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An investigation into the
nvironmental impact of polyelectrolytes
in waste water treatment plants

95—17

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PREFACE

In The Netherlands polyelectrolytes are used in various stages of the clarification process. In particular in the dewatering of activated sludge, polyectrolytes are increasingly being used to achieve higher dry solids contents. To a lesser extent, polyelectrolytes are being used in the pre-settlement and post-settlement of waste water treatment plants in order to improve the primary clarification and to prevent washing out of the sludge.

The polyelectrolytes, their monomers and by-products end up in the sludge, in the clarified water and in the surface water. In foreign countries it has been suggested several times that investigations into the possible adverse environmental effects of the polyelectrolytes and their by-products should receive attention.

The present report describes the investigation into the environmental impact of using polyelectrolytes under Dutch circumstances in waste water treatment plants. Risk assessments, based on use, properties and toxicity of polyelectrolytes and their fate in the surface water, resulting in "predicted environmental concentration (PEC)" and "no effect concentration (NEC)", do not indicate a risk. Under certain, however avoidable, circumstances ("worst case") a moderate risk may be derived for the by-products.

The investigation was assigned by the STOWA management to BKH Consultancy in Delft (members of the project team: Drs. J. Blok, Ms. Drs. C.P. Groshart,
Ms. Ir. A.L.M. Rutten and Ms. Ir. E.G. Wypkema). From STOWA the project was counselled by Ir. A.W.A. de Man, Ing. R. Kampf, Ing. G.B.J. Rijs and
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Utrecht, October 1995

Managing Director STOWA
Drs. J.F. Noorthoorn van der Kruijff

SUMMARY

A preliminary investigation has been carried out into the environmental impact of polyelectrolytes (p.e.) which are used in waste water treatment plants. To this end studies have been made of the use, properties and toxicity of p.e. and two by-products of p.e. and risk assessments have been carried out for aquatic organisms Furthermore, the occupational health aspects connected to the application of p.e. in waste water treatment plants have been elucidated.

The use and properties of p.e.

Water quality managers use p.e. mainly for sludge dewatering and to a lesser extent in sludge thickening, pre-settlement and post-settlement. In all, approximately 1400 tonnes of active p.e. are being used, 400 tonnes of which in liquid products and 1,000 tonnes in solid products. Polyelectrolytes contain by-products, among which acrylamide, mineral oils and hydroxypropionitrile.

Polyelectrolytes can be subdivided into cationic, nonionic and anionic types, based on the charge of their groups.

The mechanism of p.e. is based on de presence of these charged groups. Particularly cationic p.e. adsorb strongly to sludge.

At the moment only cationic p.e. are used in waste water treatment. In future also application of p.e. in pre-settlement is to be expected.

The toxicity of polyelectrolytes

The toxicity of (cationic) p.e. to aquatic organisms differs for each group of organisms. On fish the effect is more mechanical than chemical. There are indications that the adsorption of positively charged polyelectrolytes to the charged gill surface influence the oxygen exchange and disturb the ionic equilibrium. The effects on crustaceans are caused by the formation of aggregated p.e. which influences the mobility.

Risk assessment

An accepted method for a risk assessment is to compare concentrations of substances in an environmental compartment (PEC) with precisely those concentrations at which no effects on organisms are expected (NEC).

A first risk assessment is usually based on a "worst case" situation and a large number of assumptions. If, on this basis, risks are expected, this may be a reason to initiate further investigations in order to replace the assumptions by substantiated estimations.

Based on data on the quantities of polyelectrolytes used, the properties and information from manufacturers -using the SIMPLETREAT method- the concentrations of p.e. entering the surface water have been calculated (PEC). In this calculation the usual dosages in the pre-settlement, the sludge line and the post-settlement have been considered.

Furthermore, for the calculation assumptions have been made for adsorption, hydrolysis, biodegradability, the bonding of p.e. to humic acids and the dilution factor of the receiving surface water. Based on dilution factors in the receiving water of 5 and 32, respectively, and a concentration decrease caused by a reaction between p.e. and humic acid with a factor of 15, the p.e. concentrations in the surface water are calculated. The concentrations (PEC) calculated for systems with a high or a low sludge loading rate are presented in Table a.

Subsequently, a concentration has been derived, based on the toxicity data of the polyelectrolytes, at which after exposure no effects are expected on aquatic organisms (NEC). This derivation is based on the most toxic polyelectrolyte within the group of p.e. used by the water quality managers. The derived NEC is based on a limited data set and amounts to 1.2 µg/l (Table a).

Comparison of the calculated concentrations in the surface water (PEC) with the derived NEC shows that the PEC/NEC ratio is lower than 1 in all cases (Table a). A continuous use of p.e. in small waste water treatment plants discharging into small waters may cause a PEC/NEC of >0.1. This can be interpreted as a slight ecotoxicological risk. It is recommended to prevent an overdosage of p.e. in pre- and post-settlement.

Table a. PEC, NEC and PEC/NEC ratio for p.e.

addition point	PEC (µg/l)	NEC (µg/l)	PEC/NEC (-)
pre-settlement	0.04-0.48	1.2	0.03-0.4
sludge line	0.01-0.13	1.2	0.01-0.11
post-settlement	0.05	1.2	0.09-0.56

Both on the calculation of the PEC and on the derivation of the NEC several comments can be made. The assumptions and starting points used as well as the data on polyelectrolytes supplied by the manufactures may lead to an underestimation or an overestimation of the risk. Measurement data on concentrations in the receiving surface can enhance the accuracy of the risk estimation.

A risk assessment for two by-products of p.e. shows that these by-products, when added in the post-settlement and when discharged into small waters, form a risk to aquatic organisms (PEC/NEC = 1.86). It should be noted that the calculations are based on a "worst case" scenario and estimations of the content of by-products in p.e. are supplied by the manufacturers of p.e.

Occupational health aspects of the application

The risk of the application of polyelectrolytes depends on the form of the used p.e. (liquid, granulates, powder, pellet) and the dosing system. Exposure to liquid p.e. may irritate the skin and the eyes, but it rarely occurs.
Exposure to powdery p.e. occurs regularly during opening and changing packaging material and during eliminating malfunctions of the dosing installation. This does not cause irritation as a result of a chemical reaction, however a (mechanical) irritation of the respiratory organs by dust may occur. When using granulates or pellets the exposure is low. The by-product acrylamide and possibly also some of the other by-products may form a risk when p.e. are applied, since these products are possibly carcinogenic to man. The exposure risks can be limited by using closed dosing systems and by using liquid p.e., granulate or pellets. The use of gloves, safety glasses en (dust)masks during opening and changing packaging material and during eliminating malfunctions has to be made compulsory.

1 INTRODUCTION

In The Netherlands polyelectrolytes (p.e.) are widely used in the preparation of drinking water and in the treatment of industrial and communal wastewater. In waste water treatment plants p.e. are mainly used to improve the sludge dewatering process and to increase the dry solids content.
To a lesser extent p.e. are used in the pre- and post-settlement of waste water treatment plants to prevent washing out of the sludge or to improve pre-settlement.

The p.e., used in the purification process, can improve the separation of sludge and water. Generally this takes place by bonding of the (positively) charged groups of the p.e. to the (often negative) charge of the sludge, resulting in coagulation of the sludge particles.

P.e. end up in the activated sludge and the purified water. Polyelectrolytes end up mainly in the sludge because of adsorption. The activated sludge (surplus sludge) is dumped after drying, composting or incinerating. The use of sludge on agricultural land is decreasing. The amount of p.e. which ends up in the water phase is unknown.

In Germany and the United States the environmental impact of p.e. is questioned and it is believed that investigation into the possible adverse environmental effects of p.e. and their by-products should receive attention.

The scope of the present investigation is to examine the environmental impact of p.e. in the Netherlands. The investigation does not cover the use of p.e. for other purposes than the treatment of communal wastewater, such as the treatment of industrial wastewater and the preparation of drinking water. Furthermore, the investigation is limited to the environmental impact of p.e. on the water phase.
The following aspects have been considered:

- the use in waste water treatment plants;
- composition;
- the physical and chemical behaviour in water and the distribution over water en sludge;
- (bio)degradation and bioaccumulation;
- measurements in the effluent and/or the environment;
- effects on aquatic organisms;
- occupational health-aspects of the application;
- legislation.

The environmental impact of p.e. is judged on the basis of use, behaviour in the waste water treatment plant, concentration in the surface water, and toxicity.

In Chapter 2 of this report the procedure of the investigation is presented. A description is given of the way data on the use of p.e. were collected and of the way the environmental impact was estimated.

In Chapter 3 the collected background information on p.e. is presented. Furthermore, in this chapter a description is given of the risk assessment on which the estimation of the environmental impact is based. Chapters 4 and 5 contain the discussion and the conclusions, respectively.
Finally, in Chapter 6 the references are given.

2 PROCEDURE

2.1 General

In order to determine the environmental impact of p.e. which end up in the water phase of a waste water treatment plant and, consequently, the surface water, background information has been collected about:

- the use in waste water treatment plants;
- the composition;
- the physical and chemical behaviour in water and the distribution over water en sludge;
- (bio)degradation and bioaccumulation;
- measurements in the effluent and/or the environment;
- effects on aquatic organisms;
- occupational health-aspects of the application;
- legislation.

A number of polyelectrolytes, which are used by water quality managers, has been selected for further investigation. The collected background information has been used to perform a risk assessment, for aquatic organisms, of the selected polyelectrolytes. Based on the results of this risk assessment an opinion has been given on the environmental impact of p.e.

2.2 Background information

The use of p.e. in waste water treatment plants

An overview of the total use of p.e. in waste water treatment plants has been obtained by inquiring about both the present and the predicted use of p.e. Through a survey of ten of the larger quality managers, information has been obtained about use, places of application, applied quantities and occupational health-aspects during use.

Remaining information

The remaining information has been collected by means of:

- on-line searches in the databases ORBIT-NTIS, ORBIT-Aqualine and AQUATOX (BKH, 1992);
- referring to handbooks;
- a questionnaire to seven suppliers of p.e. asking for information on the polyelectrolytes predominantly sold to water quality managers;
- referring to some foreign organizations:
    - the Water Services Association of England and Wales in Great Britain;
    - Bundesamt für Umwelt, Wald und Landschaft in Switzerland;
    - Landesamt für Wasser und Abfall Nordrhein-Westfalen in Germany;
    - Institut für Wasser, Boden und Lufthygiene des Bundesgesundheitsamt in Germany;
    - Agence de l'eau Rhin-Meuse in France;
    - Danish Environmental Protection Agency in Denmark.

2.3 A selection of polyelectrolytes

Based on data on the use of p.e. by water quality managers, thirteen polyelectrolytes have been selected for a risk assessment, viz.:

- a liquid and a solid cationic p.e. from each of the five largest suppliers of p.e., which the water quality managers use most, including the most toxic p.e. used by the water quality managers;
- a liquid and a solid anionic p.e., which are expected to be used in pre-settlement in the future.

More detailed information on the selected p.e. was requested from the five largest suppliers of p.e. This information is confidential and therefore data have been coded. The non-coded data in this report come from open literature.

2.4 Risk assessment

In the risk assessment the concentrations to which aquatic organisms are exposed (PEC: Predicted Environmental Concentration), have been compared with precisely those concentrations at which no effects occur (NEC: No Effect Concentration). If the PEC is higher than the NEC (PEC/NEC >1) effects may occur and a risk exists.
A PEC/NEC >0.1 indicates a slight ecotoxicological risk. The risk is negligible when PEC/NEC <0.1.
The risk assessment has been carried out for the selected p.e. and two by-products of p.e., viz. acrylamide and hydroxypropionitrile.

The risk assessment is based on the addition of p.e. in waste water treatment plants on the following points:

- pre-settlement;
- sludge line
    - sludge thickening
    - sludge dewatering;
- post-settlement.

Determination of the PEC

To determine the concentrations to which aquatic organisms are exposed - the PEC - use has been made of the method of the SIMPLETREAT model developed by RIVM which is also used for the Uniform System for the Evaluation of Substances (USES) within the scope of the legislation of substances (Struijs et al., 1991). However, in this model only concentrations in the influent can be entered. In this model the amounts and the residence time of the sludge cannot be varied and hydrolysis cannot be taken into account. Therefore, the influent and effluent concentrations of p.e. and their by-products have been manually calculated in accordance with Appendix I and formula **(1)**.
For the by-products it is assumed that polyelectrolytes contain 0.1% of acrylamide and 0.05% of hydroxypropionitrile.

