. They destabilise suspensions by overcoming the repulsions between particles, allowing the particles to adhere more readily to each other. This results in larger particles which can be removed by settlement. Primary coagulants are mainly polyamines (epichlorohydrin-dimethylamine copolymers) and polyDADMACs (polydiallyldimethyl ammonium chloride).

A large proportion of polyelectrolytes in use in drinking water treatment in the UK are polyacrylamide-based flocculant aids. These are generally of higher molecular weight than coagulants and are generally anionic or nonionic in nature. Examples are shown in Table 2.1. They are used to cause stabilised particles or coagulated suspensions to form aggregates which can be removed by settlement or filtration. Polyelectrolytes may also be added to the resulting solids to facilitate dewatering, when the product may be regarded as a sludge conditioner.

Data supplied by the Environment Agency (formerly the NRA) (Table 2.2) and manufacturers (Table 2.3) show that most of the polyelectrolytes supplied in the UK (based on 1991-93 data) are cationic polyelectrolytes. Of these, approximately equal quantities are used in the treatment of sewage and sludge, and in industrial applications (mainly in the manufacture of paper and mineral processing). By comparison, much smaller quantities of cationic polyelectrolytes are used in the treatment of raw water intended for potable supply. Of the cationic products used in the treatment of wastewater, over 90% are polyacrylamide esters, although cationic polyamines are important in potable water and industrial applications. Polyelectrolytes based on natural products (alginates, tannins and modified starches) are usually anionic or non-ionic in character but have limited use in the applications of concern here.

Table 2.1 Examples of the functional groups in various types of polyacrylamide

Charge	Functional Group	Monomer reacted with acrylamide
Cationic	 $\begin{array}{l} -CH_2-CH- \\ \qquad \vert \\ \qquad CO \\ \qquad \vert \\ \qquad OC_2H_4N^+(CH_3)_3Cl^- \end{array}$	Trimethyl aminoethyl acrylate chloride
Anionic	 $\begin{array}{l} -CH_2-CH- \\ \qquad \vert \\ \qquad CO \\ \qquad \vert \\ \qquad O^- Na^+ \end{array}$	Sodium acrylate
Nonionic	 $\begin{array}{l} -CH_2-CH- \\ \qquad \vert \\ \qquad CO \\ \qquad \vert \\ \qquad NH_2 \end{array}$	Acrylamide homopolymer

2.2 Restrictions on polyelectrolyte composition and use

In the UK, a maximum dose for polyacrylamides used during drinking water treatment has been set by the DoE Committee on Chemicals and Materials of Construction for use in Public Water Supply and Swimming Pools. This is intended to limit the concentration of residual acrylamide monomer in drinking water and is applied in conjunction with a limit on the permissible concentration of acrylamide monomer in the polymer (0.025% w/w). A draft CEN standard for cationic polyacrylamides specifies the same residual acrylamide concentration for products used for treatment of waste intended for potable supply (draft BS EN 1410).

The dose for polyacrylamide in drinking water treatment must average no more than 0.25 mg l^{-1} and must never exceed 0.5 mg l^{-1}. The polyacrylamides which satisfy these limits and have been granted approval for use in the UK are listed by the Drinking Water Inspectorate (DWI 1994) as products approved under Regulation 25 of the Water Supply (Water Quality) Regulations (HMSO 1989). Limits on impurities in polyamines and polyDADMACs are not stated explicitly in the approved list (DWI 1994), although many products are approved subject to limitations on dosage.

Table 2.2 **Quantities of polyelectrolytes supplied in the UK (1991/92 and 1992/93) (Metric tonnes) (Data supplied by S. Killeen, NRA, Thames Region, Pers. Comm. 1994)**

	Cationic		Anionic		Non-ionic		Total	
Area of application	91/92	92/93	91/92	92/93	91/92	92/93	91/92	92/93
Sewage/sludge treatment	2338	2545	5	5	0	1	2343	2551
Potable water	687	699	177	170	112	119	976	988
Industrial	2196	2449	1539	1358	191	155	3926	3962
Total	5221	5693	1721	1533	303	275	7245	7501

Table 2.3 Percentage breakdown of product use by product type

Product type	Sewage/sludge treatment	Potable water	Industrial uses	All
Non-ionic/anionics:				
Polyacrylamides	5	38	37	30
Cationics:				
Polyacrylamide esters	90	38	46	55
Polyacrylamides, amide-types	<1	<1	<1	<1
'Mannichs'*	2	0	1	1
Polyamines	<1	23	10	9
PolyDADMAC (polydiallyldimethyl ammonium chloride)	2	1	6	5

* Manufactured by the Mannich reaction-modified process

Polyacrylamides used for the thickening and dewatering of sludges and for wastewater treatment are subject to Classification, Packaging and Labelling Legislation and, although they may contain higher levels of acrylamide monomer, any product containing more than 0.1% acrylamide would have to be labelled accordingly. In practice, commercial products usually contain well below 0.1% by weight of acrylamide monomer (Richards, Allied Colloids, Pers. Comm. 1996). The doses used in these processes are often two orders of magnitude larger than those applied in the treatment of potable water (generally 10-100 mg l^{-1}, Cary *et al.* 1987). Very thick waterworks sludge can be produced by the addition of polymer. It may be necessary to add 1-3 kg of polymer per tonne of dry solids (Lockyear *et al.* 1983).

2.3 Contaminants and impurities in polyelectrolytes

Synthetic polyelectrolytes contain impurities from the manufacturing process (i.e. residual monomers). Table 2.4 shows the contaminants that are known to be or may be present in synthetic polyelectrolytes (Letterman and Pero 1990). In this table, "direct evidence" for the presence of a compound implies that the determinand has been measured and its concentration in the polyelectrolyte has been reported in the literature. "Indirect evidence" implies that the determination of the compound was qualitative but not quantitative, and "speculative evidence" implies that the compound is used or possibly formed in the manufacture of the polyelectrolyte, but it is not certain whether it is found in the final product.

Table 2.4 Contaminants which may be present in synthetic polyelectrolytes (from Letterman and Pero 1990)

Polyelectrolyte	Contaminant	Evidence
Polyacrylamides	Acrylamide	Direct
	Hydroxypropionitrile	Direct
	Isobutyronitrile	Direct
EpiDMA	Epichlorohydrin	Direct
	Glycidol	Direct
	1,3-dichloro-2-propanol	Direct
	1,2-dichloropropanol	
	3-chloro-1,2-propanediol	Direct
	2,3-dichloro-1-propanol	Direct
	Dimethylamine	Inconclusive
	2-hydroxy-3-dimethyl-aminopropyl chloride	Speculative
	1,3-Bis(dimethylamino)-2-propanol	Speculative
poly(DADMAC)	Diallyldimethyl ammonium chloride	Direct
	Dimethylamine	Inconclusive
	Diallyl ether	Speculative
	Allyl chloride	Speculative
	5 Hexanal	Speculative

Table 2.5 contains a list of contaminants in polyelectrolytes which are subject to UK regulations, or which fall within the scope of draft European Standards for water treatment chemicals. They are considered to be the most important impurities in polyelectrolytes used for the treatment of drinking water.

2.4 Analysis of polyelectrolytes

Despite the existence of limits on the amount of polyelectrolyte that may be used in the treatment of drinking water, little information exists on polyelectrolyte concentrations in treated water or in the environment. This is mainly because the analysis of polyelectrolytes is a difficult analytical problem, and although many attempts have been made to resolve it, no suitable method has yet emerged.

Table 2.5 Standards for concentrations of contaminants in polyelectrolytes (products intended for potable water only)

Polyelectrolyte	Contaminant	MAC (%)	Standard or approval
Polyacrylamide	Acrylamide monomer	0.025	DWI (1994) PrEN 1407 and 1410 (1994)
Polyamine	Epichlorohydrin 1,3 dichloropropanol 1,2 dichloropropanol	0.002 0.1 0.05	PrEN 1409 (1994)
PolyDADMAC	DADMAC monomer	0.5	PrEN 1408 (1994)

MAC = Maximum allowable concentration of the contaminant in the polyelectrolyte

2.4.1 Colloid titration

When polyelectrolytes of opposite charge interact they form strong stoichiometric complexes which precipitate when the charges are neutralised. This is the principle of the colloid titration technique; the polyelectrolyte is titrated with an oppositely charged polymer and the end point is detected visually or spectrophotometrically (in the presence of a charge sensitive dye), by turbidimetry or conductivity, or by using a charge detector.

This method is unable to differentiate between different types of polyelectrolyte and is subject to interference from other sample components including natural colour causing compounds and calcium. For this reason, colloid titration is not the method of choice. A limit of detection of 1 mg l^{-1} has been quoted for cationic polyelectrolytes by Wang *et al.* (1977).

The particle charge detector uses the streaming current principle to measure the charges associated with particles in a liquid. The liquid is placed inside a PTFE cylinder and the charged particles adsorb to the walls, surrounded by counter ions in the liquid. The movement of a piston inside the cylinder forces the liquid to move causing the counter ions to be sheared away from the adsorbed particles producing a moving electrical charge (streaming current). Two electrodes in the test vessel then measure the streaming current, which depends on both the charge and concentration of particles as well as other factors such as ionic strength and pH (Jackson 1984).

The particle charge detector can be used to determine the end point in a titration of the polyelectrolyte with polyions of opposite charge. When the charges are neutralised, a polymer complex is formed and the streaming current is zero. The addition of more titrant results in a reversal of the streaming current; the particle charge detector can thus be used as an end point detector for colloid titration, although a detection limit has not been specified (Malvern Instruments Ltd. sales brochure).

2.4.2 Ionic dye complexation

In a two phase system consisting of water and a polar organic solvent such as chloroform, an ionic dye will remain in the aqueous layer. When the ionic dye and an oppositely charged substance react, a coloured complex is usually produced which has low solubility in water and dissolves preferentially in the organic phase. A spectrophotometer can be used to measure the absorbance of the polyelectrolyte/dye complex in the organic layer and therefore determine the polyelectrolyte concentration.

This method is subject to many of the problems of colloid titration methods, it is not specific for individual polyelectrolyte types, and charged complexes in the sample will interfere. The dye complex is also a problem because in many cases its extraction into the organic phase is incomplete and inconsistent. It is possible to calculate the polyelectrolyte concentration by measuring the unreacted dye in the aqueous phase; however, there are problems with this because often the unextracted complex forms a precipitate which interferes with the determination.

Parazak *et al.* (1987) developed a method which partly eliminated some of these problems. They reacted the dye Ponceau-S with a cationic polyelectrolyte in the presence of freon. The colloidal precipitate formed by the complex was insoluble in both the freon and the water and therefore collected at the freon/water interface and was removed. The concentration of polyelectrolyte was then measured using the decrease in colour intensity of the uncomplexed dye in the aqueous phase. Parazak *et al.* claimed that this method was sensitive to 0.5 to 1 mg l^{-1} for the polycations examined.

2.4.3 Spectrofluorimetry

A sensitive method for the determination of polyacrylamide was developed by Hendrickson and Neuman in 1984. The polyacrylamide was first converted to its amine derivative using the Hofmann rearrangement; the sample was reacted with NaOH and NaOCl at 1 to 3 °C and equilibrated at room temperature for 48 hours. A fluorogenic reagent (o-phthalaldehyde and 2-mercaptoethanol) was then added followed by a 30 minute equilibration period. The sample was measured in a spectrofluorimeter with excitation and emission wavelengths of 348 and 458 nm. A detection limit was reported as 20 µg l^{-1}. However, accuracy was reported as ± 70 µg l^{-1} raising concerns about the precision of the method.

Arryanto and Bark (1991) further developed this method to give an overall analysis time of two hours and a relative standard deviation of 5% at the 5 mg l^{-1} level. They used chloramine T as the oxidant and fluorescamine as the fluorogen.

2.4.4 Size exclusion chromatography

Size Exclusion Chromatography (SEC), is a high performance liquid chromatography technique that sorts molecules by their molecular size. The sample is carried through a chromatographic column by a solvent (mobile phase) and the molecules penetrate the stationary phase in varying amounts depending on their size. Because larger molecules cannot penetrate so deeply, they elute faster than smaller molecules, and the sample is separated by molecular size. In the case of polyacrylamide, a UV detector is used because amide groups absorb strongly in the UV.

SEC chromatography columns suitable for water soluble polymers have only become commercially available in recent years. Sephadex gel has been used since the 1960s for the determination of biological materials; however, analysis using this gel takes 5 to 10 hours because the gel does not have the mechanical strength necessary to withstand the high pressures involved with faster solvent flow rates. Porous silica is a newer form of column packing offering excellent mechanical and physical properties and is available in a range of pore sizes, with large pore volumes and small particle sizes. Hydrophilic rigid organic gels are also now available. These are specially designed for aqueous SEC and are very efficient, being available in very small particle sizes and therefore performing rapid separations, with good stability to pressure.