The calculation of the PEC is based on:

- adsorption according to a measured adsorption isotherm (Appendix 3);
- no adsorption of the by-products to the sludge;
- no biodegradation of p.e. or by-products in the waste water treatment plant;
- hydrolysis of the ester bonds in p.e. (Appendix 3);
- an influent concentration of : 0.2 mg/l at addition into the sludge line (Appendix 1);
  : 1 mg/l at addition in the pre-settlement;
- a hydraulic residence time in the aeration reservoir between 10 and 32 hours for systems with a high and a low sludge loading rate, respectively;
- an amount of water per population equivalent of 150 l/day;
- an amount of primary sludge per population equivalent of 40 g/day;
- an amount of secondary sludge per population equivalent of 13 g/day.

The effluent concentration at addition in the pre-settlement and the sludge line has been calculated using:

$$C_e = C_i * (1-f_1) * (1-f_2) * (1-f_3) \qquad \textbf{(1)}$$

where:

C_e = effluent concentration
C_i = influent concentration
f_1 = adsorption to primary sludge
f_2 = adsorption to secondary sludge
f_3 = hydrolysis

For additions in the pre-settlement and the sludge line the $f1$-$f3$ values are given in Table I. The derivation for these values is given in Appendix 3.

Table 1 Adsorption to primary sludge (f_1), secondary sludge (f_2) and hydrolysis (f_3) for additions in the pre-settlement and the sludge line for a high and a low sludge loading rate

addition point	loading rate	adsorption f_1 (primary sludge)	adsorption f_2 (secondary sludge)	hydrolysis f_3
pre-settlement	low	0.75	0.60	0.83
pre-settlement	high	0.75	0.70	0.52
sludge line	low	0.83	0.50	0.83
sludge line	high	0.83	0.60	0.52

The effluent concentration at the addition of p.e. in the post-settlement has been determined using the adsorption isotherm in Appendix 3 at a dosage of 1 mg/g d.s. It has been assumed that hydrolysis in this step is negligible.

The concentration in the surface water at a distance of 1000 m from the effluent discharge has been calculated using:

- dilution of the effluent in river water, expressed in percentiles over the number of treated population equivalents:
  - * 5-percentile - a dilution factor of 5;
  - * 50-percentile - a dilution factor of 32 (De Greef and De Nijs, 1990, W&M, 1991)
- taking for granted a reaction between cationic polymer and humic acid in river water. An amount of 5 mg of humic acid/litre this way yields a decrease in the concentration with a factor 15.

The calculated concentration in the surface water is equal to the concentration to which aquatic organisms are exposed (PEC).

Determination of the NEC

In order to determine the precise concentration at which no effects occur, the NEC, use has been made of the toxicity data of the selected p.e., obtained from the five largest suppliers.

The NEC has been derived from $L(E)C_{50}$s of NOECs. $L(E)C_{50}$ is the concentration at which either 50% of the test animals dies after exposure (L = lethal), or 50% of the test animals shows an effect after exposure (E = Effect). The NOEC (No Observed Effect Concentration) is the concentration at which after exposure no effect occurs in test animals. When converting an effect in test animals into an effect on the eco system level, the species diversity is determining. If sufficient data are available for the various species, the varying sensitivity can be calculated statistically. The concentration in the eco system at which no effects occur (NEC) is derived from the Maximum Permissible Risk level (MPR). In The Netherlands the definition of the MPR for the aquatic ecosystem is the concentration at which 95% of the species in the aquatic ecosystem is protected.

The derivation of the MPR has been described by Slooff et al. (1992). The method depends on the number and type of toxicity data. When at least four chronic NOECs are available for algae, Daphnia and fish, the statistical method is used. If less data are available, an extrapolation factor is applied to the lowest value. In Table 2 the used extrapolation factors are given.

Table 2 Factors applied for the derivation of a NEC for aquatic organisms (Slooff et al., 1992, OECD, 1995)

available toxicity data	extrapolation factor
a lowest acute $L(E)C_{50}$ 2) or QSAR-estimation 1) of acute toxicity	1,000
b lowest acute $L(E)C_{50}$ 2) or QSAR-estimation 1) of at least algae, crustaceans and fish	100 3)
c lowest chronic NOEC 2) or QSAR-estimation 1) of at least algae, crustaceans and fish	10 3)

1) QSAR means Quantitative Structure Activity Relationship. The toxicity of a substance is calculated on the basis of the chemical structure.

2) Chronic toxicity: during the complete life cycle or an important part of it. In general, the tests periods are longer than 96 hours.
Acute toxicity: during a relatively short part of the life cycle. In general, the test periods are shorter than 96 hours.

3) The lowest value of b) and c) is chosen, if less than three chronic NOECs are available.

From the determined NECs the lowest concentration is chosen to be used in the risk assessment.

3 RESULTS

3.1 Background information

3.1.1 The use of p.e. in waste water treatment plants

In total, the Dutch water quality managers use approximately 1,400 tonnes of active p.e. annually (1993), 366 tonnes of which in a liquid state. The remaining p.e. used, approximately 1,000 tonnes annually, are solid substances (mainly pellets). For the treatment of domestic wastewater only cationic p.e. are presently used which are composed of polyacrylamides (see section 3.1.2). The ten main water quality managers use 55 different products purchased from 8 different suppliers. From 39 products less than 25 tonnes are bought annually and from 4 products more than 100 tonnes annually. In Table 3 the present use of p.e. by the water quality managers is given.

Polyelectrolytes are mainly used for sludge dewatering by means of centrifuges, belt press filters and compartment filter presses. To a lesser extent p.e. are used for sludge thickening, pre-settlement and post-settlement (Table 3). For post-settlement p.e. are only used when -during rain water supply- the sludge is washed out.
For half of the waste water treatment plants, where p.e. are used for post-settlement during rain water supply, the post-settlement capacity will be increased. Hence, in the future the use of p.e. during post-settlement will decrease.
In Table 3 also the predicted use of p.e. for the next five years is given.

Table 3 Present and predicted use of p.e. by the Dutch water quality managers

addition point	present use (tonnes of active p.e/year)	predicted use (tonnes of active p.e./year)
pre-settlement	9	300
sludge thickening	80	600
sludge dewatering	1300	2000
post-settlement	11	6

De predicted increase in the use of p.e. during pre-settlement, sludge thickening and sludge dewatering is the result of:

- the change to other dewatering techniques:
  * centrifuges instead of belt press filters
  * direct sludge thickening;
- the application of pre-settlement;
- the increasing production of sludge caused by:
  * increasing chemical dephosphatizing;
  * increasing amount of refuse.

In the future also anionic p.e. will be used in pre-settlement.

The applied average dosages of p.e. strongly vary per waste water treatment plant. The dosages depend on the point of addition, de composition of the sludge, the percentage of active p.e. in the product and the extent to which the product dissolves in water. The variation in the average dosage per addition point is given in Table 4.

Table 4 Variation in the average dosage per addition point

addition point	average dosage of active p.e. (g/kg dry solids)
Pre-settlement	1 (g/m^3)
Sludge thickening	
flotation-thickening	1.5-2.5
belt press filter- thickening	3.7-7.0
centrifuge-thickening	2.2
gravitation-thickening	0.5-2.2
Sludge dewatering	
belt press filter	2.7-7.0
centrifuge	1.3-23
compartment filter press	5.4
Post-settlement	0.9

The maximum dosages are mostly not exactly known to the water quality managers, however they are estimated to be 130% of the average dosages.

P.e. are added as a strongly diluted solution (0,1-1%) in the sludge feed line. Practice shows that for a correct addition the operator has to manually adjust the system once or more times a day. At this moment monitoring and control equipment is available which makes it possible to maintain the adjusted addition. A daily adjustment, however, remains necessary. In view of the costs of using p.e., an over-dosage should be prevented. Moreover, in view of high dumping costs, a maximum dewatering of the sludge by means of p.e. is aimed at. The costs of using p.e. and dumping sludge are weighed against each other.

The choice of p.e. by the water quality managers is determined by:

- the price;
- the obtained dry solids content;
- the supplier's service;
- the ease of use;
- the separation efficiency.

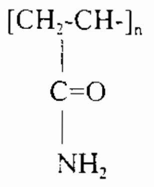
When selecting a p.e., and the various p.e. being more or less similar, the environmental and occupational health-aspects are taken into account.

In Switzerland, Denmark, England and France no investigations into the environmental impact of the use of p.e. are being conducted. In Germany p.e. have been classified by the Kommission für Wassergefährdender Stoffen and an investigation has been carried out with ^{14}C-labelled p.e.

3.1.2 The composition of polyelectrolytes

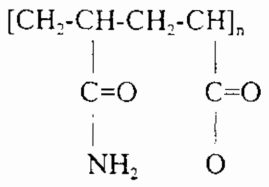
Polyelectrolytes consist of chains of monomers containing a charged group. This group characterizes the p.e. as being cationic, nonionic or anionic. At the moment the Dutch water quality managers use only cationic p.e., which are composed of polyacrylamides. Polyacrylamide as such does not contain charged groups (Fig. 1). In order to load a polyacrylamide positively of negatively, either a different substance is built in into the polymer (copolymerization) or a chemical group is bound to a side chain of the polyacrylamide.

In the future, anionic polyacrylamides will be used by the water quality managers as well for pre-settlement. In Fig. 2 the chemical structure of an anionic polyacrylamide is shown.



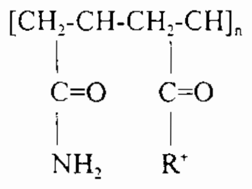
$[CH_2\text{-}CH(C{=}O)(NH_2)\text{-}]_n$

Figure 1 Polyacrylamide without a charged group



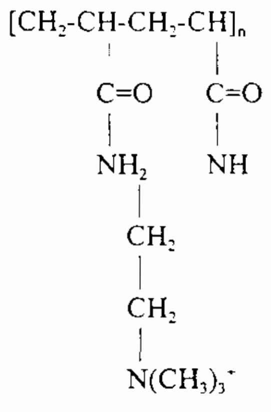
$[CH_2\text{-}CH(C{=}O)(NH_2)\text{-}CH_2\text{-}CH(C{=}O)(O)]_n$

Figure 2 Anionic polyacrylamide



$[CH_2\text{-}CH(C{=}O)(NH_2)\text{-}CH_2\text{-}CH(C{=}O)(R^+)]_n$

Figure 3 Cationic polyelectrolyte as a copolymer of acrylamide and an acrylic acid derivative

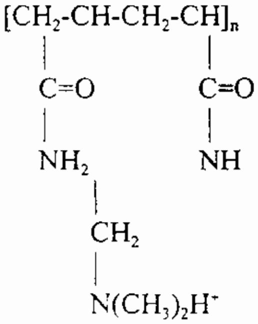


$[CH_2\text{-}CH(C{=}O)(NH_2)\text{-}CH_2\text{-}CH(C{=}O)(NH)]_n\text{-}CH_2\text{-}CH_2\text{-}N(CH_3)_3^+$

Figure 4 Cationic polyelectrolyte as a copolymer of acrylamide and a quaternized acrylic acid derivative

The water quality managers use two types of cationic polyacrylamides:

- a copolymer of acrylamide and an acrylic acid derivative (Fig. 3); prior to being build in, the acrylic acid can be quaternized (Fig. 4); the amount of acrylic acid in the polymer determines the size of the cationic charge.
- a cationic amino-methylated polyacrylamide which is being formed from the polyacrylamide with formaldehyde and dimethylamine using the Mannich-reaction and which is subsequently quaternized (Fig. 5).



$$\begin{array}{lll} \multicolumn{3}{l}{[CH_2\text{-}CH\text{-}CH_2\text{-}CH]_n} \\ | & & | \\ C=O & & C=O \\ | & & | \\ NH_2 & & NH \\ & | & \\ & CH_2 & \\ & | & \\ & N(CH_3)_2H^+ & \end{array}$$

Figure 5 Quaternized cationic amino-methylated polyacrylamide

The percentage of polymer in polyelectrolyte is usually not given by the suppliers. According to one supplier this percentage varies between 80 and 100% for the solid p.e. and between 30 and 50% for the liquid p.e.

The possible by-products of p.e. can be divided into: (remainders of) raw materials, additions and by-products which have been formed during the production process.

Raw materials

As raw material for both solid and liquid p.e. use is made of:

- acrylamide (with hydroxypropionitrile as contaminant);
- acrylic acid derivative;
- isobutyronitrile, bromate-sulphite or persulphate-nitrilotripropionamide (initiator) (Morris, 1991).

For quaternized polyacrylamides use is also made of:

- formaldehyde;
- dimethylamine;
- methylchloride;
- n-butyl-methacrylate, acrylonitrile and methyl-methacrylate (Goppers, 1976).

The concentration of these products in the end product strongly depends on the production process (Morris, 1991). According to the suppliers p.e. contain a maximum of 0.1% acrylamide. Mallevialle (1984) has measured concentrations of 0.03% acrylamide and 0.05% hydroxypropionitrile in an anionic polyacrylamide (solid material). Isobutyronitrile could not be detected (<30 mg/kg). In a liquid cationic quaternized polyacrylamide Goppers (1976) has detected three other substances, which have probably been used as raw materials. These substances are: n-butyl-methacrylate, acrylonitrile and methyl-methacrylate.

In the production of liquid p.e. polymerization takes place in an emulsion of water-in-oil. According to the suppliers the oil emulsion consists of mineral oil, paraffin-hydrocarbon or petroleum distillate. The amount of oil in a liquid p.e. depends on the extent to which the product has been dried and varies between 32 and 49%.
The waterphase is emulsified in the oilphase by emulsifiers, such as sorbitan mono-oleate (Thomas, 1991). No information on the emulsifiers present has been obtained from the suppliers. One supplier stated that liquid p.e. contains 2-3% of emulsifiers.

Additions

Additions differ per p.e. In order to minimize the polymer degradation, stabilizers are often added to solid p.e. (Morris, 1991). One supplier stated that to a solid polyelectrolyte 3-4% adipinic acid has been added. To liquid p.e. usually emulsion stabilizers are added (Morris, 1991). Another supplier has stated that to a liquid polyelectrolyte 0-4% stabilizer has been added.

By-products, formed during the production process

In order to keep the acrylamide concentration in the end product at a low level, sometimes substances are added which react with acrylamide into a saturated derivative which is assumed less toxic (Morris, 1991). Other data on by-products formed during the production process, have not been found.

3.1.3 Physical and chemical behaviour in water and the distribution over water and sludge

Cationic polyelectrolytes

The cationic p.e. used in the purification process, are capable of improving the sludge/water distribution. This takes place by an ionogeneous, irreversible bonding between the positively charged groups of p.e. and the negative charge of the sludge. This bridging effect of the p.e. results in flocculation. Polyelectrolytes can end up in the water phase if the negative charges on the sludge are occupied (too high a dosage), or if the mixing of p.e. and sludge is insufficient.
The following experiments describe the behaviour of cationic p.e.:

- in flocculation tests of active sludge with three different cationic polyacrylamides Gehr (1982) has not found p.e. in the waterphase at an addition level up to 1 g p.e./kg d.s. The maximum adsorption capacity of the active sludge varied in the tests between 2 and 10 g p.e./kg d.s. The adsorption pattern has been described by way of the Langmuir-comparison;
- in the sludge dewatering filtrate p.e. has been found at a dosage above 7.5 g/kg d.s. and a p.e. concentration of 10 mg/l using the Bentoniet-test. The test was carried out using a short conditioning time (mixing time). At an increasing conditioning time polyelectrolytes are usually no longer detectable in the filtrate. In practice (at a normal dosage) approximately 10-20 mg p.e./l is found in the leakage of pre-thickening area (STOWA, 1982);
- Schumann (1991) has found 98% adsorption to active sludge with a single addition of a cationic polyacrylamide. With the same dosage, however continuous, 81% adsorption is found. A continuous addition of cationic p.e. in the post-settlement causes in time an over-dosage. After terminating the addition, the sludge still contains poly-electrolytes for approximately 14 days. This proves that active sludge is slowly charged.

Anionic polyelectrolyte

The adsorption of anionic p.e. to both primary and active sludge is poor. Schumann (1991) has found 4% and 12% adsorption at continuous and single additions, respectively. The adsorption of anionic p.e. to cationic groups, which may be formed after precipitation of phosphate with iron, aluminum or calcium, is strong. Therefore, at simultaneous precipitation and pre-precipitation of phosphate, bonding could occur to anionic p.e.

Non-ionic p.e.

No information has been found on the behaviour of non-ionic p.e.

By-products

Acrylamide does not adsorb to primary or active sludge (Mallevialle, 1984).
The oil fraction in liquid p.e. adsorbs both to primary and active sludge. Experiments with a batch-wise addition of liquid p.e. to active sludge, carried out by one of the suppliers, showed an adsorption of the oil fraction to the sludge of more than 99.9%. Even after washing the sludge no oil has been detected in the eluate. This indicates that here an irreversible bonding may be possible as well. The filtrate turning white indicates that an overdosage may cause oil to end up in the filtrate.

No information on the behaviour in water and sludge has been found on the remaining by-products.

3.1.4 Measurements in the effluent and/or the environment

Information on p.e. concentrations in the effluent of waste water treatment plants or in the receiving surface water has not been found. For the analysis of p.e. in the effluent no analysis techniques are available at the moment.

The effluents of waste water treatment plants have been analyzed for the presence of acrylamide. In the effluent of waste water treatment plants without a clear external acrylamide source 0-0.017 mg/l acrylamide has been detected. In the effluent of waste water treatment plants with a clear acrylamide source (1 mg/l in the influent) an acrylamide concentration of 0.05-0.2 mg/l has been measured in the effluent (BUA, 1992).

3.1.5 (Bio)degradation and bioaccumulation

Polyelectrolytes

Polyelectrolytes, composed of polyacrylamides, generally are poorly biodegradable. The long polymer chains, however, can be degraded.

When the chains degrade, two steps can be distinguished:

1 degradation of the side chains;
2 degradation of the main chains.

ad 1

Polyelectrolytes composed of acrylamide and acrylic acid are converted within 24-48 hours into an anionic polymer by hydrolysis of the ester bond, separating choline. Choline is biodegradable, however, the anionic polyacrylamide is not (Schumann, 1991). According to the supplier the cationic p.e. based on polyacrylamide and polyacrylate-copolymer are very sensitive to hydrolysis. At a neutral pH and a temperature of 15°C the hydrolysis half-life time amounts to approx. two hours (SNF, 1995). A first-order hydrolysis is not reached until after 8 hours. Only p.e. with an ester bond are degraded fast by hydrolysis. According to Marroni (1995) 80% of the polyelectrolytes, used for sludge dewatering in waste water treatment plants, are of this type.

Side chains of p.e. composed of a copolymer of quaternary acrylate salts and acrylamide are not expected to degrade.

ad 2

The main chain of the polymer can be degraded by "shear forces" (strongly stirring and pumping), ozonising and biodegradation. When polyacrylamide is degraded, mainly oligomers are formed and no acrylamide (Gehr, 1990; Soponkanaporn, 1989).

The poor biodegradation of polyelectrolytes and the degradation of the polymer chains is proved by the following experiments:

- tests with ^{14}C labelled polyacrylamide during the cycle of an active sludge system showed a negligible degradation (max. 2%) to CO_2 (Schumann, 1991);
- in size exclusion chromatography tests of a polyacrylamide with quaternary ammonium bonds, the average molecular weight of solutions (1-100 mg/l) decreases in time. However, the total amount remains constant. This proves that p.e. are only degraded to oligomers. The eventual molecular weight of the solutions is between 1,000 and 10,000. The degradation is faster in solutions with low concentrations, at a higher temperature, at a basic pH and in active sludge (Sopokanaporn, 1989);
- ozonization does degrade the main chain, however, degradation to acrylamide and CO_2 does not take place. The ozonized product is not biodegradable and has a new active group (probably an aldehyde or ketone group), which combined with the amide group, yields a ring structure which cannot be specified (Suzuki, 1978);
- in biodegradation tests with solid polyacrylamides no or little degradation has been found (Suzuki, 1978, Lüttgen, 1979).

Data on bio-accumulation of p.e. have not been found.

By-products

For the biodegradation of acrylamide a bacterial population has to adapt. After this adaptation, which takes 1 to 2 days, acrylamide is completely biodegradable. In waste water treatment plants this adaptation does not or hardly takes place because of the presence of another bacterial culture. This often causes a degradation of less than 50% of acrylamide. In surface water the adaptation does take place en acrylamide is degraded into concentrations below the detection limit (BUA, 1992).

The oil fraction in liquid p.e. is readily biodegradable, which is proved by the BOD/COD-ratio of approx. 0.3 for liquid products. On the remaining by-products no data on biodegradation or bioaccumulation have been found.

3.1.6 Dilution in the surface water

The dilution factor of effluent on the surface water has been described statistically. This shows that a relatively small number of plants (10 percentile) discharges into the surface water with a low dilution factor (average 3), whereas 50 percentile of the plants discharges with an average dilution factor of 32. These statistics is based upon the numbers of plants. Exactly the small plants sometimes discharge into smaller surface waters, whereas the large plants discharge with a much higher dilution factor into the main rivers (W&M, 1991).

Den Oude (W&M, 1991) recalculated the statistics based on the number of population equivalents. This shows that a dilution factor of <5 applies for 5 percentile of the population equivalent and a dilution factor of <10 for 10 percentile.

3.1.7 Toxicity of p.e. to aquatic organisms

De toxicity of cationic, nonionic and anionic p.e. strongly differs per product and per test organism (see Appendix 2).

Cationic p.e.

De $L(E)C_{50}$ of cationic p.e. varies from 0.06-7,500 mg/l. In Table 5 the range of acute toxicity of cationic p.e. is given for fish, algae, bacteria, crustaceans and insects. Many of the data, mentioned in appendix 2, concern both selected and non-selected p.e., or products having an indistinct composition.

Table 5 $L(E)C_{50}$ of cationic p.e. for fish, algae, bacteria, crustaceans and insects

species/group	LC_{50} or EC_{50} (mg/l)
fish	0.06-1,000
algae	0.2-7,500
bacteria	0.9-7,500
crustaceans	<0.06-1,000
insects	<6.25->100

In most tests the LC_{50} or EC_{50} for fish and crustaceans is below 100 mg/l. It is not clear what causes the large differences in toxicity. Possibly the differences are caused by the difference in the products.

The Kommission für Wassergefährdender Stoffe in Germany has classified cationic p.e. in the WGK classes 2 and 3, for p.e. having a cationic charge of <15% and >15%, respectively (Hahn, 1993 a,b).

The classification in WGK class 2 is based upon the following properties:

- not biodegradable;
- no analysis in the environment possible;
- highly toxic to aquatic organisms;
- due to the bonding to sludge in the purification easily removable.

The classification in WGK class 3 is the result of the higher toxicity of cationic p.e. having a charge of >15%. The WGK-classification varies from 0-3, where 3 is the highest class. This WGK classes indicate that cationic p.e. form a moderate to high risk to the aquatic environment. However, this does not mean that a specific use is limited by the classification.

There are indications that the mechanism of cationic p.e. for fish is based on a mechanical rather than a chemical reaction (BASF, 1993). Adsorption occurs of the cationic p.e. to the anionic (negatively) charged gill surface of fish, which may influence the oxygen exchange en disturbs the ionic balance (Goodrich, 1991). According to a supplier cationic liquid polymers in diluted solutions are toxic to fish because of agglomeration on the mucous layer. The effects on aquatic organisms mainly depend on the ionic charge of the polymer (Hall and Mirenda, 1991). In fish hyperplasia in the branchia (gill) of the lamellar epithelium occurs after exposure to p.e.

Hyperplasia is a strong cell growth in the interlaminar spaces in the branchia (Hall and Mirenda, 1991).
Spraggs (1982) finds a significant change in behaviour in Salmo gairdneri (fish) after exposure to various polymers and monomers. On the basis of his investigation, Spraggs concludes that the polymers are more toxic than the monomers and the effluent of waste water treatment plants may be a risk to the ecosystem in the receiving water by the use of p.e.

The study by Hall and Mirenda (1991) shows that the toxicity of various cationic p.e. to crustaceans is not connected to the charge or molecular weight.
The effects on crustaceans are, according to Hall and Mirenda, mainly caused by the formation of aggregated p.e. in which the crustaceans get trapped. Consequently, no typical dosage-response ratio has been shown.

The bonding of cationic p.e. to humous particles

By way of field observations not many cases of poisoning of fish have been reported. This is probably caused by the bonding of cationic p.e. to negatively charged dissolved substances in the surface water, resulting in a decreasing availability of the charged p.e. for fish (Goodrich, 1991). Addition of negatively charged substances (humic acid, clay or dissolved organic substances) reduces the acute toxicity (LC_{50}) to fish and water fleas (Daphnia). Goodrich (1991) has shown that the active substance reacts in the presence of humic acid, resulting in a decrease in concentration of the active substance. At a humic content between 5 and 50 mg/l the average decrease in concentration varies for four different types of polymer between a factor 12 and 62. This decrease in concentration cannot be explained completely with the adsorption isotherm.
Humus occurs both in a dissolved form and in a suspended form in every surface water, at a concentration varying from 5 to 20 mg organic substance/litre. The macro molecules of humus and fulvinic acids contain a large number of negatively charged carboxyl groups, which strongly bond to the cationic groups of the p.e.

Nonionic p.e.