"TSK-Gel PW" (a cross linked hydrophilic polymer marketed as being suitable for the separation of nucleic acids and water soluble synthetic polymers) will elute polyacrylamides using water as a solvent.

Soponkanaporn and Gehr (1987) used Synchroprep "Catsec" 10 000 and 1000 (a macroporous silica coated with polyamine) to analyse various anionic, cationic and nonionic acrylamide based polyelectrolytes. They used 0.25M potassium hydrogen phosphate at pH 3 as a mobile phase, with UV detection at 200 nm. By using a 1000 µl injection volume, the authors achieved a detection limit of 1 mg l^{-1}, although they stated that lower detection limits could be achieved for purely qualitative analysis.

The problem with SEC is that the sample often elutes as a series of different molecular weight compounds, so although the method is useful for characterisation of the compounds, quantitative determination is difficult. Leung *et al.* (1987) solved this problem by using a TSK SEC column with exclusion limits smaller than the polyelectrolyte molecular size, so that the polyelectrolyte eluted as a single peak at the exclusion limit of the column. This meant that SEC cold be used as a quantitative technique. Leung *et al.* (1987) also used ultrafiltration to preconcentrate the polyacrylamide, the sample was then evaporated to dryness and dissolved in mobile phase before analysis. The lower detection limit of the method was claimed to be 4 mg l^{-1} (in the sample) although concentrations as low as 0.5 mg l^{-1} have been detected with this method at WRc (Bailey, pers. comm.).

2.4.5 Summary

The methods can be summarised as shown in Table 2.6.

Of all the techniques, size exclusion chromatography (SEC) is the most promising. It is simple in execution and sensitive and has been used to effect by several authors (Gehr and Soponkanaporn 1990, Leung *et al.* 1987, Aizawa *et al.* 1990). However, like all the methods described, it is not specific for polyelectrolytes. Furthermore, the lower limit of detection is in the region of 0.2 to 0.5 mg l^{-1} which may not be sufficiently sensitive for some applications (e.g. drinking water) and it may be subject to interferences in environmental samples from naturally occurring polymers.

Table 2.6 Summary of analytical methods

Method	Limit of detection (mg l^{-1})	Specificity
Colloid titration	1.0 mg l^{-1} (Wang and Langley 1977)	{ Any colloids or charged solutes (including { colour) will interfere.
Ionic dye complexation	0.5-1.0 mg l^{-1} (Parazak *et al.* 1987)	
Spectrofluorimetry	20±70 µg l^{-1} reported (Hendrickson and Newman 1984)	Probably most specific method because it involves converting the amide to amine and then reacting with fluorogenic reagent.
Size exclusion chromatography	4 mg l^{-1} (Leung *et al.* 1987)	Measures any high molecular weight compound (1×10^6 - 20×10^6) which absorbs in the UV range. Some naturally occurring high molecular weight compounds may interfere.

3. ENTRY INTO THE AQUATIC ENVIRONMENT

3.1 Polyelectrolytes

3.1.1 Potential for environmental contamination

The potential for polyelectrolytes entering surface waters arises from point sources such as outlet pipes from wastewater treatment plants, water treatment works or industrial effluent outfalls. Diffuse inputs can virtually be ignored. Under normal operating conditions and using the optimum polyelectrolyte dose, residual polyelectrolyte concentrations are expected to be very low. In water treatment works, the common practice of recycling the supernatants from sludge treatment back to the head of the works means that polyelectrolyte residuals will usually be contained within the plant.

Other potential sources of contamination including overdosing, accidental spillage, disposal of supernatant from dewatering of sludges and, conceivably, leaching from treated sludges applied to land. These different potential sources of contamination are discussed in more detail below.

3.1.2 Effects of dosing

The type and dose of polyelectrolyte required for a particular application can be determined by either laboratory or plant trials. The optimum dose is often determined on pilot plants or at the treatment works itself (Bannister 1985) and thus the final selection is usually based upon practical experience.

Cationic polyelectrolytes will sorb to the negative charges present in sludges (this is the basis of their coagulating or flocculating properties). However, it is conceivable for cationic polyelectrolytes to remain within aqueous waste streams if the negative charge on the sludge are occupied (the polyelectrolyte is applied at an excessively high dosage) or if the sludge and polyelectrolyte are inadequately mixed. Studies on the flocculation of activated sludge by cationic polyelectrolytes (Gehr and Henry 1982) only detected polyelectrolytes in the water phase when applied at rates between 2 and 10 g polyelectrolyte kg^{-1} dry solids. None were detected at lower application rates.

WHO (1973) cited in Singh (1985) reported that, when water entering a drinking water treatment plant was dosed with 0.3 mg l^{-1} of polyacrylamide, the polymer concentration had decreased to 0.026 mg l^{-1} after coagulation-sedimentation, 0.002-0.01 mg l^{-1} after rapid sand filtration and below 0.002 mg l^{-1} after activated carbon treatment. Earlier work by Black *et al.* (1965) indicated that up to 95% (85% in 30 seconds) of a cationic polyelectrolyte (polyDADMAC labelled with C^{14}) was adsorbed in 30 minutes by coagulation alone. However, the latter study is 30 years old and may not have used a reliable method for assessing polyelectrolyte adsorption. Lockyear *et al.* (1983) indicated that in the treatment of waterworks sludge, as long as the actual dose used was within 50% of the optimum, no polyelectrolyte would be expected to be discharged with the supernatant into the aquatic environment. Lurie and Rebhun (1994) reported that about

20% of the cationic and nonionic copolymer and 85% of the anionic polymer was associated with the aqueous phase after flocculation of activated sludge solids; however, their data relate to atypical conditions indicative of gross overdosing.

No data on sorption on non-ionic polyelectrolytes has been found but Schumann (1991, cited in STOWA 1995) demonstrated only poor sorption of an anionic polymer to activated sludge. However, such products could be strongly sorbed following treatment with inorganic flocculants to remove phosphate.

3.1.3 Sludge dewatering

Filtrates resulting from sludge dewatering have been found to contain measurable concentrations of cationic polyelectrolyte in tests where dosages in excess of 7.5 g kg^{-1} dry solids and a short conditioning time were employed (STOWA 1995).

3.1.4 Spillage

The few cases of environmental contamination by polyelectrolytes used in the treatment of water or wastewater are believed to have resulted from spillages from storage tanks or conducting pipework for diluted polymer in wastewater treatment plants (Allied Colloids, pers. comm.). This would seem to be the most likely source of environmental contamination. We might expect contamination due to spillage to result in acute, i.e. short-term, exposure of aquatic life.

3.1.5 Supernatants arising from sludge dewatering

Supernatants produced from treating sludges with polyelectrolytes are normally recycled back to the head of the treatment works. Therefore, any residual polyelectrolytes will tend to be contained within the plant.

3.1.6 Leaching from treated sludges

Leaching from sludges spread onto agricultural land is unlikely to be a significant source of polyelectrolytes in water because of the strong sorption onto soil particles. A large proportion of treated sludge would be incinerated anyway.

3.1.7 Conclusions

On balance, under normal operating conditions and using the optimum polyelectrolyte dose, no residual cationic polyelectrolyte is likely to be present in effluents arising from water or wastewater treatment plants. By comparison, anionic polyelectrolytes may show more potential to remain unadsorbed and thereby the risks of entering watercourses are higher. Accidental spillage is probably the most significant route of entry into watercourses.

3.2 Residual monomers

An additional possible source of environmental contamination results from the release of residual monomer, such as acrylamide, into surface waters. Brown *et al.* (1982) showed that little degradation of the acrylamide monomer occurred during primary or final settlement in a sewage treatment works, whilst an approximately 50% loss was recorded in both the activated sludge tanks and the biological filter beds. Thus, a large percentage of the monomer degradation occurs during biological treatment, suggesting that biodegradation may play an important role in removal.

Brown *et al.* (1980a and b) also reported that acrylamide did not adsorb onto sediment or sludges, and may therefore enter the aquatic environment through leaching in effluent treatment processes or runoff from sludges applied to agricultural land. Croll *et al.* (1974) have also reported that acrylamide may pass unchanged through a waterworks. Krautter *et al.* (1986) reported that acrylamide is highly soluble in water (2 kg l^{-1} quoted by Brown *et al.* 1980a), and it is rapidly degraded in surface water and sediments by a wide range of natural microbial communities. Nevertheless, field studies indicate concentrations may persist (Section 4.2.2).

3.3 Measured environmental concentrations

No data have been located concerning the concentrations of polyelectrolytes in the aquatic environment which might indicate small releases to surface water. However, some data are available on the levels of the acrylamide monomer found in the aquatic environment and in discharges released to surface waters (summarised in Table 3.1). Acrylamide was detected at levels of <5 µg l^{-1} in both river-water and tap-water in areas where polyacrylamides were used in the treatment of potable water (Brown and Rhead 1979). Low concentrations (<20 µg l^{-1}) have been detected in sewage effluent from treatment facilities at which polyacrylamides were not used and in a number of other industrial sites (Croll *et al.* 1974, Jewel *et al.* 1978). Higher concentrations are evident in effluents arising from acrylamide manufacturing plants and from wastewater treatment plants receiving acrylamide-containing waste. However, there is no evidence of acrylamide entering surface waters as a result of using polyelectrolytes as process chemicals or for water/wastewater treatment. With the advent of products containing smaller quantities of acrylamide (typically less than 0.1% by weight), the reported concentrations can be expected to be higher than would be found now, but no data are available.

Table 3.1 Acrylamide concentrations in water samples

Location	Source of sample	Concentration ($\mu g\ l^{-1}$)	Reference
Municipal water treatment	River water	3.4	1
Municipal water treatment	Tap-water	4.5	1
Sewage works	Effluent	2.3 - 17.4	1
Clay pit	Effluent	16	2
Clay pit	Stream-water	1.2	2
Acrylamide manufacture	Wastewater effluent	1100	2
Acrylamide manufacture	Treated effluent	280	2
Pulp mill	Effluent	0.47 - 1.2	2
Coal mine	Coal-washing effluent	1.8	2
Coal mine	Tailings Lagoon	39 - 42	2
Reservoir	During polyacrylamide waterproofing	4	3
Sewage works (no acrylamide source)	Effluent	0 - 17	4
Sewage works (with acrylamide source in influent)	Effluent	50 - 200	4

References:

1 Brown and Rhead (1979)
2 Croll *et al.* (1974)
3 Jewett *et al.* (1978)
4 BUA (1993), cited in STOWA (1995)

4. FATE AND BEHAVIOUR IN THE AQUATIC ENVIRONMENT

The fate and behaviour of polyelectrolytes is an important consideration when assessing the environmental risk posed by polyelectrolytes and any residual monomers. In this section, we show that environmental exposure to polyelectrolytes may be ameliorated by:

- abiotic hydrolysis;
- biodegradation;
- sorption to suspended solids and dissolved organic matter;
- gelling behaviour in water.

Conversely, interactions with other substances to produce potentially more toxic substances also warrant some consideration. For example, chlorine added to drinking water (and, potentially, to wastewater) for disinfection purposes could react with residual polyelectrolytes to form toxic by-products such as chloroform (Feige *et al.* 1980, Amy and Chadik 1983), although the use of chlorine in wastewater treatment is not widespread.

4.1 Fate and behaviour of polymers

4.1.1 Abiotic degradation

Soponkanaporn and Gehr (1989) studied the degradation due to ageing (storage for 30 days at either 20 or 27 °C), ozonation, chlorination and biological processes of a commercially available cationic ester-type polyacrylamide (acrylamide and dimethyl-aminoethyl acrylate quaternised with methyl chloride). The extent of degradation of the polyelectrolyte over a period of time was followed by size exclusion chromatography (see Section 2.4). In general, degradation rates increased with decreasing polyelectrolyte concentration, increasing pH and increasing temperature. Complete degradation (i.e. to carbon dioxide and other low molecular weight compounds) only occurred as a result of biodegradation, and then only when the polyelectrolyte had not been previously reacted with ozone or chlorine.