The LC_{50} of nonionic p.e. for crustaceans varies from 0.08 to 53 mg/l and for fish from 8 to 3,500 mg/l. It is not clear what causes the large differences in toxicity.
The Kommission für Wassergefährdender Stoffe in Germany has classified nonionic p.e. together with anionic p.e. in the WGK-class 2 (Hahn, 1993c). This means that nonionic p.e. form a moderate risk to the aquatic environment. However, this does not mean that by this classification a specific use of these substances for the preparation of potable water, the treatment of surface water and the treatment of waste water is restricted.

The classification in WGK-class 2 is based upon the following properties of nonionic p.e.:

- not biodegradable;
- highly toxic to fish and algae;
- no analysis possible in the environment.

No information has been found on the mechanism underlying the toxicity of nonionic p.e.

Anionic p.e.

The LC_{50} of anionic p.e. for crustaceans varies from 0.06 to >3,333 mg/l. The LC_{50} for fish varies from 18 to 811 mg/l. It is not clear what causes the large differences in toxicity. The Kommission für Wassergefährdender Stoffe in Germany has classified anionic p.e. together with nonionic p.e. in WGK-class 2 (Hahn, 1993c). Hence, anionic p.e. form a moderate risk to the aquatic environment.
No information has been found on the mechanism underlying the toxicty of anionic p.e.

Selected cationic and anionic p.e.

The toxicity values of the selected p.e., obtained from the suppliers, are given in Table 6. No data on toxicity has been obtained of the selected anionic products.

The $L(E)C_{50}$ of the selected cationic p.e. varies from 0.12 to 190 mg/l. The difference in toxicity is caused by, i.a. a difference in sensitivity of test organisms and a difference in test circumstances and test procedures. Table 7 shows the variation of the $L(E)C_{50}$ of selected liquid and solid cationic p.e. per group of organisms. The toxicity of liquid and solid p.e. to fish is in the same order of magnitude.

Table 6 Toxicity values of a liquid and a solid cationic p.e. from five different suppliers, and a solid and a liquid anionic p.e.

product[2]	type of p.e.	species	criterion	test period (h)	concentration (mg/l)
a2	liquid cationic	Crangon crangon (saltwater crustacean)	LC_{50}	96	190
d1	liquid cationic	no data			
b1	liquid cationic	Daphnia magna (crust.) Salmo gairdneri (fish) Lepomis macrochirus (fish) Salmo gairdneri (fish)	LC_{50} LC_{50} LC_{50} LC_{50}	48 96 96 96	0.28 0.3 0.7 42[1]
e2	liquid cationic	bacterium bacterium	EC_{50} EC_{10}	- -	1.8 36.6
b2	liquid cationic	Lepomis macrochirus (fish) Salmo sp. (fish) Daphnia sp. (crust.)	LC_{50} LC_{50} LC_{50}	96 96 48	2.5 0.94 0.12
c1	liquid cationic	Pimephalis promelas (fish) Brachydanio rerio (fish) Daphnia (crust.)	LC_{50} LC_{50} LC_{50}	- 48 48	44.3 6.88 2
a1	solid cationic	no data			
c2	solid cationic	Pimephalis promelas (fish) Pimephalis promelas (fish) Ceriodaphnia (crust.) Ceriodaphnia (crust.)	LC_{50} LC_{50} LC_{50} LC_{50}	48 96 24 48	2.01 1.75 0.5 0.45
e1	solid cationic	algae bacterium Daphnia sp. (crust.) Leuciscus idus melanotus (fish)	NOEC EC_{50} EC_{50} LC_{50}	- - - 96	<1 0.9 70 0.75
d2	solid cationic	no data			
b4	solid cationic	Oncorhynchus mykiss (fish) Lepomis macrochirus (fish) Oncorhynchus mykiss (fish) Pimephalis promelas (fish) Daphnia magna (crust.) Ceriodaphnia dubia (crust.)	LC_{50} LC_{50} LC_{50} LC_{50} EC_{50} EC_{50}	96 96 96 96 48 48	5.7[1] 4.8 0.47 5.2 24 11
a3	liquid anionic	no data			
b3	solid anionic	no data			

[1] humic acid added in test

[2] coded for each supplier

Table 7 $L(E)C_{50}$ of liquid and solid cationic p.e. for fish, algae and bacteria and crustaceans

species/group	LC_{50} or EC_{50} of liquid p.e. (mg/l)	LC_{50} or EC_{50} of solid p.e. (mg/l)
fish	0.3-44.3	0.47-5.2
algae and bacteria	1.8	0.9
crustaceans (fresh water)	0.12-2	0.45-70
crustaceans (salt water)	190	-

3.1.8 Toxicity of the by-products to aquatic organisms

The toxicity data of the by-products of p.e. are shown in Table 8.

Table 8 Toxicity of the by-products of p.e.

product	species	group	criterion	concentration (mg/l)	ref.
acrylamide	Photobacterium phosphoreum	bacterium	$EC_{50\ \mathrm{luminescence}}$	13.500	1
	Selenastrum capricornutum	algae	EC_{50} cell growth	72	1
	Daphnia magna	crust.	48 h LC_{50}	160	1
			48 h EC_{50}	98	1
	Mysidopsis bahia (salt water)	crust.	96 h LC_{50}	78	1
			28 d NOEC lethality	2.0	1
			28 d NOEC reproduction	4.4	1
	Paratanytarsus parthenogenetica	insect	48 h LC_{50}	410	1
	Various fish	fish	9 d LOEC feed behaviour	56	2
			96 h LC_{50}	124-160	1
			EC_{50} behaviour	85-88	1
	Heteropneustes fossilis	fish	48 h LC_{50}	87	1
	Rasbora heteromorpha	fish	96 h LC_{50}	130	1
	Salmo trutta	fish	48 h LC_{50}	400	1
	Carassius auratus	fish	24 h LC_{50}	460	1
	Salmo gairdneri	fish	14 d NOEC lethality	25	1
			14 EC liver damage	25	1
			LC_{50}	140	4
			EC_{50} dev.behaviour	8	4
hydroxypropionitrile	Lepomis macrochirus	fish	96 h LC_{50}	0.9	3
	Pimephalis promelas	fish	96 h LC_{50}	0.9	3
	Poecilia reticulata	fish	96 h LC_{50}	1.37	3
	Lagodon rhomboides	fish	24 h LC_{50}	0.215	3
polyacrylate	Leusiscus idus	fish	48 h NOEC	210	5
methylmethacrylate	Pimephalis promelas	fish	96 h LC_{50}	130	5
ethylacrylate	not defined	fish	72 h LC_{50}	5	5
	Artemia salina (salt water)	crust.	24 h LC_{50}	12	5
acrylate	Pseudomonas putida	bacterium	tox. threshold	41	3
	Microcystis aeruginosa	cyano bacterium	tox. threshold	0.15	3
	Scenedesmus quadricauda	green algae	tox. threshold	18	3

tox. thresh. = toxicity limit at which cell growth inhibition occurs (= EC5)

1) BUA, 1993

2) Criddle, 1990

3 Verschueren, 1983

4) Spraggs, 1982

5) BKH, 1992

The acute toxicity (LC_{50}) of the monomer acrylamide varies from 72 to 460 mg/l for algae, crustaceans, insects and fish. This makes acrylamide moderately to slightly toxic (>1 mg/l and >100 mg/l, respectively). Acrylamide is less toxic than p.e.
Acrylamide is slighly toxic to bacteria. The chronic toxicity (NOEC) of acrylamide is less by a factor of 10-30 than the acute toxicity and it varies from 2.0 to 25 mg/l with effects on lethality, reproduction and growth. A field study of insects in a small river shows that 0.05 mg/l of acrylamide results in a decrease in population growth en species diversity after 6 hours of exposure. After three weeks only the waterbeetle Hydropsyche instabilis could be detected. After four and eight weeks recolonization occurs of a few species with low densities (WHO/IPCS, 1985). The field study proves that very low concentrations of acrylamide can have effects.

The acute toxicity of hydroxypropionitrile varies from highly toxic (< 1 mg/l) to moderately toxic (0.2-1.4 mg/l).
The acute toxicity of acrylate varies from highly toxic to moderately toxic, as well.
Ethylacrylate is moderately toxic, whereas methylmethacrylate and polyacrylate are slightly toxic (>100 mg/l). This might indicate that the toxicity decreases with the chain length of the acrylates. The toxicity of hydroxypropionitrile and acrylates is at the same order of magnitude as the toxicity of polyelectrolytes.

No data have been found on the toxicity of other by-products of p.e. The toxicity of petroleum distillate and mineral oils is hard to determine because of the diversity in the composition of the various oil-like products.

3.1.9 Occupational health-aspects of the application

Polyelectrolytes

When regarding the occupational health aspects of the use of p.e., liquid and solid products should be distinguished. Solid products are powder, granules or pellets.

Most liquid polyelectrolytes are classified as substances which irritate skin and eyes. Contact with liquid p.e., however, is not very likely. Only malfunctions and during connection of p.e. to the dosing system, contact may be possible with the (concentrated) product. Wearing safety glasses and gloves has to be made compulsory during these activities.

Solid products do not irritate the skin, the eyes or the respiratory organs. Contact with solid products and particularly powdery products, is more likely than with liquid products. Especially during connection of packaging material containing the p.e. to the dosing system dust may be formed. When this dust is inhaled, the respiratory organs may get irritated. This irritation, however, is not chemical but mechanical. If water is present in the area of dust formation, p.e. may form a slippery substance and, hence, a risk of slipping.
When the so-called "big bags" were introduced, the number of possible contacts with solid p.e. were reduced considerably. By using granular products and pellets the formation of dust is reduced.

By-products

Besides the active material, various by-products occur. In a number of cases these by-products are more hazardous to man, than the active material itself. In Appendix 4 the effects of the various by-products are described in more detail.

The byproduct acrylamide is included in the Dutch list of carcinogenic substances and it is covered by the supplementary Registration Act for carcinogenic substances (see 4.5). For the supplementation to the Registration Act for substances which may damage the reproduction, it is advised to link this to the registration of for instance acrylamide, since mutagenous substances may affect the reproduction (SZW, 1995).

3.1.10 Legislation regarding polyelectrolytes

In order to determine the environmental risks of substances, information is needed on p.e. en their by-products. The present legislation may offer a possibility to oblige suppliers to give data.
Polyelectrolytes are covered by the legislation for polymers.

For polymers the Dutch legislation for substances is still under development. The OECD (Organisation for Economic Co-operation and Development) is working on definitions for polymers, viz. the formulation of parameters and criteria for the assessment of the environmental impact of polymers, and the development of methods to determine these parameters. In various countries polymer products are registered by producers under the terms of a legislation for substances. Each country has different registration procedures.

On an EC-level new chemical substances have to be registered with the government under the terms of Directive 79/831/EEC, before being internally marketed.
This legislation does not cover polyelectrolytes since these substances have been on the market for a long time and are not considered to be new substances.
From 1993 onwards environmental data have to be supplied of already existing chemicals (before 1981) under the terms of Directive 793/93/EEC.

From these existing substances, more than 100,000, initial attention is focused on the High Production Volume (HPV) substances. By means of the available data, lists are compiled of substances, which should have priority within the EC-policy, because of their risk for man and/or environment.
In 1994 a first priority list has been drafted, which does not include the relevant p.e. The next priority list is to be drafted at the end of 1995 based on data from the so-called HEDSET (the database containing the environmental data from the suppliers), for substances mentioned in Annex I of the Directive 793/93/EEC.
Polyelectrolytes are not included in the Annex, whereas acrylamide is. By order of the EC, a risk assessment will be carried out for substances in the priority list.

Within the scope of the Chemical Substances Act (CSA) in The Netherlands a list of substances for special attention and a list of priority substances have been drafted. Neither of these lists include polyelectrolytes. Under the terms of the Water Pollution Act actions can be taken if questions arise on the environmental impact of substances which may end up in the surface waters and in the sediment.

3.2 Risk assessment

In the following sections risk assessments are described for the selected cationic p.e., for acrylamide and hydropropionitrile. Because of insufficient data no risk assessments have been made for anionic p.e. and other by-products.

The risk assessment has been performed in accordance with the description in section 2.4.

3.2.1 Risk assessment for cationic p.e.

The calculation of the Predicted Environmental Concentration (PEC) for cationic p.e.

For the dosage in the primary clarifier and the sludge line the p.e. concentrations in the effluent have been calculated manually, in accordance with the method of the SIMPLETREAT model (Appendix 1).

For the dosage in the secondary clarifier the p.e. concentrations in the effluent has been read with the aid of the adsorption isotherm in Figs. 6 and 7 (Appendix 3). The calculated concentrations in the effluent are given in Table 9.
By applying dilution factors for 5 percentile and 50 percentile, these effluent concentrations result in concentrations in the surface water (PEC); these are given in Table 9 as well.
In practice p.e. are usually added in the sludge dewatering phase. At this point a concentration in the surface water is calculated of 0.01-0.13 µg/l.