The study showed that hydrolysis could be extensive but was pH-dependent: at an initial concentration of 1 mg l^{-1} and pH 6, the cationic co-polymer was completely degraded after 4 days at 27 °C via hydrolysis, but when the concentration was increased to 10 mg l^{-1}, even after 30 days, some of the initial polymer remained even after 30 days, although the amount remaining is not known. However, increasing the pH to 9 resulted in the higher concentration of polymer being degraded in 4 days. At pH 3 very little degradation had occurred after 30 days, suggesting that acid hydrolysis is a much slower process than alkaline hydrolysis. As there was no change in total peak area it could be assumed that none of the polymer had been degraded to carbon dioxide and that no monomers were formed (Soponkanaporn and Gehr 1989). A study conducted by Allied Colloids on the cationic polyelectrolytes Zetag 57 (Allied Colloids, Internal Technical

Report) again demonstrates a higher rate of hydrolysis (as judged by colloid titration and reduction in cationic value) at low concentrations (5 mg l^{-1}) than at high concentrations (500 mg l^{-1}) and at pH 8.5 compared to pH 6. Hydrolysis was virtually complete after 6 h under optimal conditions (5 mg l^{-1}; pH 8.5). The rapid hydrolysis of ester-type polyacrylamides at pH values above 8 has also been noted (Allied Colloids, internal reports). This reaction has also been shown to occur in natural waters especially those of medium and high alkalinity. Finally, circumstantial evidence for the importance of hydrolysis as a loss mechanism emerges from toxicity studies on aged solutions, shown in Table A6. The cationically charged side-chains are cleaved off to form low molecular weight alcohols (Figure 4.1) and the remaining polymer becomes increasingly insoluble, with the loss of cationic charge, thereby rendering it non-bioavailable.

It is clear that hydrolysis of ester-type polyelectrolytes will be an important loss mechanism which can rapidly reduce exposure concentrations in receiving waters in the short-term, at least under alkaline conditions, and would be expected to reduce the risk of chronic exposure to an insignificant level in most cases. Depending on the residence time in a wastewater treatment plant, much of the hydrolysis may have occurred before the wastewater is actually discharged. STOWA (1995) estimate that between 52% and 83% hydrolysis of a cationic ester-type polyacrylamide/polyacrylate copolymer might be expected within a treatment plant, depending on the residence time (10-32 h) and assuming a thoroughly mixed system.

We should remember that losses due to hydrolysis will be of much greater importance for ester-type polyelectrolytes than for other types of polyelectrolyte. However, we have already shown that this is, by far, the most widely used product type, especially in the treatment of wastewaters and sludges (Table 2.3).

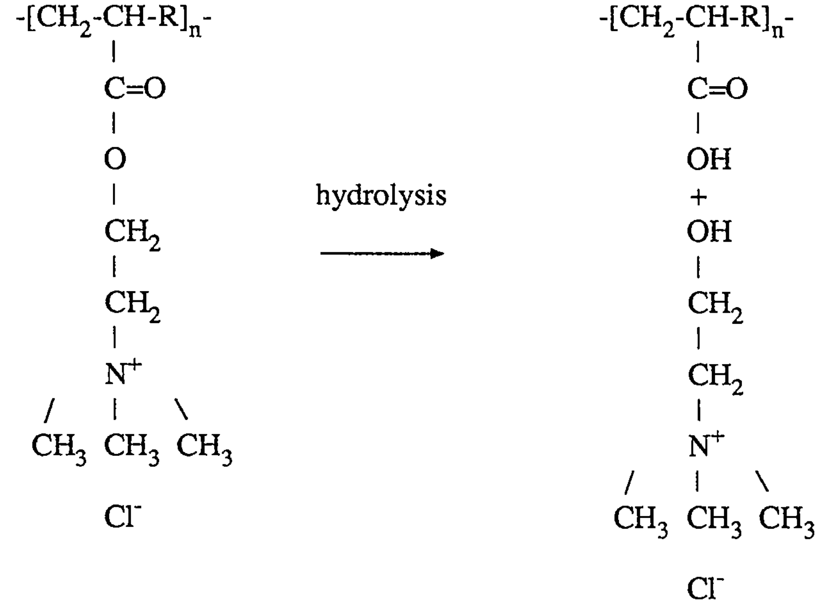


Figure 4.1 Hydrolysis of ester-type polyacrylamides

4.1.2 Biodegradation

Soponkanaporn and Gehr (1989) investigated the biodegradation of the cationic copolymer (a copolymer of acrylamide and dimethyl-aminoethyl acrylate quaternised with methyl chloride) inoculated with bacterial seed from an activated sludge plant. The rate of biodegradation was found to increase with decreasing polyelectrolyte concentration, increasing pH and increasing temperature, reflecting the conditions which favour abiotic hydrolysis. Acrylamide monomer was not produced during degradation (Soponkanaporn and Gehr 1989).

At an initial polymer concentration of 1 mg l^{-1} and at 20 °C the addition of bacterial seed led to the reduction of the polymer after 10 days. This rate was considerably faster than that for the polymer stored at 20 °C without the addition of the seed (30 days), but slower than for samples stored at 27 °C (4 days). Thus the temperature affected polymer degradation more than the addition of bacterial seed. At a concentration of both 1 and 10 mg l^{-1} polyelectrolyte, complete removal of total organic carbon had occurred by the end of the experimental period of 30 days, indicating that the bacteria are capable of utilising the polymer as a carbon source and converting it to carbon dioxide (Soponkanaporn and Gehr 1989). These authors also studied the biodegradation rate of the chlorinated polymer. At 10 mg l^{-1} hardly any degradation was reported after 28 days, and the authors suggest that this is due to the formation of some compounds during chlorination that are either toxic to the micro-organisms, and/or resistant to degradation.

Nonionic and anionic polymers of a similar structure (i.e. polyacrylamide and sodium polyacrylate) were studied by Suzuki *et al.* (1978). Both polymers were reported to be highly resistant to biodegradation due to the presence of constituent amide and carboxylic functional groups. Concentrations used in this experiment were >1000 mg l^{-1}, which are far in excess of those likely to occur in aquatic systems. Using ^{14}C-labelled polyacrylamide, activated sludge gave rise to less than 2% conversion to CO_2 (Schumann 1991, cited in STOWA 1995).

In view of their tendency to sorb to solids (Section 4.1.3) anaerobic biodegradation of cationic polyelectrolytes would be of interest but no data are available. As far as aerobic biodegradation is concerned, the data indicate modest rates of removal of cationic polymers from water.

4.1.3 Sorption

Removal of cationic polyelectrolytes from water due to sorption to solids and suspended solids represents another important loss mechanism. Reduced bioavailability as a result of interactions with dissolved organic substances such as humic and fulvic acids, are also important in the context of environmental exposure to polyelectrolytes, at least for cationic polyelectrolytes. The evidence comes from a variety of sources, described below.

Sorption of cationic polyelectrolytes is the basis for their properties as coagulants or flocculants. The process is generally recognised to be extremely rapid, as reflected by jar tests for sorption lasting only a few seconds (Allied Colloids, pers. comm.) and is irreversible (Akers 1972). Narkis and Rebhun (1975, 1977) have investigated the kinetics of adsorption of cationic polyelectrolytes with clay suspensions and humic and fulvic acids. They showed that the polyelectrolyte reacts by means of charge neutralisation to form stable colloids. In mixed systems, reaction with humic and fulvic acids is preferential although, at low pH, the decreased dissociation of the humic and fulvic acids leads to reduced reaction with polyelectrolyte (Narkis and Rebhun 1977). It follows that there is a greater risk of residual cationic polyelectrolyte occurring in waters of low pH where sorption may be reduced.

There is also a considerable body of evidence from laboratory toxicity tests which demonstrate how the bioavailability of cationic polyelectrolytes can apparently be markedly reduced by sorption to humic materials and clays. Cary *et al.* (1987) studied the effect of suspended solids (such as bentonite, ilite, kaolin and silica) and dissolved organic carbon substances (humic, fulvic and tannic acids) on the toxicity of cationic polyamines. Acute LC50s were obtained for the waterflea, *Daphnia magna* (48 hour tests) and the fathead minnow, *Pimephales promelas* (96 hour tests) using four different cationic polymers of varying molecular weight and charge density. Acute toxicities for both species with all 4 polymers were all less than 0.5 mg l^{-1}. By adding a variety of suspended solids and dissolved organics at various concentrations it was shown that the toxicities were decreased, in the majority of cases by between 10 and 100 times. The presence of dissolved organic substances clearly reduced the toxicity more than the presence of suspended solids (Tables A3 and A4).

In experiments by Goodrich *et al.* (1991), four different concentrations of humic acid were added to solutions of four different cationic polyelectrolytes (epichlorohydrin-dimethylamine and acrylamide-2-(N,N,N)-trimethyl ammonium ethacrylate chloride) before the acute LC50 tests were carried out. It can be seen from Table A6 that a strong correlation exists between toxicity and the humic acid concentration of the water. A concentration of 5 mg l^{-1} humic acid was found to significantly reduce the toxicity of polymers, and a higher concentration of 50 mg l^{-1} reduced toxicity 33- to 75-fold.

McDonald (1971 in Biesinger and Stokes 1986) showed that fish survived in a suspension of cationic polyamine, as long as particles were present to adsorb the polymer. In fact, some fish populations seemed healthier and had increased feeding rates after the addition of flocculants. However, if the water turbidity is already low, then the polyelectrolyte may clog the fish gills resulting in suffocation.

Hall and Mirenda (1991) carried out an experiment to determine the toxicity of a cationic polymer (45% charge density) to the waterflea *Daphnia magna* and the fathead minnow *Pimephales promelas* exposed to a range of concentrations of humic acid. Increases in humic acid concentration in the dilution water progressively decreased the toxicity to both species, and the addition of 60 mg l^{-1} humic acid (equivalent to 9.6 mg l^{-1} of TOC) reduced toxicity to *D. magna* and *P. promelas* by two orders of magnitude (Table A5). Similar observations were reported in studies made available by SNF (Marroni, Pers. Comm.). Table A6 shows the effect of adding humic acid to solutions of a cationic polyacrylamide, Floerger FO 4550, on its acute toxicity to zebrafish (*Brachydanio rerio*) and also the reduction in toxicity which resulted when test solutions were aged prior to exposure. This decline in toxicity on ageing was attributed to abiotic hydrolysis of the polymer (see Section 4.1.1). Biesinger and Stokes (1986) reported that the toxicity of an unspecified cationic polymer to the fathead minnow (*P. promelas*) could also be reduced by the addition of anionic polymer or clay. The cationic polymer was added at a concentration of 10 mg l^{-1}, and it was found that 11 and 20 mg l^{-1} anionic polymer were needed to completely detoxify the cationic polymer for *D. magna* and *P. promelas*, respectively. The amounts of clay needed to detoxify 5 mg l^{-1} of cationic polymer were between 80 and 320 mg l^{-1}, depending on the type of clay. Finally, based on studies using a range of unspecified cationic polymers, Nabholz and Zeeman (1991, Pers. Comm.) report toxicity reductions of 94-fold for compounds with charge densities of approximately 2.4 cations/1000 molecular weight when 10 mg l^{-1} humic acid was added to test solutions. Smaller reductions were evident for polymers which contained a high proportion of low molecular weight polymers.

The ameliorating effect of the presence of humic acids, DOC and suspended solids has led the US EPA to require testing of high molecular weight (>1000) cationic polyelectrolytes in the presence of water amended with 10 and 20 mg l^{-1} humic acid, in addition to tests performed in unadulterated water containing less than 2 mg l^{-1} TOC (Nabholz and Zeeman 1991; Pers. Comm.). The former tests are intended to provide an assessment of hazard under realistic exposure conditions while the 'clean water' tests provide an estimate of 'intrinsic' toxicity. In the US EPA scheme, testing under chronic exposure conditions may be required if there is no effect of humic acid on acute toxicity. If toxicity is reduced in the presence of humic acid, sediment toxicity tests may be triggered. Nevertheless, unpublished work by Rogers and Witt (1989; cited in Pers. Comm. from Nabholz and Zeeman 1991) indicates no toxicity to sediment-dwelling organisms for compounds with charge densities of around 3.0 cations/1000 molecular weight. This suggests that such polymers will not normally be bioavailable to either pelagic or benthic organisms in the field.

4.1.4 Gelling

If solid product is spilled directly into a watercourse, it will usually fail to disperse and dissolve but instead will form gel aggregates, unless it becomes mixed vigorously as soon as it enters the water (Technical and Processing Data on Zetag and Magnafloc, Allied Colloids TPD 2000). This characteristic will further reduce the risk of environmental exposure if the dry product was spilled.

4.1.5 Reaction with other substances

Chlorination of water containing polyelectrolytes produced some compounds which were toxic to the bacteria from an activated sludge, and were also resistant to hydrolysis. When a concentration of 1, 10 and 100 mg l^{-1} of the polyelectrolyte was exposed to ozone for up to 60 minutes, the authors found that ozone could not completely degrade the polymer, even at the lowest concentration. These authors and Suzuki *et al.* (1978) both observed that ozone-induced degradation only occurred at alkaline pH values. In the light of these results, the authors suggest that chlorination is not recommended for effluents containing high polymer concentrations, and neither chlorination or ozonation will improve the biodegradability of the polymer.

Soponkanaporn and Gehr (1989) estimated that at pH 7 the chloroform concentration resulting from a dose of 1 mg l^{-1} polyacrylamide could be as high as 28 µg l^{-1} in samples of drinking water. Acrylamide monomer is much more reactive with chlorine than the polymers, and Mallevialle *et al.* (1984) found that 1 mg l^{-1} acrylamide yielded 800 µg l^{-1} of trihalomethanes (THMs), including chloroform, after 24 hours. In the Dangerous Substances Directive (CEC 1988) the maximum allowable concentration of chloroform for the protection of all uses of fresh and marine waters is 12 µg l^{-1}. These data suggest that if wastewaters or effluents from wastewater treatment plants containing polyelectrolytes are chlorinated, the chloroform standard in waterbodies might be exceeded.

4.1.6 Conclusions

To summarise, there is evidence for a number of processes which will have the effect of reducing concentrations of polyelectrolytes in water, especially cationic polyelectrolytes. The most significant of these are losses due to sorption onto dissolved and suspended materials. Hydrolysis, especially under alkaline conditions, can also be expected to be a significant loss mechanism.

4.2 Fate and behaviour of monomers

The most widely used monomer in polyelectrolyte production is acrylamide, and all the data concerning the fate and behaviour of polyelectrolyte monomers are for this substance.

4.2.1 Abiotic degradation

Brown *et al.* (1980a) found that owing to the hydrophilic nature of acrylamide, no significant adsorption by natural sediments, industrial and sewage sludges, clays, peat, cationic, anionic and hydrophobic resins was found. The authors suggest that the major processes for the removal of acrylamide from waterbodies should, therefore, be biological and chemical degradation, although entrainment of acrylamide into sludges during flocculation using polyacrylamides is possible.

4.2.2 Biodegradation

Brown *et al.* (1980a) and Croll *et al.* (1974) have reported that a wide range of bacteria are able to to degrade acrylamide, but that lag periods of several days may occur before significant losses occur.

Krautter *et al.* (1986) in summarising the work of other authors, reported that acrylamide is biodegraded by a wide range of natural microbial communities under various conditions. In non-acclimated river water, 50% removal occurred in about 4 days, whereas for acclimated river water 50% removal occurred in less than 24 hours.

Brown *et al.* (1982) found no significant degradation when a river was continuously dosed with acrylamide for 74 days, although some increase in the ability to degrade acrylamide was evident in samples taken further downstream towards the end of the study. The reason for this lack of degradation may be due to the fact that this study was undertaken during the winter and spring months when biological activity was low and degradation rates were, therefore slower. In waters receiving continuous discharges of effluents containing acrylamide, it is likely that the microbial communities present may be more capable of degrading acrylamide than those present at sites which do not receive such discharges.

5. AQUATIC TOXICITY OF POLYELECTROLYTES

A large number of studies have been carried out on the aquatic toxicity of polyelectrolytes, and the salient points are summarised below.

5.1 Mode of toxic action

The surface of fish gills carries a negative charge to which cationic polyelectrolytes will readily bind due to electrostatic attraction. It is likely that the mortality of fish is the result of lamella fusion of gills causing suffocation or reduction in oxygen transfer affecting the internal ionic balance. This is supported by a microscopic examination of the gills of fathead minnows (*Pimephales promelas*) carried out by Biesinger and Stokes (1986), who found that the lamella epithelium of the gills exhibited a 'fuzzy' appearance after exposure to cationic polyelectrolytes. Biesinger and Stokes (1986) concluded that this binding effect was the reason why cationic polymers are generally more toxic to aquatic organisms than anionic or non-ionic polyelectrolytes. However, chelation of certain nutrients has also been implicated in the toxicity of anionic polymers to algae (Nabholz and Zeeman 1991, Pers. Comm.).

Because uptake across membranes can effectively be discounted (Section 5.2), the toxic effects of polyelectrolytes can usually be attributed to interactions with the surfaces of aquatic organisms.

5.2 Bioaccumulation

We would expect only soluble polymers to interact with biological membranes and only products with low molecular weights would be capable of crossing membranes, where some systemic toxicity is possible. Bioaccumulation of high molecular weight polymers (>1000) can be discounted. This applies to virtually all polyelectrolytes described in this review which cover the range 10 000-several million. Finally, any toxic effects of insoluble polymers would probably be attributable to physical effects (e.g. clogging of fish gills) and would not be dependent on chemical structure.

Data provided by Allied Colloids (Norman, Pers. Comm.) show that octanol water partition coefficients of five cationic polyelectrolytes were less than 1.0, indicating little tendency to partition from water into the octanol phase, even if transfer across biological membranes was possible. The test report describes difficulties in interpretation caused by aggregations of the polymers but we can safely assume there is little or no potential for bioaccumulation.

5.3 Acute toxicity to aquatic life

5.3.1 Summary of available data

Many studies have been undertaken to investigate the toxicity of polyelectrolytes to aquatic life. A large proportion of these have been carried out on behalf of manufacturers and are commercially sensitive. For this review, a large amount of commercial data has been made available on behalf of the TEGEWA Polyelectrolyte Producers Group and this has been supplemented by data published in the open literature. By far the majority of the data are for cationic polyelectrolytes and their effects on fish and crustaceans. Much smaller datasets are available for non-ionic and anionic polyelectrolytes.

All the available data are summarised in Tables 5.1 and 5.2 for freshwater and marine organisms, respectively. They are confined to studies in which substances such as humic and fulvic acids and clays were not added, and therefore, they represent a 'worst case' situation with respect to aquatic toxicity, at least for the cationic polyelectrolytes (Section 4.1.3).

Table 5.1 Summary of the toxicity of polyelectrolytes to freshwater organisms

Product type	Taxon	n	Range of EC_{50}/LC_{50} values (mg l^{-1})	Median EC_{50}/LC_{50} (mg l^{-1})
Cationic	Algae	11	0.2 - 636.0	57.0
	Invertebrates	85	0.04 - 450.0	3.9
	Fish	114	0.06 - 1000.0	0.89
Anionic	Algae	2	2.0 - >1000.0	n/a
	Invertebrates	10	17.0 - 3333.0	345.0
	Fish	13	18.0 - 811.0	37.2
Non-ionic	Algae	1	1081.0	n/a
	Invertebrates	7	15.3 - 1733.0	53.0
	Fish	9	8.0 - 4220.0	100 - 500

Table 5.2 Summary of the toxicity of polyelectrolytes to marine organisms

Product type	Taxon	n	Range of EC_{50}/LC_{50} values (mg l^{-1})	Median EC_{50}/LC_{50} (mg l^{-1})
Cationic	Algae	1	0.2	n/a
	Invertebrates	1	960.0	n/a
	Fish	3	1000.0 - 2370.0	n/a
Anionic	Algae	3	>1000.0	n/a
	Invertebrates	6	15.0 - 400.0	30.0
	Fish	1	>1000.0	n/a
Non-ionic	No data			

The data shown in Tables 5.1 and 5.2 refer to EC_{50} or LC_{50} concentrations in acute or (rarely) chronic toxicity tests. In the fish and invertebrate tests the measured endpoints are usually survival or immobilisation but for the algal studies, growth inhibition is normally the measured endpoint. The wide range of reported effect concentrations is noteworthy reflecting the effects of structural variations (Section 5.3.2) and the wide range of test species, exposure durations, endpoints and test conditions used. By presenting all the available data as ranges of effect concentrations from separate studies, and calculating the corresponding median values, the relative sensitivities of different groups of organisms become readily apparent.

Some lower EC_{50} values (i.e. higher toxicities) than those shown in Table 5.1 have been reported for anionic polyacrylamides. Values as low as 0.06 mg l^{-1} and 0.4 mg l^{-1} to the water flea, *Daphnia pulex*, and fathead minnow, *Pimephales promelas*, respectively, were reported by Hall and Mirenda (1991). However, these point estimates were based on binominal interpolation of the test data and so are associated with wide confidence intervals. Furthermore, their data show no consistent relationship between charge density and toxicity. These factors, coupled with the fact that they indicate toxicity at least two orders of magnitude greater than other studies suggests they are probably anomalous and have therefore not been used in the risk assessment.

The data for non-ionic polymers to fish also indicate a wide range of toxicities but, in this case, the lowest reported LC_{50} values do not appear to be outliers. It is interesting to note that the lowest LC_{50} values were obtained in separate studies although both studies used rainbow trout, hinting that this may be a particularly sensitive species.

The medians shown in Table 5.1 probably provide the most meaningful picture of the relative toxicities of the different product types, indicating consistently lower toxicities with non-ionic and anionic polyelectrolytes. The US EPA classification scheme for polyelectrolytes regards non-ionic polymers as being of 'low' concern but anionic polymers can inhibit growth of unicellular algae as a result of chelation of nutrients. In these cases, toxicity may be reduced by the addition of Ca^{2+}. As far as cationic products are concerned, the data show that fish are generally more sensitive than invertebrates (predominantly *Daphnia* sp.) which are, in turn, more sensitive than algae. Distributions of toxicity data to freshwater organisms resulting from the more hazardous cationic polyelectrolytes are illustrated in Figure 5.1.

The dataset from toxicity tests using marine organisms (Table 5.2) is too small to permit an evaluation of the relative sensitivities of different classes of organisms to different types of polyelectrolytes.

5.3.2 Factors affecting toxicity

Structural/charge properties

The literature reveals marked effects of structural factors, and especially cationic charge characteristics, on the aquatic toxicity of cationic polyelectrolytes.

Hall and Mirenda (1991) studied the acute toxicity of 34 wastewater treatment polyelectrolytes as three distinctive charge types (cationic, anionic and non-ionic) to *Daphnia pulex* (water flea) and *Pimephales promelas* (fathead minnow). Cationic polyelectrolytes were by far the most toxic polyelectrolytes to *Pimephales* (Table A8), with toxicity increasing with positive charge density (Figure 5.2). Similarly, data provided by Allied Colloids (Norman, Pers. Comm. 1995) shows a clear relationship between cationic charge density of five polymers and their acute toxicities to golden orfe and *Daphnia*, but not algae. There is no convincing evidence to indicate that increasing negative charge density in anionic polyelectrolytes results in greater toxicity.

The US EPA have devised a classification scheme for the hazard assessment of polymers, including polyelectrolytes, based on (i) their molecular weight and (ii) charge characteristics. The scheme makes use of Structure-Activity Relationships (SARs) to predict the toxicity of certain classes whilst for others, practical testing is required, as shown below:

Compound class	Hazard assessment
Low molecular weight (<1000) polymers	
a) Neutral (nonionic) polymers	Predicted on basis of functional group
b) Anionic polymers	Predicted on basis of functional group and/or by comparison with analogues
c) Cationic polymers	Predicted on basis of functional group and/or by comparison with related compounds, e.g. quaternary ammonium compounds
d) Amphoteric polymers	Classified according to balance of positive and negative charges and hazard assessed accordingly
High molecular weight (>1000) polymers	
a) Neutral (nonionic) polymers	Low concern
b) Anionic polymers	Polycarboxylic acids: moderate toxicity to algae due to chelation of nutrients. Toxicity can be offset by addition of Ca^{2+}
c) Cationic polymers	Of greatest concern. Toxicity to fish and *Daphnia* increases exponentially with increasing cationic charge density, reaching an asymptote at ca. 2.5 cations/1000 molecular weight Toxicity ameliorated by addition of humic acids. Testing scheme involves tests with and without addition of humic acid and possible sediment toxicity or chronic water column tests
d) Amphoteric polymers	Classified according to balance of positive and negative charges and hazard assessed accordingly

Species effects

Biesinger and Stokes (1986) carried out studies exposing 4 aquatic organisms *Daphnia magna*, a gammarid *Gammarus pseudolimnaeus*, a midge *Paratanytarsus* sp. and the fathead minnow *P. promelas* to a variety of cationic, anionic and non-ionic polymers. Of the 15 cationic polymers, several exhibited high acute toxicity to gammarids, and midges were found to be much less sensitive to these polyelectrolytes, with the lowest reported 48 hour LC50 for midges of <6.25 mg l^{-1}, and 96 hour LC50 values for gammarids of 8.1 mg l^{-1} (both for polymer G). The wide range of LC50s shown in their results (Table A1) reflects inter-specific differences and also the effect of structural and charge properties of the polymer on its aquatic toxicity, as discussed above.

Exposure conditions

Goodrich *et al.* (1991) compared the results of 96 hour toxicity tests using *O. mykiss* (rainbow trout) exposed to different experimental conditions and four different polymers. The polymers under examination were found to be more toxic in a flow-through regime than in static conditions. Ninety-six hour LC50s under static conditions varied between 0.27-0.78 mg l^{-1}. However, in flow-through conditions, much higher toxicities were evident, with 96 hour LC50s of between 0.043-0.38 mg l^{-1}. Most of the fish deaths occurred during the first seven days of the experiment so only small changes to estimates of toxicity resulted when the exposure period was extended.

The effects of ageing on the toxicity of solutions containing certain cationic polyelectrolytes has already been described (Section 4.1 and Table A8), where hydrolysis was implicated as the reason for lower toxicity in aged solutions. Losses due to hydrolysis would also explain the higher measured toxicities in flow-through tests compared with static tests (Goodrich *et al.* 1991).