Table 9 Calculated PEC for dosage in pre-settlement, sludge thickening, sludge dewatering and post-settlement

addition point	loading rate	dosage*** (g/kg d.s.)	concentration in the filtrate*** (mg/l)	concentration in the influent (mg/l)	concentration in the effluent (mg/l)	PEC* (µg/l)
pre-settlement	low	1 (mg/l)	-	1	0.017	0.04-0.23
pre-settlement	high	1 (mg/l)	-	1	0.036	0.08-0.48
sludge line**	low		20	0.2	0.003	0.01-0.04
sludge line**	high		20	0.2	0.01	0.02-0.13
post-settlement		1	-	4 to post-settlement	0.05	0.10-0.67

* range is the result of different dilution factors (see section 2.4)
** based on addition in sludge dewatering
*** see Appendix 1, calculation of the concentration

Derivation of the No Effect Concentration (NEC) for cationic p.e.

Data on the toxicity of the selected cationic p.e. which are used by the water quality managers, are included in Table 6. For the selected cationic p.e. less than four chronic NOEC values are available. Therefore, for the calculation of the NEC extrapolation factors, as described in Ch. 2, were used.

In order to derive the NEC the toxicity data of solid and liquid p.e. were combined and the lowest toxicity value was selected.
From the various selected cationic p.e. the LC_{50} for Daphnia sp. (0.12 mg/l) is the lowest. According to Table 2 an extrapolation factor of 1,000 ought to be used since an $L(E)C_{50}$ value for the algae group is absent.

For algae a NOEC of <1 mg/l has been found, however. Moreover, for bacteria an LC_{50} of 0.9 mg/l has been found. Based on these additional data it is justified to apply an extrapolation factor of 100, resulting in a NEC of 0.0012 mg/l.

PEC/NEC ratio for cationic p.e.

Comparison of the various PEC and NEC gives the PEC/NEC ratios, where the PEC is the calculated concentration in the surface water and the NEC is the concentration at which no effect on aquatic organisms is expected.
The calculated PEC/NEC ratios, for a dosage of p.e. at de four different points, are given in Table 10. All PEC/NEC ratios are smaller than 1. This means no risk to aquatic organisms.

Table 10 PEC/NEC ratios for additions of cationic p.e. at different points in the purification process

addition point	loading rate	PEC/NEC ratio
pre-settlement	low	0.03-0.19
pre-settlement	high	0.07-0.40
sludge line*	low	0.01-0.03
sludge line*	high	0.02-0.11
post-settlement	-	0.09-0.56

* based on addition in the sludge dewatering phase.

3.2.2 Risk assessment for two by-products

The calculation of the Predicted Environmental Concentration (PEC) for acrylamide and hydroxypropionitrile

The calculation of the concentrations acrylamide and hydroxypropionitrile in the influent is based on p.e. containing 0.1% acrylamide and 0.05% hydroxypropionitrile as a percentage of active p.e.

Assuming that acrylamide and hydroxypropionitrile do not degrade in waste water treatment plants and that no adsorption to sludge occurs, the concentration in the effluent is equal to that in the influent. De assumption that acrylamide does not degrade is a worst-case approach. The calculated concentration in the influent and effluent are given in Table 11.

The concentrations in the effluent, when the various dilution factors are applied, result in concentration in the surface water (PEC), given in Table 11.

Table 11 The calculated concentration of the by-products acrylamide and hydroxypropionitrile in the influent and effluent, and the calculated PEC

addition point	dosage p.e. (mg/g d.s.)	concentration in influent and effluent (µg/l)		PEC (µg/l)	
		acrylamide	hydroxypropionitrile	acrylamide	hydroxypropionitrile
pre-settlement	1 (mg/l)	1	0.5	0.03-0.2	0.016-0.1
sludge line	10	0.2	0.1	0.006-0.04	0.003-0.02
post-settlement	1*	4	2	0.125-0.8	0.063-0.4

• 4 mg/l in post-settlement.

Derivation of the No Effect Concentration (NEC) for acrylamide and hydroxypropionitrile

Data on the toxicity of acrylamide have been found for bacteria, algae, crustaceans and fish (Table 8). Chronic NOECs are available for crustaceans and fish. Acute L(E)C$_{50}$ are available for fish, crustaceans, algae and bacteria.
Derivation of the NEC is based on an extrapolation factor of 10 on the lowest NOEC, or an extrapolation factor of 100 on the lowest EC$_{50}$. The lowest NOEC found amounts to 2.0 mg/l and the lowest EC$_{50}$ found amounts to 72 mg/l. Extrapolation with a factor of 10 and 100 results in NEC-values of 0.2 and 0.7 mg/l, respectively. Of these, the lowest value of (0.2 mg/l) is chosen as NEC.

For hydroxypropionitrile only data on the acute toxicity have been found. For the derivation of the NEC an extrapolation factor of 1,000 is applied to the lowest LC$_{50}$ of 215 µg/l, resulting in a NEC of 0.215 µg/l.

PEC/NEC ratio for acrylamide and hydroxypropionitrile

The calculated PEC/NEC ratios are given in Table 12.
For additions in the pre-settlement, sludge line and post condensation, PEC/NEC ratios have been calculated for acrylamide which are much lower than 1. The acrylamide present in the p.e. does not form a potential risk to aquatic organisms.

For additions of p.e. in the pre-settlement and the sludge line, a PEC/NEC ratio has been calculated for hydroxypropionitrile which is lower than 1. This indicates that addition at this point does not form a risk to aquatic organisms.
When adding p.e. in the post-settlement, the PEC/NEC ratios are higher than 1, with a dilution factor of 5 for small installations which discharge into smaller waters (5 percentile). This means that addition on these points (only just) forms a risk to aquatic organisms. Simultaneous addition of p.e. at more points may be a risk to aquatic organisms.

It should be noted that degradation of hydroxypropionitrile and adsorption of hydroxypropionitrile to sludge have not been taken into account, and that the highest extrapolation factor had to be used.

Table 12 Calculated PEC/NEC ratio for the by-products acrylamide and hydroxypropionitrile

addition point	PEC/NEC acrylamide	PEC/NEC hydroxypropionitrile
pre-settlement	0.00015-0.001	0.46-0.074
sludge line	0.00003-0.0002	0.01-0.09
post-settlement	0.0006-0.004	0.29-1.86

4 DISCUSSION

4.1 Environmental impact

This preliminary investigation only covers the use of p.e. at waste water treatment plants. The use of p.e. in all other processes, such as drinking water production and treatment of industrial waste water has been left out. Moreover, this investigation was restricted to the spreading of p.e. by way of the water line.
P.e. and possibly also their by-products adsorb strongly to sludge. The by-product acrylamide does not adsorb to sludge. The treatment and use of sludge may cause a risk to other environmental compartments (air, ground water and soil).

The risk assessment was only carried out for cationic p.e. and two by-products of p.e. For the anionic p.e. and other by-products of p.e. data are absent. A risk assessment for these substances, however, should also be carried out.

The risk to aquatic organisms has been determined by comparing the (calculated) concentration of p.e. in the surface water (PEC) with a derived concentration which is "safe" to aquatic organisms (NEC). Both the calculation of the PEC and the derivation of the NEC were based on a "worst-case", to which comments can be made.

4.2 Comments to the calculation of the PEC

Approach according to a model

The concentration of p.e. in the surface water does not originate from measurements in surface water, but is derived according to a model from a number of data on p.e. dosages at waste water treatment plants and from data supplied by manufacturers of p.e. according to a model.

When calculating the concentration in the influent, percentages filtrate in the influent have been assumed of 1 and 5% in the sludge dewatering and the sludge thickening, respectively. In practice other filtrate percentages in the influent may occur on account of central sludge dewatering, variable sludge growth and a variable percentage of dry solids. This leads to an other PEC and with that an other PEC/NEC ratio, which will primarily deviate in upward direction.

Dosage of p.e.

When calculating the PEC influent concentrations have been assumed of 1 mg p.e./l in the pre-settlement, 0.04 mg p.e./l in the sludge thickening, 0.2 mg p.e./l in the sludge dewatering, and a dosage of 1 g p.e./kg d.s. in the post-settlement.
In practice other dosages can be used, which leads to an other PEC and with that to an other PEC/NEC ratio, which can deviate both in upward or downward direction.

- when underdosing in the sludge thickening, the adsorption percentage of p.e. to sludge is increased from 90% to 98% (Schumann, 1991). The underdosing may lead to a overestimation of the calculated PEC/NEC ratio.

- In the sludge dewatering an overdosage is often used because a high dry solids percentage of the sludge is desirable.

Overdosage causes a decrease in the adsorption percentage in the sludge dewatering from 95% to 90%, which leads to an underestimation of the calculated PEC/NEC ratio with a factor of 2 when dosing in the sludge dewatering. Overdosing should therefore be prevented.

Degradability

For the calculation of the PEC fast hydrolysis of cationic polyacrylamides with an esterbond has been assumed.
According to Schumann (1991) it is true that p.e. are hydrolysed to choline and an anionic polyacrylamide, but this anionic polyacrylamide is poorly degradable.
The toxicity is of this degradation product is not clear.
Non-ester types of p.e. do not hydrolyse.

Purity of p.e.

When calculating the PEC of acrylamide and hydroxypropionitrile contents in p.e. of 0.1% and 0.05%, respectively, have been assumed. In reality these contents possibly deviate in upward or downward direction, which has consequences for the PEC.

4.3 Comments to the derivation of the NEC

The derivation of the NEC is based on the extrapolation factors used in the Uniform System for the Evaluation of Substances (USES). In the USES three extrapolation factors are distinguished:

- a factor of 10 for the extrapolation of data for one species to the ecosystem;
- a factor of 10 for extrapolation of data on acute effects to chronic effects;
- a factor of 10 when little data are available.

The first factor is always used in the derivation of a NEC. The second factor is only used when data on acute effects are used. The third factor is used when data for one or more of the groups of fish, algae and crustaceans are absent. The extrapolation factor used for the derivation of the NEC may vary from 10 to 1,000 (10 * 10 * 10). The level of the extrapolation factors (10) has been chosen arbitrary, but it is used for the derivation of the NEC in many risk assessments. Also the choice for the use of (a maximum of) three extrapolation factors is arbitrary, but it is applied often.

Most of the toxicity data have been found in documents obtained from the suppliers of p.e. These documents do not include information on the circumstances under which toxicity tests have been carried out, and on test procedures used. The toxicity data possibly are too high or too low, which can result in, respectively, an underestimation or an overestimation of the NEC. However, when the toxicity data obtained from suppliers are compared with toxicity data from the literature no major differences are found.

The toxicity of the various p.e. varies strongly. The risk assessment is based on toxicity data of the selected polyelectrolyte which was the most toxic. Many p.e. are less toxic, which may cause the NEC to be too low.

For the total group of the cationic polyelectrolytes some chronic toxicity data are known for fish, daphnia and algae. This concerns polyamine derivatives which do not hydrolyse, so that application in pre-settlement or post-settlement may cause an effluent concentration between 20 and 100 µg/l. The lowest NOEC for this group is 0.1 mg/l. If the safety factor of 10 is applied hereon (according to table 2), then the NEC will be 10 µg/l.

4.4 Comments to the risk assessment of the by-products

The by-products occurring in p.e. have not been specified sufficiently to be able to carry out a complete risk assessment. The risk assessment for hydroxypropionitrile indicates that by-products can form a potential risk under certain circumstances. The oil fraction of the p.e. adsorbs mainly to sludge and is usually readily degradable. More detailed specification and monitoring of the by-products occurring in the product can only be done by way of certification. Because a legal framework is lacking for this, it is not to be expected that this will happen in the near future.

It is assumed that the by-products mentioned, acrylamide and hydroxypropionitrile, do not adsorb to sludge and do not degrade. This is a worst case approach. Paragraph 3.1.5, however, shows that acrylamide does degrade after adaptation of the sludge and in the surface water. For hydroxypropionitrile this is not known. This may implicate an over-estimation of the PEC/NEC.

4.5 Occupational health-aspects of the application

The risks of the application of p.e. in waste water treatment plants depend strongly on the form (solid or liquid) and on the dosing system. The risk also depends on the composition of the product. In particular the presence of by-products may cause risks.

In The Netherlands acrylamide is included on the list of carcinogenic substances. The exposure to this substance should be as low as possible, and should in any case not exceed the threshold limit value (in Dutch: MAC-waarde). For carcinogenic substances on the workfloor, in addition to the "ordinary" registration, a supplementary registration obligation applies. This supplementary registration is compulsory for a carcinogenic substance containing product, if the concentration of the carcinogenic substance is equal to or greater than 0.1% (weight percent) of the product. According to manufacturers of p.e. the concentration of acrylamide in p.e. is less than 0.1%.