5.3.3 Sub-lethal effects of polyelectrolytes

Compared with the dataset for short-term effects on survival and immobilisation, data concerning sub-lethal toxicity are limited.

Biesinger and Stokes (1986) reported that the species diversity in an algal mesocosm containing 10 species of algae was affected by the presence of a cationic polyelectrolyte. By day 62, *Scenedesmus obliquus* (a green alga) comprised 98.02% of the algal population in the highest concentration (31 mg l^{-1}), compared to 59.98% in the control vessel. The two most common algal species at the start of the test (*Ankistrodesmus* sp. and *Chlamydomonas reinhardtii*), which comprised approximately 28% of the population in the highest concentration, had declined to 0.04 and 0.53% of the cell numbers after 62 days.

Cationic polymers might be expected to cause sub-lethal effects at lower concentrations than the other types of polymers. Sub-lethal toxicity for cationic polyelectrolytes appears to occur if the water turbidity is low, when fish gills may become clogged resulting in suffocation (McDonald 1971, in Biesinger and Stokes 1986). Rainbow trout (*O. mykiss*) were found to avoid water containing cationic polymers (acrylamide and polydimethyl-diallyl-ammonium chloride) if given the choice between a channel containing polyelectrolyte and another containing no polyelectrolyte (Spraggs *et al.* 1982). They reported 50% avoidance at concentrations of 0.8 and 0.43 mg l^{-1} for these two polymers, respectively.

Although Goodrich *et al.* (1991) reported sub-lethal effects on the growth of rainbow trout after 28 days exposure to an acrylamide/acrylate ester copolymer, no details are given as to what effects were noted or the concentration needed to cause them. Extending the exposure period from 4 to 28 days had very little effect on the survival rate of fish in this study in a flow-through experiment, designed to maintain concentrations of the test chemical.

Significant impairment of the reproduction of *D. magna* was reported by Biesinger *et al.* (1976) at concentrations of a cationic polyacrylamide as low as 0.2 mg l^{-1} in a static 21 day study (Table A2). The highest concentration which had no effect on reproduction was 0.1 mg l^{-1}. The corresponding concentrations after 21 days for the other two cationic polyelectrolytes were both 1 mg l^{-1} (Table A2).

The data available in the literature show that long-term toxicity of aquatic organisms to cationic polyelectrolytes occurs at about the same order of magnitude as acute toxicity, indicating a low acute:chronic ratio. There is no evidence that prolonged exposure allows other modes of toxic action to be expressed.

5.4 Summary of aquatic toxicity of polyelectrolytes

In terms of their toxicities to aquatic life, it is clear that cationic polyelectrolytes pose a more serious potential hazard than non-ionic or anionic products. Fish also appear to be the most sensitive taxon to cationic polyelectrolytes but algae are sensitive to anionic polyelectrolytes. Within the cationic polyelectrolytes, a very large range of toxicities have been reported reflecting, in probable order of importance:

- cationic charge density;
- the presence of dissolved organic matter and clays;
- the species tested;
- the frequency with which test solutions are replaced.

Exposure duration appears to be of little consequence and the acute:chronic ratio is probably low as a result. The lowest credible adverse effect concentrations are from studies with cationic polyelectrolytes where acute EC_{50}/LC_{50} values as low as 0.04-0.06 have been reported in studies with *Daphnia* (Hall and Mirenda 1991) and bluegill sunfish, *Lepomis macrochirus* (Cary *et al.* 1987).

As noted previously, the presence of humic and fulvic acids or clays can markedly reduce bioavailability (and therefore toxicity), and this must be taken into account in any assessment of the risk of environmental damage resulting from polyelectrolytes entering surface water.

Figure 5.1 Frequency distribution plots illustrating the toxicities of cationic polyelectrolytes to different organisms

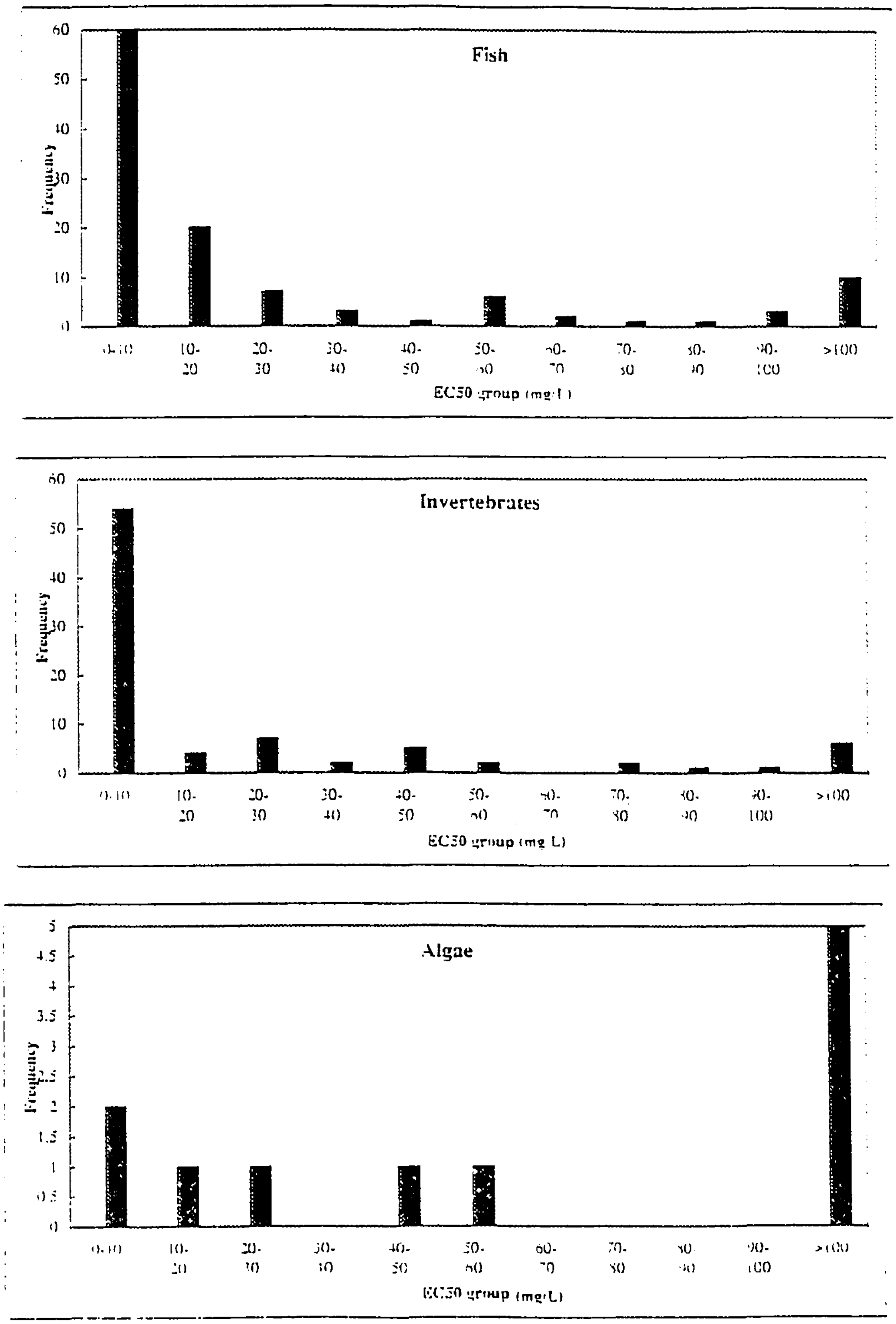
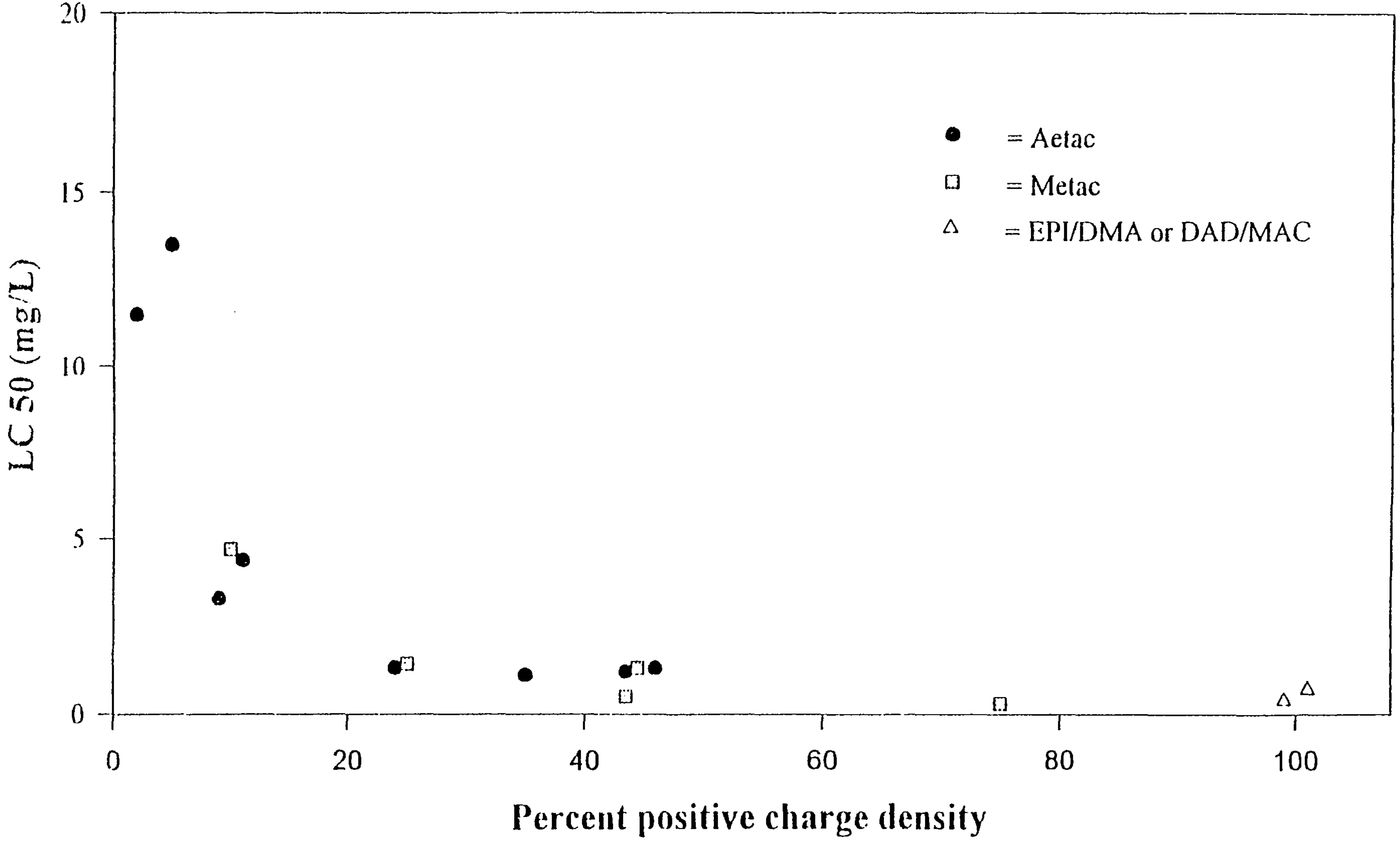


Figure 5.2 Influence of cationic polyelectrolyte charge density on acute toxicity to fathead minnow (*Pimephales promelas*) [from Hall and Mirenda 1991)



6. ECOTOXICITY OF IMPURITIES AND BY-PRODUCTS

Two other concerns arise when considering the potential risk that polyelectrolytes pose to the environment. The first is the potential presence of impurities in the finished product and the degradation products formed. Examples of such contaminants are the acrylamide monomer and epichlorohydrin used in the production of polyacrylamide and epichlorohydrin-dimethylamine copolymer, respectively. The second concern is the possibility that the polyelectrolyte may react with other chemicals used in the treatment process to form harmful by-products. An example of this is the possibility of polyelectrolytes reacting with chlorine to produce chloroform.

6.1 Impurities

Letterman and Pero (1990) investigated the contaminants present in polyelectrolytes used in the United States for the treatment of drinking water and the by-products formed. The polyelectrolytes are similar to those used in the United Kingdom. The study investigated the possible presence of residual monomers; reagents used to form the monomers; by-products of the reaction of monomer with other chemicals; and miscellaneous chemicals used in the production process such as solvents and salts as contaminants of the finished polymer. The study was restricted by the need to preserve the commercial confidentiality of the manufacturers. However, Letterman and Pero (1990) concluded that a wide variety of contaminants may potentially be present in the finished polyelectrolyte some of which are harmful to mammalian and aquatic life above certain concentrations. The compounds of most concern are the acrylamide monomer used in the production of anionic, cationic and non-ionic polyacrylamides, and epichlorohydrin used in forming cationic epichlorohydrin- dimethylamine copolymers. For products used in the treatment of potable water supplies, there is a limit of 0.025% acrylamide monomer. Although there is no limit on the amount of acrylamide present in products used for the treatment of sludges or wastewaters, most products used for this purpose contain less than 0.1% w/w acrylamide (TEGEWA Polyacrylamide Products Group, Pers. Comm.).