5 CONCLUSIONS

The risk assessment shows that a continuous use of p.e. in the pre-settlement or post-settlement results for 5 percentile of the treated waste water discharged into a small surface water, in an estimated risk expressed in PEC/NEC, of 0.19-0.56. It should be noted that in these cases, where the surface water has a slow flow rate, after 1000 m hydrolysis will lead to a further decrease in the concentration in the surface water.

When used in the sludge line and at waste water treatment plants discharging into a larger surface water, the PEC/NEC ratio is clearly much lower than 1 and the risk is negligible.

The risk assessment based on data that have been supplied by manufacturers of p.e. shows that only in continuous use of p.e. in small waste water treatment plants discharging into smaller waters, there may be a PEC/NEC ratio > 0.1 as a result of the use of p.e. This could be interpreted as a minor ecotoxicologic risk. In these cases, the discharge of remaining BOD, ammonium and sludge (containing metals) will already cause a considerable effect on the aquatic ecosystem. Consequently, the effect of p.e. addition, resulting in a better effluent quality for BOD and suspended matter, will be positive rather than negative. In these cases caution should be taken in dosing polyelectrolytes in the pre-settlement and post-settlement.
It is not to be expected that somewhere in The Netherlands visible negative effects of p.e. on the ecosystem can be found.

A number of assumptions has been made in the method used for risk assessments in order to estimate both the p.e. concentration in the effluent and the toxicity.
Particularly measurement data on p.e. concentrations in the receiving surface water and data on the chronic toxicity of p.e. may contribute to a better risk assessment of p.e. for the aquatic organisms.

The presence of by-products in p.e. can only lead to a risk to aquatic organisms for dosages of p.e. in the post-settlement of small installations, which discharge on small waters (5 percentile). In the method used for the risk assessment a "worst case"situation has been assumed, which might lead to an overestimation of the risks. Mostly, the remaining by-products are not sufficiently specified to estimate their risks.

The risk to the user of p.e. depends on its form (solid or liquid) and on the dosing system. Particularly by-products in p.e. may cause risks to the user. Direct contact with p.e. should be avoided in order to reduce the risk.

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Appendices

Appendix 1

Calculation of the p.e. concentrations in the influent

Calculation of the p.e. concentrations in the influent

Pre-settlement

When adding p.e. in the pre-settlement all of the added amount ends up in the influent. Calculations are based on a dosage of 1 mg p.e./l in the influent. The concentration in the effluent is calculated manually based on the method of the SIMPLETREAT model.

Sludge line

When adding p.e. during sludge thickening and sludge dewatering only the p.e. present in the filtrate ends up in the influent. The p.e. concentration in the influent can be calculated based on the p.e. concentration in the filtrate and the contribution of the various filtrate flows in the influent. The filtrate of the sludge dewatering forms approximately 1% of the influent volume flow. The filtrate of the sludge thickening forms approximately 5% of the influent volume flow.

The concentration in the filtrate of the sludge thickening can be read from the adsorption isotherm in Figures 6 and 7 from Appendix 3.
Based on a p.e. concentration in the sludge of 5 g p.e./kg d.s. this amounts to 0.7 mg/l.

In practice in the leakage of sludge dewatering rest activity of 20 mg p.e./l is found (STOWA, 1982). Based on this, when dosing in the sludge dewatering, a concentration in the filtrate of 20 mg/l is assumed.

Thus, when dosing, the concentration of p.e. in the influent is in:

- the sludge thickening (0.7 mg/l * 5% =) 0.04 mg/l;
- the sludge dewatering (20 mg/l * 1% =) 0.2 mg/l.

For the calculation in the sludge line the "worst-case" situation is assumed by choosing 0.2 mg/l as starting-point.

The concentration in the effluent is calculated manually based on the method of the SIMPLETREAT model.

Post-settlement

Addition of p.e. in the post-settlement only takes place during rainwater supply (RWS). Therefore, it may be assumed that the supplied sludge contains no p.e. The average dosage applied is
1 g p.e./kg d.s. and the dry solids concentration in the supply amounts to 4 g d.s./l on average. Hence, the average dosage applied is 4 mg p.e./l. According to the adsorption isotherm of Appendix 3 the equilibrium concentration in the solution is 0.05 mg/l. Hydrolysis is negligible with that.

Appendix 2

Overview of the toxicity data for p.e.

Overview from literature of the toxicity of various polyelectrolytes

Type	Activity	Name of substance	Org.Group	Species	Time in h	Conc. in mg/	Crit	Effect/Remarks	Reference
ANIONIC P.E.									
anion.	-30%	AA AE5	Crustaceans	Daphnia pulex	48	0.06	LC50	-	Hall & Mirenda 1991
anion.	-8%	AA AE1	Crustaceans	Daphnia pulex	48	0.09	LC50	-	Hall & Mirenda 1991
anion.	-20%	AA AE2	Crustaceans	Daphnia pulex	48	0.11	LC50	-	Hall & Mirenda 1991
anion.	-30%	AA AE4	Crustaceans	Daphnia pulex	48	0.39	LC50	-	Hall & Mirenda 1991
anion.	-30%	AA AE6	Crustaceans	Daphnia pulex	48	0.41-0.62	LC50	-	Hall & Mirenda 1991
anion.	-30%	AA AE3	Crustaceans	Daphnia pulex	48	0.66	LC50	-	Hall & Mirenda 1991
anion.		Dow AP-30	Crustaceans	Daphnia magna	96	17	LC50	static test	Biesinger, 1976
anion.	40%	a1	Crustaceans	Paratya australiensis	96	180	LC50	-	Supplier a
anion.	50%	a1	Crustaceans	Crangon crangon	96	230	LC50	-	Supplier a
anion.	bead	a2	Crustaceans	Crangon crangon	96	280	LC50	-	Supplier a
anion.		Dow AP-30	Crustaceans	Daphnia magna	48	345	LC50	static test	Biesinger, 1976
anion.	40%	a3	Crustaceans	Crangon crangon	96	460	LC50	-	Supplier a
anion.	50%	a4	Crustaceans	Paratya australiensis	96	490	LC50	-	Supplier a
anion.	40%	a1	Crustaceans	Crangon sp.	96	720	LC50	-	Supplier a
anion.	50%	a5	Crustaceans	Crangon crangon	96	790	LC50	-	Supplier a
anion.	45%	a3	Crustaceans	Crangon crangon	96	>3333	LC50	-	Supplier a
anion.		d1	Plants	Barley	-	>50	NOEC	sprout/root yield	Supplier d
anion.	gel	a6	Fish	Salmo gairdneri	96	18	LC50	-	Supplier a
anion.	-30%	AA AE5	Fish	Pimephales promelas	96	20.97	LC50	-	Hall & Mirenda 1991
anion.	-30%	AA AE4	Fish	Pimephales promelas	96	28.42	LC50	-	Hall & Mirenda 1991
anion.	40%	a1	Fish	Armed bullhead	96	35	LC50	-	Supplier a
anion.	-30%	AA AE3	Fish	Pimephales promelas	96	36	LC50	-	Hall & Mirenda 1991
anion.	-8%	AA AE1	Fish	Pimephales promelas	96	37.23	LC50	-	Hall & Mirenda 1991
anion.	-20%	AA AE2	Fish	Pimephales promelas	96	40.43	LC50	-	Hall & Mirenda 1991
anion.	-30%	AA AE6	Fish	Pimephales promelas	96	55.11	LC50	-	Hall & Mirenda 1991
anion	bead	a7	Fish	Salmo gairdneri	96	115	LC50	-	Supplier a
anion	gel	a8	Fish	Salmo gairdneri	96	130	LC50	-	Supplier a
anion.	gel	a6	Fish	Salmo gairdneri	96	421	LC50	-	Supplier a
anion	gel	a8	Fish	Salmo gairdneri	96	740	LC50	-	Supplier a
anion	50%	a1	Fish	Salmo gairdneri	96	811	LC50	-	Supplier a

Overview from literature of the toxicity of various polyelectrolytes (continued)

Type	Activity	Name of substance	Org.Group	Species	Time in h	Conc. in mg/l	Crit.	Effect/Remarks	Reference
KATIONIC P.E.									
kation.		d2	Algae	-	-	<1	NOEC	(OECD 201)	
kation.		d3	Algae	-	-	>1	NOEC	(OECD 201)	
kation.		poly-dimethyl-diallyl-ammonium chloride	Algae	Selenastrum capricornutum		0.2	EC50	inhibition	Spraggs, 1982
kation.		acrylamide copolymer	Algae	Selenastrum capricornutum		2	EC50	inhibition	Spraggs, 1982
kation.		e1	Anaerobic sludge		72	22	NOEC	TOC,CSB,gasification	Supplier e
kation.		e2	Anaerobic sludge		3	22-44	LOEC	-	Supplier e
kation.		e2	Anaerobic sludge		6	22-44	LOEC	75% eff.TOC,gasification	Supplier e
kation.		e1	Anaerobic sludge		72	44	LOEC	20% eff.TOC,CSB,gasification	Supplier e
kation.		e1	Anaerobic sludge		48	44	LOEC	40% eff.TOC,CSB,gasification	Supplier e
kation.		e2	Anaerobic sludge		24	44	NOEC	TOC,CSB,gasification	Supplier e
kation.		e3	Anaerobic sludge		24-72	176	NOEC	TOC,CSB,gasification	Supplier e
kation.		d2	Bacteria	-	-	0.9	EC50	MKH 913 mg/l(DEV 18)	Supplier d
kation.		d4	Bacteria	-	-	0.9	EC50	MKH 913 mg/l(DEV 18)	Supplier d
kation.		d2	Bacteria	-	-	0.9	EC50	MKH >5000 mg/l(DEV 18)	Supplier d
kation.		d5	Bacteria	-	-	1.8	EC50	mhk=36.6 mg/l dev 18	Supplier d
kation.		d6	Bacteria	Pseudomonas putida	24	15	EC50	dev 18	Supplier d
kation.		d3	Bacteria	Protozoa	-	22	EC50	(Erlanger Ziliatentest)	Supplier d
kation.		d7	Bacteria	-	-	235	EC50	MHK-1875 mg/l dev 18)	Supplier d
kation.		acrylamide copolymer	Bacteria	Microtox		250	EC50	-	Spraggs, 1982
kation.		poly-dimethyl-diallyl-ammonium chloride	Bacteria	Microtox		7500	EC50	-	Spraggs, 1982
kation.	gel	a9	Crustacea	Daphnia magna	48	0.06	EC0	-	Supplier a
kation.		Superfloc 330	Crustacea	Daphnia magna	21 d	0.1	NOEC	reproduction	Biesinger, 1976
kation.		Superfloc 330	Crustacea	Daphnia magna	21 d	0.2	LOEC	reproduction	Biesinger, 1976
kation.		CAlgaeon M500	Crustacea	Daphnia magna	21 d	1	NOEC	reproduction	Biesinger, 1976
kation.		Magnifloc 570 C	Crustacea	Daphnia magna	21 d	1	NOEC	reproduction	Biesinger, 1976
kation.		CAlgaeon M500	Crustacea	Daphnia magna	21 d	2	LOEC	reproduction	Biesinger, 1976
kation.		Magnifloc 570 C	Crustacea	Daphnia magna	21 d	2	LOEC	reproduction	Biesinger, 1976
kation.		Superfloc 330	Crustacea	Mysis relicta	14 d	<0.06	LC50	flow through	Biesinger, 1976
kation.	45%	Metac CE3	Crustacea	Daphnia pulex	48	0.06	LC50	-	Hall & Mirenda 1991
kation.	6%	Aetac CE7	Crustacea	Daphnia pulex	48	0.06	LC50	-	Hall & Mirenda 1991
kation.	15.4% a	D poly(dimethyldiallylammonium) chloride	Crustacea	Daphnia magna	48	0.08	LC50	-	Cary et al 1987
kation.	45%	Metac CE4	Crustacea	Daphnia pulex	48	0.08-0.12	LC50	-	Hall & Mirenda 1991

Overview from literature of the toxicity of various polyelectrolytes (continued)

Type	Activity	Name of substance	Org.Group	Species	Time in h	Conc. in mg/l	Crit.	Effect/Remarks	Reference
KATIONIC P.E.									
kation.	-	Polymer K	Crustacea	Daphnia magna	48	0.09	LC50	-	Biesinger & Stokes 1986
kation.	75%	Metac CE5	Crustacea	Daphnia pulex	48	0.1	LC50	-	Hall & Mirenda 1991
kation.	-	Polymer I	Crustacea	Daphnia magna	48	0.13	LC50	-	Biesinger & Stokes 1986
kation.	10%	Aetac CE8	Crustacea	Daphnia pulex	48	0.15	LC50	-	Hall & Mirenda 1991
kation.	100%	EPI/DMA CS2	Crustacea	Daphnia pulex	48	0.16	LC50	-	Hall & Mirenda 1991
kation.	8.3% a	B poly(dimethylvinylpyridinium)chloride	Crustacea	Daphnia magna	48	0.17	LC50	-	Cary et al 1987
kation.	15.4% a	D poly(dimethyldiallylammonium)chloride	Crustacea	Daphnia magna	48	0.17	LC50	-	Cary et al 1987
kation.	2%	Aetac CE6	Crustacea	Daphnia pulex	48	0.17	LC50	-	Hall & Mirenda 1991
kation.		Superfloc 330	Crustacea	Daphnia magna	7 d	<0.19	LC50	flow through	Biesinger, 1976
kation.	25%	Metac CE2	Crustacea	Daphnia pulex	48	0.19	LC50	-	Hall & Mirenda 1991
kation.	45%	Aetac CE11	Crustacea	Daphnia pulex	48	0.19-1.1	LC50	-	Hall & Mirenda 1991
kation.	15.4% a	D poly(dimethyldiallylammonium)chloride	Crustacea	Daphnia magna	48	0.2	LC50	-	Cary et al 1987
kation.	25%	Aetac CE9	Crustacea	Daphnia pulex	48	0.2	LC50	-	Hall & Mirenda 1991
kation.	45.7% a	A quaternized polyalkanolamine	Crustacea	Daphnia magna	48	0.21	LC50	-	Cary et al 1987
kation.	35%	Aetac CE10	Crustacea	Daphnia pulex	48	0.21	LC50	-	Hall & Mirenda 1991
kation.	10%	Metac CE1	Crustacea	Daphnia pulex	48	0.22	LC50	-	Hall & Mirenda 1991
kation.	-	Polymer F	Crustacea	Daphnia magna	48	0.24	LC50	-	Biesinger & Stokes 1986
kation.	100%	EPI/DMA CS1	Crustacea	Daphnia pulex	48	0.26	LC50	-	Hall & Mirenda 1991
kation.	45%	Metac CE4	Crustacea	Daphnia pulex	48	0.26-0.04	LC50	-	Hall & Mirenda 1991
kation.		b1	Crustacea	Daphnia magna	48	0.28	LC50		Supplier b
kation.		Superfloc 330	Crustacea	Limnocalanus macrurus	96	0.29	LC50	static	Biesinger, 1976
kation.	-	Polymer G	Crustacea	Daphnia magna	48	0.32	LC50	-	Biesinger & Stokes 1986
kation.	45%	Aetac CE12	Crustacea	Daphnia pulex	48	0.32-0.63	LC50	-	Hall & Mirenda 1991
kation.		Superfloc 330	Crustacea	Daphnia magna	48	0.34	LC50	static	Biesinger, 1976
kation.		Superfloc 330	Crustacea	Mysis relicta	96	0.5	LC50	static	Biesinger, 1976
kation.	-	Polymer O	Crustacea	Daphnia magna	48	0.5	LC50	-	Biesinger & Stokes 1986
kation.	45%	Aetac CE14	Crustacea	Daphnia pulex	48	0.57	LC50	-	Hall & Mirenda 1991
kation.		CAlgacon M500	Crustacea	Daphnia magna	48	0.65	LC50	static	Biesinger, 1976
kation.	-	Polymer H	Crustacea	Daphnia magna	48	0.71	LC50	-	Biesinger & Stokes 1986
kation.	-	Polymer B	Crustacea	Daphnia magna	48	0.77	LC50	-	Biesinger & Stokes 1986
kation.	100%	DAD/MAC CS3	Crustacea	Daphnia pulex	48	0.77	LC50	-	Hall & Mirenda 1991
kation.	45%	Aetac CE13	Crustacea	Daphnia pulex	48	0.98	LC50	-	Hall & Mirenda 1991
kation.		Superfloc 330	Crustacea	Daphnia magna	21 d	1.1	LC50	static	Biesinger, 1976
kation.	-	Polymer E	Crustacea	Daphnia magna	48	1.2	LC50	-	Biesinger & Stokes 1986
kation.	-	Polymer L	Crustacea	Daphnia magna	48	1.84	LC50	-	Biesinger & Stokes 1986
kation.		Magnifloc 570 C	Crustacea	Daphnia magna	21 d	1.85	LC50	static	Biesinger, 1976

Overview from literature of the toxicity of various polyelectrolytes (continued)

Type	Activity	Name of substance	Org.Group	Species	Time in h	Conc. in mg/l	Crit.	Effect/Remarks	Reference
KATIONIC P.E.									
kation.	100%	DAD/MAC CS4	Crustacea	Daphnia pulex	48	2	LC50	-	Hall & Mirenda 1991
kation.		CAlgaeon M500	Crustacea	Limnocalanus macrurus	96	2	LC50	static	Biesinger, 1976
kation.		Magnifloc 521C	Crustacea	Daphnia magna	96	2.1	LC50	static	Biesinger, 1976
kation.		CAlgaeon M500	Crustacea	Daphnia magna	21 d	2.85	LC50	static	Biesinger, 1976
kation.		Magnifloc 521C	Crustacea	Daphnia magna	48	3.7	LC50	static	Biesinger, 1976
kation.		CAlgaeon M500	Crustacea	Mysis relicta	96	>4	LC50	static	Biesinger, 1976
kation.	bead	a10	Crustacea	Daphnia magna	48	4.6	EC50	-	Supplier a
kation.		Gendriv 162	Crustacea	Daphnia magna	96	<6.2	LC50	static	Biesinger, 1976
kation.	-	Polymer J	Crustacea	Daphnia magna	48	6.78	LC50	-	Biesinger & Stokes 1986
kation.	-	Polymer G	Crustacea	Gammarus pseudolimnaeus	96	8.1	LC50	-	Biesinger & Stokes 1986
kation.	75%	MF CS5	Crustacea	Daphnia pulex	48	12.13	LC50	-	Hall & Mirenda 1991
kation.	-	Polymer O	Crustacea	Gammarus pseudolimnaeus	96	12.5	LC50	-	Biesinger & Stokes 1986
kation.	-	Polymer M	Crustacea	Daphnia magna	48	12.59	LC50	-	Biesinger & Stokes 1986
kation.	-	Polymer M	Crustacea	Gammarus pseudolimnaeus	96	21	LC50	-	Biesinger & Stokes 1986
kation.	-	Polymer E	Crustacea	Gammarus pseudolimnaeus	96	22.8	LC50	-	Biesinger & Stokes 1986
kation.	-	Polymer B	Crustacea	Gammarus pseudolimnaeus	96	31.6	LC50	-	Biesinger & Stokes 1986
kation.	-	Polymer L	Crustacea	Gammarus pseudolimnaeus	96	33.4	LC50	-	Biesinger & Stokes 1986
kation.	70%	Mannich CS7	Crustacea	Daphnia pulex	48	41.58	LC50	-	Hall & Mirenda 1991
kation.		Gendriv 162	Crustacea	Daphnia magna	48	42	LC50	static	Biesinger, 1976
kation.	70%	Mannich CS8	Crustacea	Daphnia pulex	48	45.96	LC50	-	Hall & Mirenda 1991
kation.	70%	Mannich CS10	Crustacea	Daphnia pulex	48	46.24	LC50	-	Hall & Mirenda 1991
kation.	70%	Mannich CS6	Crustacea	Daphnia pulex	48	51.71	LC50	-	Hall & Mirenda 1991
kation.		d7	Crustacea	Daphnia	-	70	EC50	(OECD 202)	Supplier d
kation.		d3	Crustacea	Daphnia	-	70	EC50	(OECD 201)	Supplier d
kation.		d2	Crustacea	Daphnia	-	70	EC50	(OECD 202)	Supplier d
kation.		d4	Crustacea	Daphnia	-	ca 70	LC50	(OECD 202)	Supplier d
kation.	70%	Mannich CS9	Crustacea	Daphnia pulex	48	70.08	LC50	-	Hall & Mirenda 1991
kation.	-	Polymer N	Crustacea	Daphnia magna	48	70.71	LC50	-	Biesinger & Stokes 1986
kation.	-	Polymer N	Crustacea	Gammarus pseudolimnaeus	96	85.2	LC50	-	Biesinger & Stokes 1986
kation.	-	Polymer A	Crustacea	Daphnia magna	48	>100	LC50	-	Biesinger & Stokes 1986
kation.	-	Polymer H	Crustacea	Gammarus pseudolimnaeus	96	>100	LC50	-	Biesinger & Stokes 1986
kation.	-	Polymer I	Crustacea	Gammarus pseudolimnaeus	96	>100	LC50	-	Biesinger & Stokes 1986
kation.	-	Polymer D	Crustacea	Daphnia magna	48	>100	LC50	-	Biesinger & Stokes 1986
kation.	-	Polymer C	Crustacea	Daphnia magna	48	>100	LC50	-	Biesinger & Stokes 1986
kation.	-	Polymer F	Crustacea	Gammarus pseudolimnaeus	96	>100	LC50	-	Biesinger & Stokes 1986
kation.	-	Polymer K	Crustacea	Gammarus pseudolimnaeus	96	>100	LC50	-	Biesinger & Stokes 1986
kation.	-	Polymer D	Crustacea	Gammarus pseudolimnaeus	96	102.9	LC50	-	Biesinger & Stokes 1986

Overview from literature of the toxicity of various polyelectrolytes (continued)

Type	Activity	Name of substance	Org.Group	Species	Time in h	Conc. in mg/l	Crit.	Effect/Remarks	Reference
KATIONIC P.E.									
kation.	bead	a11	Crustacea	Daphnia magna	48	110	EC50	-	Supplier a
kation.	-	Polymer J	Crustacea	*Gammarus pseudolimnaeus*	96	112.25	LC50	-	Biesinger & Stokes 1986
kation.	-	a14	Crustacea	Crangon crangon	96	190	LC50	-	Supplier a
kation.	50%	a15	Crustacea	Crangon crangon	96	190	LC50	-	Supplier a
kation.	gel	a12	Crustacea	Daphnia magna	48	200	EC50	-	Supplier a
kation.	gel	a13	Crustacea	Daphnia magna	48	450	EC50	-	Supplier a
kation.	gel	a9	Crustacea	Daphnia magna	48	1000	EC100	-	Supplier a
kation.	-	Polymer G	Insect	Paratanytarsus	48	<6.25	LC50	-	Biesinger & Stokes 1986
kation.	-	Polymer E	Insect	Paratanytarsus	48	26.9	LC50	-	Biesinger & Stokes 1986
kation.	-	Polymer F	Insect	Paratanytarsus	48	50	LC50	-	Biesinger & Stokes 1986
kation.	-	Polymer B	Insect	Paratanytarsus	48	>100	LC50	-	Biesinger & Stokes 1986
kation.	-	Polymer M	Insect	Paratanytarsus	48	>100	LC50	-	Biesinger & Stokes 1986
kation.	-	Polymer D	Insect	Paratanytarsus	48	>100	LC50	-	Biesinger & Stokes 1986
kation.	-	Polymer H	Insect	Paratanytarsus	48	>100	LC50	-	Biesinger & Stokes 1986
kation.	-	Polymer I	Insect	Paratanytarsus	48	>100	LC50	-	Biesinger & Stokes 1986
kation.		d8	Plants	Barley	-	>50	NOEC	sprout/root yield	Supplier d
kation.		Zetag 74	Fish	Salmo gairdneri	-	0.54	LOEC		Criddle, 1990
kation.	bead	a11	Fish	Leuciscus idus	48	1	LC0	-	Supplier a
kation.		d9	Fish	-	-	-		CBSb5=240/CSB=1160 mg/l	Supplier d
kation.	8.3% a	poly(dimethylvinylpyridinium)chloride B	Fish	Lepomis macrochirus	96	0.06	LC50	-	Cary et al 1987
kation.	8.3% a	*poly(dimethylvinylpyridinium)chloride B*	Fish	Lepomis macrochirus	96	0.082	LC50	-	Cary et al 1987
kation.	45.7% a	quaternized polyalkanolamine A	Fish	Pimephales promelas	96	0.16	LC50	-	Cary et al 1987
kation.	8.3% a	poly(dimethylvinylpyridinium)chloride B	Fish	Lepomis macrochirus	96	0.17	LC50	-	Cary et al 1987
kation.	8.3% a	poly(dimethylvinylpyridinium)chloride B	Fish	Lepomis macrochirus	96	0.18	LC50	-	Cary et al 1987
kation.	45.7% a	quaternized polyalkanolamine A	Fish	Pimephales promelas	96	0.18	LC50	-	Cary et al 1987
kation.		Purifloc C31	Fish	Salmo gairdneri	96	0.185	LC50		Manual of acute tox
kation.		poly-dimethyl-diallyl-ammonium chloride	Fish	Salmo gairdneri		0.2	EC50	evasive behaviour	Spraggs, 1982
kation.	8.3% a	poly(dimethylvinylpyridinium)chloride B	Fish	Lepomis macrochirus	96	0.22	LC50	-	Cary et al 1987
kation.	15.4% a	poly(dimethyldiallylammonium)chloride D	Fish	Pimephales promelas	96	0.25	LC50	-	Cary et al 1987
kation.		b1	Fish	Salmo gairdneri	96	0.3	LC50		Supplier b
kation.	8.3% a	poly(dimethylvinylpyridinium)chloride B	Fish	Lepomis macrochirus	96	0.3	LC50	-	Cary et al 1987
kation.	15.4% a	poly(dimethyldiallylammonium)chloride D	Fish	Pimephales promelas	96	0.3	LC50	-	Cary et al 1987
kation.		Superfloc 330	Fish	Salvelinus namaycush	11 d	0.31	LC50	flow through	Biesinger, 1976
kation.	45.7% a	*quaternized polyalkanolamine A*	Fish	Lepomis macrochirus	96	0.32	LC50	-	Cary et al 1987
kation.		*Superfloc 330*	Fish	Salmo gairdneri	14 d	0.34	LC50	flow through	Biesinger, 1976
kation.		Purifloc C31	Fish	Chinook salmon	96	0.357	LC50	-	Manual of acute tox