The ecotoxicity of acrylamide and the other compounds mentioned above are discussed in Sections 6.1.1-6.1.3.

6.1.1 Acrylamide monomer

It has been estimated that up to 70% of the polyelectrolytes used in the treatment of water and wastewater are based upon the acrylamide monomer (Letterman and Pero 1990).

The available data from laboratory studies suggests that the acrylamide monomer is of low to moderate acute toxicity to aquatic crustaceans and fish, with reported effects occurring in the range 85-410 mg l^{-1} (Krautter *et al.* 1986, Spraggs *et al.* 1982). All the available toxicity data for acrylamide are presented in Table A9.

Only one field study is available but it is important because it indicates that invertebrates may be much more sensitive to acrylamide than is suggested by the results of acute exposures in the laboratory. Over a period of about 10 weeks during Autumn and Winter, Brown *et al.* (1982) continually released a concentration of 6 µg l^{-1} acrylamide into a small river supplemented on three occasions by further additions of acrylamide resulting in peak concentrations of between 31.5 and 50.5 µg l^{-1} for 6 hour periods. This regime had an adverse effect (in terms of diversity and drift) on most species of aquatic invertebrates, with a few species being unaffected. The only species on which a negative result was not experienced was the caddisfly larva (*Hydropsyche instabilis*), which actually increased in numbers over the test period. The reduction in species diversity was temporary with some recovery evident 5 weeks after the dosing had been discontinued. Although the study was carried out during winter and an appropriate reference (control) survey is absent, the study does provide evidence of adverse effects of acrylamide at much lower concentrations than has been found to cause any other effect in laboratory studies. Such a discrepancy between acute laboratory and field studies might be expected for a compound with a mode of action which causes sub-lethal effects. Acrylamide is a known neurotoxin and it is conceivable that this caused behavioural effects and the observed invertebrate drift. Such effects would almost certainly go undetected in laboratory acute studies.

6.1.2 Acrylic acid

Bringmann and Kuhn (1977) reported that a concentration of >18 mg l^{-1} acrylic acid (as the sodium salt) inhibited cell multiplication in the green alga *Scenedesmus quadricauda*. This indicates that acrylic acid is of moderate toxicity to algae.

Juhnke and Lüdemann (1978) found that a much higher concentration was necessary to cause an effect to fish. The LC50 (exposure period was not reported) to golden orfe (*Leuciscus idus*) was reported as 315 mg l^{-1} indicating low toxicity to this species.

6.1.3 Epichlorohydrin

Epichlorohydrin is used in the production of epichlorohydrin-dimethylamine copolymer, a cationic polyelectrolyte extensively used as a primary coagulant. Epichlorohydrin is a potential EC List 1 substance and is included on the North Sea reference list of dangerous substances. The US EPA has set a maximum free epichlorohydrin level of 0.01% in the polymer and a maximum dose of 20 mg l^{-1} (Pontius 1991).

Epichlorohydrin has a low octanol-water partition coefficient suggesting that it has little tendency to bioaccumulate (Krijgsheld and Van Der Gen 1986). The toxicity data indicate that it is of moderate toxicity to aquatic organisms with LC_{50} values for a range of freshwater and marine fish species between 12 and 35 mg l^{-1} and a 24 h EC_{50} to *Daphnia magna* of 30 mg l^{-1} (Krijgsheld and Van Der Gen 1986).

6.2 Chloroform formation

The formation of chloroform during the reaction of chlorine with a variety of polyelectrolytes has been reported.

In the UK the concentration of chloroform permissible in the aquatic environment is controlled by DoE Regulations (The Surface Waters (Dangerous Substances) (Classification) Regulations 1989) implementing the Dangerous Substances Daughter Directive for chloroform (CEC 1988). A standard of 12 µg l^{-1} chloroform is laid down for the protection of fresh and waters.

Chlorination of a commercially available cationic copolymer of acrylamide and dimethyl-aminoethyl resulted in the formation of chloroform at a rate which was dependent on the polyelectrolyte concentration as well as the pH. An initial polymer concentration of 1 mg l^{-1} at pH 3 with a chlorine dose of 20 mg l^{-1} produced 12.5 µg of chloroform per mg of polymer after 12 days. This increased to 28 and 58 µg of chloroform per mg of polymer at pH 7 and 9, respectively (Soponkanaporn and Gehr 1989).

The results of Soponkanaporn and Gehr (1989) are in line with the work of other investigators. For example Feige *et al.* (1980) reported chloroform production of 3-15 µg mg^{-1} for cationic copolymers of epichlorohydrin and dimethylamine and for anionic and non-ionic polyacrylamides. Keiser and Lawrence (1977) and Amy and Chadik (1983) obtained values of 0.3 and <0.6 µg mg^{-1} for non-acrylamide polymers after reaction periods of 96 hours and 4 hours respectively.

In further studies the chlorination of 1 mg l^{-1} of polyacrylamide at pH 4 and 7 resulted in haloform concentrations of 8.8 and 14.6 µg mg^{-1}, respectively. At pH 10 this increased to a maximum of 30.3 µg mg^{-1} supporting previous work that found an increased haloform formation at higher pHs (Aizawa *et al.* 1990).

Studies also indicated that the lower the carboxylate substitution on a polyelectrolyte the greater the risk of formation of haloforms. However, only 1-10% of the total haloforms formed is as chloroform, the rest of the products being a wide variety of other haloforms (Aizawa *et al.* 1990).

Mallevialle *et al.* (1984) reported that a copolymer of acrylamide and sodium acrylate used in the treatment of potable water had little reactivity with chlorine. The presence of contaminants, though, did raise questions about the possible production of harmful by-products. Chlorination of 1 mg l^{-1} of acrylamide produced 800 µg trihalomethane l^{-1} after 24 hours, compared to the 7-8 µg trihalomethane l^{-1} produced by chlorinating 5 mg l^{-1} of an anionic copolymer of acrylamide and sodium acrylate. As acrylamide was only present at a concentration of 100 ng l^{-1} at the recommended maximum polymer dosage of 0.5 mg l^{-1} for potable water treatment, this application of the polymer should pose no problems to the environment with regard to chloroform production.

6.3 Summary of the environmental risk posed by acrylamide monomer

The preceding sections show that acrylamide can have adverse effects on invertebrate communities in the field at concentrations of between 31.5 and 50.5 µg l^{-1} (Brown *et al.* 1982). This represents a much greater hazard than is indicated from acute toxicity tests carried out in the laboratory, which typically generate LC_{50}s to fish and crustaceans between 85 and 410 mg l^{-1}, several orders of magnitude higher than the effect concentrations seen in the field. This difference may reflect a sub-lethal toxic mode of action of acrylamide which is not detectable in short-term laboratory experiments designed to monitor lethal responses. Coupled with the high water solubility of acrylamide, low sorption to sediment and suspended solids, and equivocal information on its persistence in water, these findings raise concerns about the hazard to aquatic life posed by this compound.

The published data on the occurrence of acrylamide in surface waters is limited to a few measurements reported fifteen to twenty years ago (Croll *et al.* 1974, Jewett *et al.* 1978, Brown and Rhead 1979). Only two values relate to surface waters, both of which would indicate environmental concentrations an order of magnitude below those reported to cause invertebrate drift. Recent unpublished data generated by WRc (Dillon, Pers. Comm.) shows concentrations of between 2 and 6.5 µg l^{-1} acrylamide in the waste liquors arising from the conditioning of waterworks sludges with polyelectrolytes prior to dewatering. Some of these waste liquors may be discharged to surface waters but there, they would receive further dilution. Although these results suggest this use of polyelectrolytes is not likely to result in adverse concentrations of acrylamide in surface waters in the vicinity of water treatment works, the available data are sparse and there are no data for other applications of polyelectrolytes, e.g. in wastewater treatment.

Clearly, there is some uncertainty about the true hazard posed by acrylamide to aquatic life and its occurrence in surface waters. A better appreciation of environmental concentrations of acrylamide around wastewater, sewage and water treatment works which employ polyelectrolytes would be necessary before a proper assessment of its environmental risk can be made. This might be coupled with further investigations into the sub-lethal effects of acrylamide if measured concentration exceed, or are close to, those which have been reported to be associated with invertebrate drift.

7. PRIORITISATION OF POLYELECTROLYTES

7.1 Prioritisation schemes

A number of schemes for prioritising chemicals according to their environmental risks have been developed. These vary according to the purpose for which they have been developed but all share a common aim to classify substances in terms of their potential harm. The central questions common to such classification schemes are:

- What is the likelihood of environmental exposure?
- How persistent is the chemical?
- What harm does the chemical cause to living organisms?

Such schemes tend to classify chemicals into one of the following groups (cited in Hedgecott 1993):

- Those with no or low likelihood of environmental hazard.
- Those with a high likelihood of environmental hazard.
- Those with uncertain likelihood of environmental hazard and which require further study.

WRc has developed a prioritisation scheme for DoE for the selection of candidate List I substances that are potentially hazardous to aquatic life (Hedgecott and Cooper 1991). In this scheme, chemicals are assigned a final priority category (i.e. high, medium or low environmental risk) but the order of priority within each category is not defined. The argument in support of this approach is that the amount and quality of data currently available, and our present understanding of chemical hazard, are inadequate, and that a 'broad brush' approach is therefore most appropriate (Hedgecott 1993).

The selection procedure assesses environmental risk on the basis of chemical toxicity, bioaccumulation, persistence, and quantities employed as shown in Figure 7.1 and Table 7.1.

Figure 7.1 Prioritisation scheme for polyelectrolytes

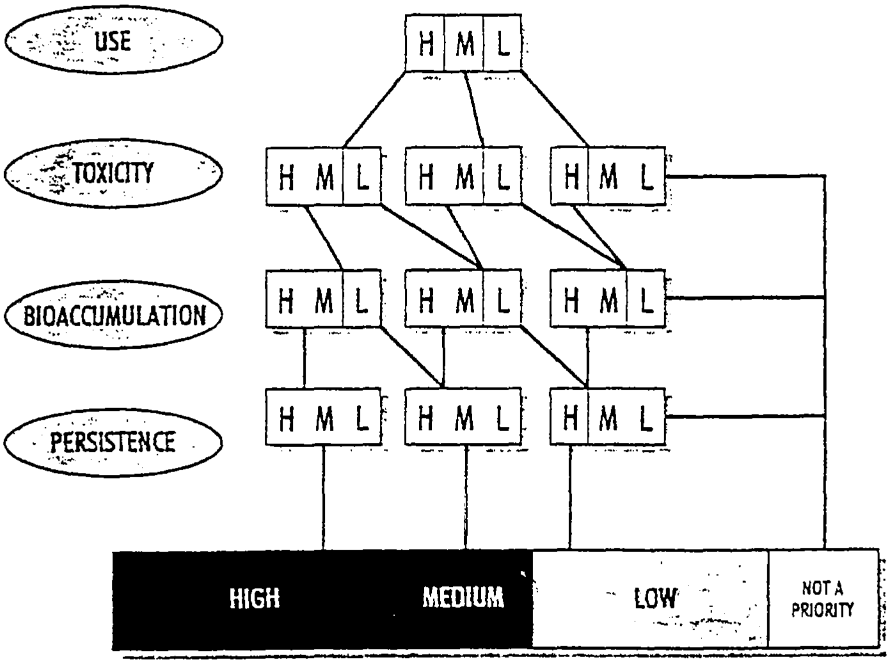


Table 7.1 Classification criteria for properties used in prioritisation

Property	Classification 'Low'	 'Medium'	 'High'
Usage (tonnes p.a.)	<1000	1000 - 10 000	>10 000
Toxicity (LC_{50}, mg l^{-1})	>100	100 - 1.0	<1.0
Bioaccumulation (log K_{ow})	<2.0	2.0 - 3.5	>3.5
Persistence (half-life, days)	<10	10 - 100	>100

7.2 Prioritisation of polyelectrolytes for EQS development

7.2.1 Introduction

As far as the uses described in this report are concerned, the most important polyelectrolyte products may be classified as follows. These account for approximately 99% of all polyelectrolytes used in the treatment of water and wastewater (Table 2.2).

1. Polyacrylamides
    1.1 Anionic
    1.2 Non-ionic
    1.3 Cationic
2. Other cationic products
    2.1 Polyamines
    2.2 Poly(DADMAC)s

The following prioritisation is based on this classification of polyelectrolytes. We have ignored any possible contribution made by residual monomers. Most data relating to the toxicity of polyelectrolytes are concerned with short term exposure. Data concerning long term exposure are limited, but those studies that are available indicate that the acute to chronic ratio is low and so no additional hazard as a result of chronic exposure is expected.

7.2.2 Usage of polyelectrolytes

Information on usage are based on the data given in Tables 2.2 and 2.3 for usage in 1992/93. Because the available information on usage are broken down by application rather than product type, the following tonnages for each product type have been inferred from the data available, as shown in Table 7.2.

Table 7.2 Approximate breakdown of product usage (tonnages)

Product type	% of all polyelectrolytes in 1992/93*	Tonnage in 1992/93+
1. Polyacrylamides		
1.1 Anionic	30$	1533
1.2 Non-ionic		275
1.3 Cationic	55	4126
2. Other cationic products		
2.1 Polyamines	9	675
2.2 Poly(DADMAC)s	5	375

* From Table 2.1
\+ From Table 2.2
$ Assumed that all anionic and non-ionic products are of this type

This approach assumes that the breakdown given in Table 2.2 is applicable to the 1992/93 tonnages given in Table 2.1. It applies only to polyelectrolytes used in the treatment of wastewater and potable water and so product in storage or manufacture is excluded.

On the basis of this assessment, the cationic polyacrylamides would attract a 'medium' usage rating. The risks of contaminating a watercourse are discussed in Section 3.1 but, for the purposes of prioritisation, no one application (treatment of sewage/sludge, water treatment, or treatment of industrial effluent) has been considered to pose a greater risk of environmental exposure than another. Nevertheless, as discussed later (Section 7.2.5), the applications and tonnages of non-ionic and anionic polyelectrolytes would almost certainly result in lowers risks of environmental exposure compared to cationic polyelectrolytes. Based simply on tonnages, the non-ionic products fall into the 'low' use category whilst the anionics just fall into the 'medium' category (Table 7.1).

Because it is based simply on tonnages, the prioritisation scheme does not consider the concentrations of polyelectrolytes which may be expected to occur in surface waters as a result of normal (or abnormal) operating conditions. A risk assessment using predicted environmental concentrations of cationic polyelectrolytes and monomers arising from the treatment of wastewaters (STOWA 1995) concluded that there was little risk of acute toxicity at the concentrations which could be expected to occur. This assessment is useful in highlighting operating conditions which might erode the safety margin between toxic concentrations of polyelectrolyte and predicted concentrations in the environment.

7.2.3 Toxicity

The toxicity of polyelectrolytes is highly dependent on charge characteristics and especially charge density. The range of acute toxicities are summarised in Tables 5.1 and 5.2 and the lowest credible acute EC_{50}/LC_{50} values for the different classes for fish and invertebrates are shown in Table 7.3.

Table 7.3 Lowest credible acute EC_{50}/LC_{50} values for polyelectrolytes

		Acute toxicity (EC_{50}/LC_{50}, mg l^{-1})	
Product type		Fish	*Daphnia*
1.	Polyacrylamides		
1.1	Anionic	18.0	17.0
1.2	Non-ionic	8.0	15.3
1.3	Cationic	0.4	0.04
2.	Other cationic products		
2.1	Polyamines	0.06	-
2.2	Poly(DADMAC)s	0.16	0.21

Due to the wide range of toxicities which is often evident (Tables 5.1 and 5.2) these values may not be representative of the majority of products within that class. They also take no account of losses due to sorption: toxicity may be reduced by 1-2 orders of magnitude when dissolved organic matter such as humic or fulvic acids are present (Section 4.1). Furthermore, whilst there is an extensive dataset for cationic products, toxicity data for non-ionic and anionic products are comparatively sparse and not always comprehensively documented.

Although most surface waters will contain dissolved organic substances, this factor has not been included here but has been taken into account in the estimation of the persistence of polyelectrolytes in surface water (Section 7.2.5). The toxicity values in Table 7.3 therefore represent the intrinsic hazard posed by polyelectrolytes to aquatic life and certainly represent a 'worst case' situation. On the basis of these toxicity values, the anionic and non-ionic products would be regarded as 'medium' toxicity, and the cationic polyelectrolytes (polyacrylamides, polyamines and poly(DADMAC)s) would attract a 'high' toxicity rating.

7.2.4 Bioaccumulation

There are no reported data on the bioaccumulation of polyelectrolytes by aquatic organisms, although conventional assessments of bioaccumulation properties of cationic polyelectrolytes based on octanol-water partitioning suggest no tendency to partition out of water (Norman, Pers. Comm.). Furthermore, it is generally recognised that large molecules (chain length or cross sectional area >9.5A) or molecules which are sorbed to dissolved organic matter or suspended particles are unable to cross biological membranes and bioaccumulate. Certain ionised molecules may also be excluded (Barron 1990). All these characteristics would apply to cationic, and possibly, anionic polyelectrolytes. Furthermore, Norman (Allied Colloids, Pers. Comm. 1995) notes that cationic polyelectrolytes are not absorbed by the gastrointestinal tract and are insoluble in lipids. There is also circumstantial evidence to suggest that the toxic effects of cationic polyelectrolytes result from interactions with external membranes. Together, these observations would suggest that an appropriate classification of bioaccumulation would be 'Low'.

7.2.5 Persistence

The available data for abiotic and biotic degradation of polyelectrolytes are restricted to certain cationic products, but this is the group which would be most hazardous to aquatic life (Sections 7.2.2-7.2.3).

Hydrolysis is dependent on pH, temperature and polymer concentration but rates of loss under realistic conditions are likely to be significant, especially as concentrations are reduced by dilution. Abiotic hydrolysis would be expected to be more rapid in hard, alkaline waters than in soft waters. Probably, the tendency of polyelectrolytes to sorb to dissolved and suspended organic matter is a more significant factor affecting their availability in surface waters. There is an extensive dataset showing the amelioration of the toxicity of cationic polyelectrolytes in the presence of humic acid and other compounds (Section 4.1). Reductions of toxicity to fish and invertebrates typically range between 10 and 100-fold for cationic polyacrylamides and poly(DADMAC) products.

Although few studies have measured polyelectrolyte half-lives under field or simulated field conditions, the combination of abiotic hydrolysis, biodegradation and especially losses due to sorption would have a very considerable impact on bioavailability in the water column. It is conceivable that cationic polyelectrolytes may persist in sediments but they are unlikely to be bioavailable to benthic organisms. Although sorption of anionic and non-ionic polyelectrolytes would, of course, occur in treatment of potable or wastewater, losses of any residual polyelectrolyte in surface waters are likely to be of smaller magnitude than for cationic polymers because of the predominantly net negative charge associated with most natural sediments and suspended solids (Simkiss 1995). Nevertheless, since anionic and non-ionic polymers are used more in the treatment of potable water than in treatment of sludges and sewage, the risks of residual polymer entering water courses are probably smaller than for polymers used in wastewater treatment. This coupled with the smaller quantities used (Table 2.2) would be expected to reduce the risk of exposure to hazardous concentrations of non-ionic and anionic products.

For cationic polyelectrolytes, a 'low' persistence classification is clearly appropriate. For anionic and non-ionic polyelectrolytes, there is rather more uncertainty about the extent of losses due to the sorption or degradation but this is counter-balanced to some extent by an expectation that smaller amounts would enter surface waters in the first place. For these classes, a 'medium' persistence classification is considered appropriate.

7.2.6 Conclusions

Although polyelectrolytes are widely used in close proximity to surface waters, it is only the cationic polymers which pose a significant hazard to aquatic life. However, their bioavailability will be greatly reduced under field conditions especially when compared to the conditions operating in standard laboratory 'clean water' toxicity tests. Furthermore, all polyelectrolytes will have little or no tendency to bioaccumulate. Table 7.4 summarises the risks posed by different types of polyelectrolyte to aquatic life. Despite the high toxicities and comparatively large amounts of cationic polyelectrolytes used, the range of loss mechanisms operating in natural waters would be expected to virtually eliminate any risk to aquatic life. For this reason they are not considered a priority for EQS development.

The anionic and non-ionic polyacrylamides are also not a priority for EQS development by virtue of their relatively low toxicity to aquatic life and the smaller quantities used, especially non-ionic products, despite uncertainties about their persistence in surface water.

It is important to point out that the prioritisation scheme employed here was intended to assess the environmental risks posed by single substances. It is also applicable for groups of substances exhibiting similar toxicological properties or behaviour in the environment. We have seen that polyelectrolytes can exhibit a very wide range of toxicities, even within a product type. This necessitates the use of a 'worst case' estimate of toxicity which may not be representative of most other examples of that product type. Furthermore, data on hydrolysis or biodegradation has been extrapolated from a few reported examples to apply to all polyelectrolytes within a particular produce type. In the case of cationic polyelectrolytes, the dominating influence of sorption as a removal mechanism reduces this source of uncertainty. However, as noted above, a lack of data on environmental fate of anionic polyelectrolytes introduces a greater degree of uncertainty into the assessment of risk posed by examples of this product type.

The environmental risks posed by any residual acrylamide also remain uncertain. An investigation of environmental concentrations of acrylamide in surface waters in the vicinity of discharges where polyelectrolytes are employed would be useful. This information could then be compared with existing data on effect concentrations to ascertain whether a significant risk is likely or not. Based on predicted environmental concentrations of acrylamide and hydroxypropionitrile arising from the use of polyelectrolytes for wastewater treatment, STOWA (1995) concluded that a small risk to aquatic life may indeed occur under certain operating conditions. This warrants further attention.

Table 7.4 Prioritisation of polyelectrolytes

Product type	Usage	Toxicity	Bioaccumulation	Persistence	Priority
1. Polyacrylamides					
1.1 Anionic	M	M	L	M	not a priority
1.2 Non-ionic	L	M	L	M	not a priority
1.3 Cationic	M	H	L	L	not a priority
2. Other cationic products					
2.1 Polyamines	L	H	L	L	not a priority
2.2 Poly(DADMAC)s	L	H	L	L	not a priority

8. CONCLUSIONS

1. Polyelectrolytes are widely used in the UK, and although no data are available on the amounts used, there are data for the amounts supplied for different applications. In the UK, 7501 metric tonnes of polyelectrolytes were supplied in 1992/93. Of these, the largest group are the cationic polymers which account for 5693 tonnes supplied to the UK in this period. Similar quantities are used for the treatment of sewage and sewage sludges and for the treatment of industrial wastes, with potable water treatment a relatively minor application. By comparison, smaller quantities of non-ionic and anionic polyelectrolytes are used and these mainly in the treatment of water intended for potable supply.

2. Several analytical methods are available with limits of detection typically in the order of 1 mg l^{-1}. However, most are not specific and are prone to interference from other substances. The most useful methods are size exclusion chromatography and derivatisation of polyelectrolyte followed by spectrofluorometric detection.

3. Biodegradation and abiotic hydrolysis contribute to the removal of polyelectrolytes, especially in alkaline conditions. Temperature was found to be an important factor in controlling the biodegradation rate. In a natural waterbody, complete degradation of cationic polyelectrolytes will occur within a few weeks. There is little information available on the degradation of non-ionic and anionic polyelectrolytes.

4. Sorption of cationic polyelectrolytes to dissolved and suspended organic matter and clays represents an important mechanism for removal from the water column. Such binding is thought to be irreversible and bound residues appear not to pose a hazard to sediment dwelling organisms. There are no data on such losses in the field but laboratory studies reveal reductions in toxicity of 10-100 fold for cationic polyelectrolytes. Losses of anionic and non-ionic polyelectrolytes by this mechanism in surface waters are unlikely to be as significant.

5. Polyelectrolytes, especially those with molecular weights in excess of 1000, will not bioaccumulate.

6. Polyacrylamides contain residual acrylamide which may be released into surface waters. Acrylamide appears to be highly toxic to aquatic invertebrates in the field, in marked contrast to laboratory studies. This may reflect a sub-lethal mode of action of acrylamide which is not detected in acute laboratory studies. The environmental risk posed by acrylamide is unclear because of a lack of data on concentrations in surface waters. Such data would be helpful in determining whether residual acrylamide should be subject to further control.

7. The toxicity of polyelectrolytes to freshwater and saltwater organisms varies widely according to the chemical composition of the individual polymer and test conditions, with reported EC_{50}/LC_{50} values occurring between 0.04->1000 mg l^{-1}. Cationic polymers are more toxic to aquatic life than anionic and non-ionic polyelectrolytes. Even within product types a wide range of toxicities is reported. Within the cationic polymers, much of this variation in toxicity can be explained by differences in charge density, with toxicity increasing as cationic charge density increases.

8. The risks to aquatic life posed by the more hazardous cationic polyelectrolytes are considerably diminished by losses due to sorption and degradation. There is some uncertainty about the extent to which non-ionic and anionic polyelectrolytes will be lost in surface waters but their much lower toxicities and the smaller tonnages used mean they are probably of little environmental concern.

9. Using the prioritisation procedure recommended by Hedgecott (1993), none of the polyelectrolyte classes are judged to be a priority for EQS derivation.

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APPENDIX A

AQUATIC TOXICITY DATA FOR POLYELECTROLYTES AND ACRYLAMIDE

Table A1 The acute toxicity of cationic polyelectrolytes to selected aquatic organisms (mg l^{-1}) (Biesinger and Stokes 1986)

Polymer	Water flea[1] 48 hr LC50	Fathead minnows[2] 96 hr LC50	Midges[3] 48 hr LC50	Gammarids[4] 96 hr LC50
Polymer A	>100.00	>100.00		
Polymer B	0.77	>100.00	>100.00	31.6
Polymer C	>100.00	>100.00		
Polymer D	>100.00	7.4	>100.00	102.9
Polymer E	1.2	0.88	26.9	22.8
Polymer F	0.24	2.87	50.0	>100.00
Polymer G	0.32	1.00	<6.25	8.10
Polymer H	0.71	2.46	>100.00	>100.00
Polymer I	0.13	3.74	>100.00	>100.00
Polymer J	6.78	9.47		112.25
Polymer K	0.09	6.82		>100.00
Polymer L	1.84	5.7		33.4
Polymer M	12.59	2.18	>100.00	21.0
Polymer N	70.71	2.72		85.2
Polymer O	0.50	1.05		12.5

Notes:

[1] *Daphnia magna*
[2] *Pimephales promelas*
[3] *Paratanytarsus parthenogeneticus*
[4] *Gammarus pseudolimnaeus*

Data are not available on the individual results for the 10 anionic and 3 non-ionic polymers tested by these authors

Table A2 Chronic toxicity of three cationic polyelectrolytes to aquatic organisms (Biesinger *et al.* 1976)

Species	Polyelectrolyte	Test conditions	Exposure period	Effect[a]	Concentration (mg l^{-1})
Daphnia magna Waterflea	Superfloc 330	static	21 days	LC50	1.1
Daphnia magna Waterflea	Superfloc 330	static	21 days	NOEC reproduction	0.1
Daphnia magna Waterflea	Superfloc 330	static	21 days	Significant impairment of reproduction	0.2
Daphnia magna Waterflea	Calgon M-500	static	21 days	LC50	2.85
Daphnia magna Waterflea	Calgon M-500	static	21 days	NOEC reproduction	1.0
Daphnia magna Waterflea	Calgon M-500	static	21 days	Significant impairment of reproduction	2.0
Daphnia magna Waterflea	Magnifloc 570C	static	21 days	LC50	1.85
Daphnia magna Waterflea	Magnifloc 570C	static	21 days	NOEC reproduction	1.0
Daphnia magna Waterflea	Magnifloc 570C	static	21 days	Significant impairment of reproduction	2.0

Notes:

a. Effect:
LC50 = concentration causing mortality to 50% of the test organisms
NOEC = effect observed to have no effect on the test organisms

Table A3 Reduction in acute toxicities relative to standard laboratory water test results, of selected cationic polyelectrolytes to the waterflea (*Daphnia magna*) and to fathead minnows (*Pimephales promelas*) in the presence of suspended solids and dissolved organic compounds (Cary *et al.* 1987)

	Compound A		Compound B		Compound C		Compound D	
Substrate	Waterflea[1]	Fathead minnow[1]	Waterflea[1]	Fathead minnow[1]	Waterflea[1]	Fathead minnow[1]	Waterflea[1]	Fathead minnow[1]
Bentonite[2]	96 x	46 x	>101 x	36 x	75 x	26 x	36 x	14 x
Illite[2]	4.8 x	6.9 x	44 x	1.6 x	6.9 x	3.8 x	6.0 x	1.2 x
Kaolin[2]	4.3 x	2.6 x	2.9 x	1.5 x	11 x	2.6 x	5.5 x	0.87 x
Silica[2]	1.2 x	2.2 x	4.5 x	1.6 x	1.5 x	1.7 x	0.70 x	0.85 x
Tannic acid[3]	83 x	29 x	>101 x	36 x	100 x	26 x	59 x	14 x
Lignin[3]	137 x	24 x	>101 x	19 x	50 x	14 x	>77 x	8 x
Humic acid[3]	50 x	40 x	94 x	36 x	63 x	16 x	37 x	14 x
Lignosite[3]	28 x	18 x	>101 x	21 x	59 x	15 x	39 x	8 x
Fulvic acid[3]	70 x	14 x	52 x	19 x	48 x	15 x	11 x	9 x

Notes:

Compounds A-D are described in the notes of Table A4

1 Results = 48 hr LC50 for the waterflea, 96 hr LC50 for fathead minnows.
2 Test conducted with 50 mg l^{-1}
3 Test conducted with 10 mg l^{-1}

Table A4 **Humic acid modification of the toxicity of cationic polymers to Rainbow trout fingerlings (Goodrich *et al.* 1991)**

Treatment	LC50 (mg l^{-1})			
	24 hr	48 hr	72 hr	96 hr
A-1	1.39	0.76	0.65	0.59
A-1 + 0.05 mg HA l^{-1}	1.29	0.85	0.53	0.35
A-1 + 0.5 mg HA l^{-1}	ND	1.55	1.29	1.29
A-1 + 5.0 mg HA l^{-1}	14.63	11.09	9.65	9.65
A-1 +50.0 mg HA l^{-1}	44.35	44.35	44.35	44.35
A-2	0.77	0.36	0.28	0.27
A-2 + 0.05 mg HA l^{-1}	0.43	0.35	0.35	0.35
A-2 + 0.5 mg HA l^{-1}	0.69	0.46	0.35	0.35
A-2 + 5.0 mg HA l^{-1}	4.50	2.79	2.77	2.77
A-2 +50.0 mg HA l^{-1}	44.35	23.77	22.18	22.18
A-3	1.06	0.89	0.82	0.78
A-3 + 0.05 mg HA l^{-1}	0.74	0.65	0.60	0.56
A-3 + 0.5 mg HA l^{-1}	1.39	0.98	0.69	0.69
A-3 + 5.0 mg HA l^{-1}	5.54	5.54	5.54	5.54
A-3 +50.0 mg HA l^{-1}	44.35	25.47	25.47	25.47
B-2	0.71	0.68	0.66	0.66
B-2 + 0.5 mg HA l^{-1}	1.22	1.22	1.22	1.22
B-2 + 5.0 mg HA l^{-1}	9.73	9.73	9.73	9.37
B-2 +50.0 mg HA l^{-1}	38.92	38.92	38.92	38.92

Notes:

ND = not determined
HA = humic acid

Descriptions of polymers:

A-1	Epichlorohydrin-dimethylamine mol.wt = 10 000 daltons
A-2	Epichlorohydrin-dimethylamine mol.wt = 50 000 daltons
A-3	Epichlorohydrin-dimethylamine mol.wt = 200 000-250 000 daltons
B-2	Acrylamide-2-(N,N,N)-trimethyl ammonium ethylacrylate chloride 39% charge density

Table A5 Results of CE4 toxicity test conducted with varying concentrations of humic acid in the dilution water (Hall and Mirenda 1991)

	LC50 (95% confidence interval, mg l^{-1})	
Humic acid in dilution water mg l^{-1} [a]	*D. magna*	*P. promelas*
0	0.1 (0.037-0.37) 0.26 (0-1.85)	0.81 (0.37-1.11)
2	0.45 (0.19-1.11)	1.10 (0.74-1.85)
10	1.18 (0.19-1.85)	6.00 (4.44-8.88)[b]
20	4.14 (1.11-5.55)[c]	12.50 (9.25-18.5)[b]
40	7.20 (3.70-29.6)[d]	48.55 (44.4-59.2)[b]
60	13.38 (11.1-22.2)[d]	64.01 (59.2-74.0)[b]

Notes:

a Humic acid source resulted in TOC concentrations = 16% of the nominal humic acid concentration
b Denotes *P. promelas* LC50 value that is significantly different from the LC50 tests without humic acid
c Denotes *D. pulex* LC50 value that is significantly different from the lowest LC50 tests without humic acid
d Denotes *D. pulex* LC50 value that is significantly different from the highest *D. pulex* LC50 in tests without humic acid.

Table A6 The effects of different test waters and ageing of test solutions on the acute toxicity of a cationic polyacrylamide (Floerger FO 4550) to zebrafish (*Brachydanio rerio*)

Exposure conditions			
Test water	Ageing period of test solutions	End point	Concentration (mg l^{-1})
Groundwater	0 h	96 h LC_{50}	0.87
Groundwater	6 h	24 h LC_{50}	8.7
Groundwater	12 h	24 h LC_{50}	42.3
River water	0 h	96 h LC_{50}	4.37
Groundwater + 5 ppm humic acid	6 h	24 h LC_{50}	78.0
Groundwater + 5 ppm humic acid	12 h	24 h LC_{50}	187.0

Table A7 Comparison of acute static nonrenewal toxicity and acute flow-through toxicity of polyelectrolytes to rainbow trout *O. mykiss* (Goodrich *et al.* 1991)

	LC50 (mg l^{-1}) for various exposure periods			
	24 hr	48 hr	72 hr	96 hr
Polymer A-1				
Static	1.39	0.76	0.65	0.59
Flow-through	ND	0.054	0.054	0.043
Ratio	-	14.0	11.9	13.9
Polymer A-2				
Static	0.77	0.36	0.28	0.27
Flow-through	0.36	0.28	0.13	0.10
Ratio	2.1	1.3	2.2	2.8
Polymer A-3				
Static	1.06	0.89	0.82	0.78
Flow-through	0.35	0.32	0.25	0.16
Ratio	3.0	2.7	3.2	5.0
Polymer B-2				
Static	0.71	0.68	0.66	0.66
Flow-through	ND	0.41	0.38	0.38
Ratio	-	1.7	1.7	1.7

Notes:

See Table A6 for descriptions of the polymers
ND = not determined

Table A8 **Differences in the toxicity of different charge types of polyelectrolytes to the waterflea (*Daphnia pulex*) and the fathead minnow (*Pimephales promelas*) (Hall and Mirenda 1991)**

		Acute toxicity (mg l^{-1})[1]	
Polymer	Molecular weight	*Daphnia pulex*	*Pimephales promelas*
Cationic emulsion	3-8 x 10^6	0.06-0.98	0.4 - 13.49
Anionic emulsion	9-18 x 10^6	0.06-0.66	20.97 - 85.11
Non-ionic emulsion	8 x 10^6	0.08-0.15	63.63

Notes:

1. Acute toxicity:
   48 hours for *Daphnia pulex*
   96 hours for *Pimephales promelas*

Table A9 Acute toxicity of acrylamide to aquatic organisms

Species	Exposure period	Effect[a]	Concentration (mg l^{-1})	Reference
CRUSTACEANS				
Daphnia magna Waterflea	48 hours	LC50	160	1
Daphnia magna Waterflea	48 hours	EC50 (immobilisation)	98	1
Daphnia magna Waterflea	48 hours	EC50 (immobilisation)	100 - 130	2
Daphnia magna Waterflea	48 hours	NOEC	60	1
Paratanytarsus partenogenetica midge larvae	48 hours	LC50	410	1
Paratanytarsus partenogenetica midge larvae	48 hours	EC50 (immobilisation)	230	1
Paratanytarsus partenogenetica midge larvae	48 hours	NOEC	60	1

Table A9 continued

Species	Exposure period	Effect[a]	Concentration (mg l^{-1})	Reference
FISH				
Oncorhynchus mykiss rainbow trout	96 hours	LC50	110	1
Oncorhynchus mykiss rainbow trout	96 hours	EC50 (loss of equilibrium)	88	1
Oncorhynchus mykiss rainbow trout	96 hours	NOEC	37	1
Pimephales promelas fathead minnow	96 hours	LC50	120	1
Pimephales promelas fathead minnow	96 hours	EC50 (loss of equilibrium)	86	1
Pimephales promelas fathead minnow	96 hours	NOEC	41	1
Lepomis macrochirus bluegill sunfish	96 hours	LC50	100	1

Table A9 continued

Species	Exposure period	Effect[a]	Concentration ($mg\ l^{-1}$)	Reference
Lepomis macrochirus bluegill sunfish	96 hours	EC50 (loss of equilibrium)	85	1
Lepomis macrochirus bluegill sunfish	96 hours	NOEC	35	1
Brachydanio rerio Zebrafish	24 hours	LC50	283	2

Notes:

a = Effects:
LC50 = concentration causing 50% mortality of test organisms
EC50 = concentration causing a specific effect on 50% of the test organism
NOEC = Concentration having no effect on the test organisms

References:

1. Krautter *et al.* (1986)
2. Raveyts *et al.* (1985)