Overview from literature of the toxicity of various polyelectrolytes (continued)

pe	Activity	Name of substance	Org.Group	Species	Time in h	Conc. in mg/l	Crit.	Effect/Remarks	Reference
KATIONIC P.E.									
kation.	-	Polymer B2	Fish	Salmo gairdneri	72	0.384	LC50	flow through	Goodrich, et al, 1991
kation.	-	Polymer B2	Fish	Salmo gairdneri	96	0.384	LC50	flow through	Goodrich, et al, 1991
kation.		acrylamide copolymer	Fish	Salmo gairdneri		0.4	EC50	evasive behaviour	Spraggs, 1982
kation.	75%	Metac CE5	Fish	Pimephales promelas	96	0.4	LC50	-	Hall & Mirenda 1991
kation.	-	Polymer B2	Fish	Salmo gairdneri	48	0.406	LC50	flow through	Goodrich, et al, 1991
kation.		poly-dimethyl-diallyl-ammonium chloride	Fish	Salmo gairdneri		0.43	LC50	-	Spraggs, 1982
kation.		Purifloc C31	Fish	Salmo gairdneri	96	0.446	LC50	-	Manual of acute tox
kation.	8.3% a	poly(dimethylvinylpyridinium)chloride B	Fish	Lepomis macrochirus	96	0.45	LC50	-	Cary et al 1987
kation.	15.4% a	poly(dimethyldiallylammonium)chloride:D	Fish	Pimephales promelas	96	0.46	LC50	-	Cary et al 1987
tion.		Purifloc C31	Fish	Pimephales promelas	96	0.49	LC50	-	Manual of acute tox
ation.	45.7% a	quaternized polyalkanolamine A	Fish	Lepomis macrochirus	96	0.5	LC50	-	Cary et al 1987
kation.	45.7% a	quaternized polyalkanolamine A	Fish	Lepomis macrochirus	96	0.5	LC50	-	Cary et al 1987
kation.	45%	Metac CE4	Fish	Pimephales promelas	96	0.52-0.78	LC50	-	Hall & Mirenda 1991
kation.		Purifloc C31	Fish	Pimephales promelas	96	0.56	LC50	-	Manual of acute tox
kation.	8.3% a	poly(dimethylvinylpyridinium)chloride B	Fish	Lepomis macrochirus	96	0.58	LC50	-	Cary et al 1987
kation.	45%	Metac CE4	Fish	Pimephales promelas	96	0.58-0.34	LC50	-	Hall & Mirenda 1991
kation.	45.7% a	quaternized polyalkanolamine A	Fish	Ictalurus punctatus	96	0.59	LC50	-	Cary et al 1987
kation.	8.3% a	poly(dimethylvinylpyridinium)chloride B	Fish	Ictalurus punctatus	96	0.63	LC50	-	Cary et al 1987
kation.	45.7% a	quaternized polyalkanolamine A	Fish	Lepomis macrochirus	96	0.64	LC50	-	Cary et al 1987
kation.	-	Polymer B2	Fish	Salmo gairdneri	96	0.661	LC50	Static	Goodrich, et al, 1991
kation.	-	Polymer B2	Fish	Salmo gairdneri	72	0.661	LC50	Static	Goodrich, et al, 1991
kation.	-	Polymer B2	Fish	Salmo gairdneri	48	0.675	LC50	Static	Goodrich, et al, 1991
kation.	100%	EPI/DMA CS2	Fish	Pimephales promelas	96	0.68	LC50	-	Hall & Mirenda 1991
kation.		Purifloc C31	Fish	Ictalurus punctatus	96	0.68	LC50		Manual of acute tox
kation.		b1	Fish	Lepomis macrochirus	96	0.7	LC50		Supplier b
kation.	-	Polymer B2	Fish	Salmo gairdneri	24	0.705	LC50	Static	Goodrich, et al, 1991
kation.	100%	DAD/MAC CS3	Fish	Pimephales promelas	96	0.74	LC50	-	Hall & Mirenda 1991
kation.		d2	Fish	Leuciscus idus melanotus	96	0.75-5.5	LC50	(OECD 203)	Supplier d
kation.		d2	Fish	Brachydanio rerio	96	0.75-5.5	LC50	(OECD 203)	Supplier d
kation.		acrylamide copolymer	Fish	Salmo gairdneri		0.8	LC50	-	Spraggs, 1982
kation.	45%	Aetac CE14	Fish	Pimephales promelas	96	0.81	LC50	-	Hall & Mirenda 1991
kation.	100%	EPI/DMA CS1	Fish	Pimephales promelas	96	0.86	LC50	-	Hall & Mirenda 1991
kation.	-	Polymer E	Fish	Pimephales promelas	96	0.88	LC50	-	Biesinger & Stokes 1986
kation.	100%	DAD/MAC CS4	Fish	Pimephales promelas	96	0.88	LC50	-	Hall & Mirenda 1991
kation.	45%	Metac CE4	Fish	Pimephales promelas	96	0.93	LC50	-	Hall & Mirenda 1991
kation.	-	Polymer G	Fish	Pimephales promelas	96	1	LC50	-	Biesinger & Stokes 1986
kation.		d3	Fish	Leuciscus idus melanotus	96	ca 1	LC50	(OECD 203)	Supplier d

Overview from literature of the toxicity of various polyelectrolytes (*continued*)

Type	Activity	Name of substance	Org.Group	Species	Time in h	Conc. in mg/l	Crit.	Effect/Remarks	Reference
KATIONIC P.E.									
kation.		d4	Fish	Brachydanio rerio	96	ca 1	LC50	-	Supplier d
kation.		d3	Fish	Brachydanio rerio	96	ca 1	LC50	(OECD 203)	Supplier d
kation.		d4	Fish	Leuciscus idus melanotus	96	ca 1	LC50	-	Supplier d
kation.	bead	a10	Fish	Ictalurus punctatus	96	1-10	LC50	-	*Supplier a*
kation.	-	a16	Fish	Fish	-	1-100	LC50	-	Supplier a
kation.	-	a17	Fish	Fish	-	1-100	LC50	-	Supplier a
kation.	70%	Mannich CS	Fish	Pimephales promelas	96	1.04	LC50	-	Hall & Mirenda 1991
kation.	45.7% a	quaternized polyalkanolamine:A	Fish	Lepomis macrochirus	96	1.05	LC50	-	Cary et al 1987
kation.	35%	Aetac CE10	Fish	Pimephales promelas	96	1.05	LC50	-	*Hall & Mirenda 1991*
kation.	-	Polymer O	Fish	Pimephales promelas	96	1.05	LC50	-	Biesinger & Stokes 1986
kation.	bead	a10	Fish	Leuciscus idus	48	1.1	LC50	-	Supplier a
kation.		Magnifloc 521C	Fish	Salmo gairdneri	14 d	1.1	LC50	flow through	Biesinger, 1976
kation.	45%	Aetac CE13	Fish	Pimephales promelas	96	1.17	LC50	-	Hall & Mirenda 1991
kation.	70%	Mannich CS10	Fish	Pimephales promelas	96	1.19	LC50	-	Hall & Mirenda 1991
kation.		Purifloc C31	*Fish*	*Lepomis macrochirus*	96	1.24	LC50		Manual of acute tox
kation.	45%	Aetac CE11	Fish	Pimephales promelas	96	1.3	LC50	-	Hall & Mirenda 1991
kation.	70%	Mannich CS9	Fish	Pimephales promelas	96	1.36	LC50	-	Hall & Mirenda 1991
kation.	*gel*	*a9*	Fish	Leuciscus idus	48	1.4	LC50	-	Supplier a
kation.	45%	Metac CE3	Fish	Pimephales promelas	96	1.41	LC50	-	Hall & Mirenda 1991
kation.	25%	Metac CE2	Fish	Pimephales promelas	96	1.41	LC50	-	Hall & Mirenda 1991
kation.	25%	Aetac CE9	Fish	Pimephales promelas	96	1.45	LC50	-	Hall & Mirenda 1991
kation.		Purifloc C31	Fish	Lepomis macrochirus	96	1.47	LC50		Manual of acute tox
kation.	*70%*	*Mannich CS7*	*Fish*	*Pimephales promelas*	96	1.48	LC50	-	Hall & Mirenda 1991
kation.		d7	Fish	Brachydanio rerio	96	2	LC50	(OECD 203)	Supplier d
kation.		Superfloc 330	Fish	Salmo gairdneri	96	2.12	LC50	static	Biesinger, 1976
kation.	-	Polymer M	Fish	Pimephales promelas	96	2.18	LC50	-	Biesinger & Stokes 1986
kation.	-	Polymer H	Fish	Pimephales promelas	96	2.46	LC50	-	Biesinger & Stokes 1986
kation.	-	*Polymer N*	*Fish*	*Pimephales promelas*	*96*	*2.72*	*LC50*	-	*Biesinger & Stokes 1986*
kation.	bead	a18	Fish	Salmo gairdneri	96	2.8	LC50	-	Supplier a
kation.	45%	Aetac CE12	Fish	Pimephales promelas	96	2.81	LC50	-	Hall & Mirenda 1991
kation.		Superfloc 330	Fish	Salvelinus namaycush	96	2.85	LC50	static	Biesinger, 1976
kation.	-	Polymer F	Fish	Pimephales promelas	96	2.87	LC50	-	Biesinger & Stokes 1986
kation.	70%	Mannich CS6	Fish	Pimephales promelas	96	*3.29*	*LC50*	-	*Hall & Mirenda 1991*
kation.	-	Polymer I	Fish	Pimephales promelas	96	3.74	LC50	-	Biesinger & Stokes 1986
kation.	10%	Metac CE1	Fish	Pimephales promelas	96	4.7	LC50	-	Hall & Mirenda 1991
kation.	10%	Aetac CE8	Fish	Pimephales promelas	96	4.49-3.29	LC50	-	Hall & Mirenda 1991
kation.	gel	a12	Fish	Leuciscus idus	48	5.4	LC50	-	Supplier a

Overview from literature of the toxicity of various polyelectrolytes (continued)

Type	Activity	Name of substance	Org.Group	Species	Time in h	Conc. in mg/l	Crit.	Effect/Remarks	Reference
KATIONIC P.E.									
kation.		d7	Fish	Leuciscus idus melanotus	96	5.5	LC50	(OECD 203)	Supplier d
kation.		CAlgaeon M500	Fish	Salvelinus namaycush	96	5.7	LC50	static	Biesinger, 1976
kation.	-	Polymer L	Fish	Pimephales promelas	96	5.7	LC50	-	Biesinger & Stokes 1986
kation.		CAlgaeon M500	Fish	Salmo gairdneri	96	6.15	LC50	static	Biesinger, 1976
kation.	-	Polymer K	Fish	Pimephales promelas	96	6.82	LC50	-	Biesinger & Stokes 1986
kation.	-	Polymer D	Fish	Pimephales promelas	96	7.4	LC50	-	Biesinger & Stokes 1986
kation.		Magnifloc 521C	Fish	Salmo gairdneri	96	8.7	LC50	static	Biesinger, 1976
kation.	-	Polymer J	Fish	Pimephales promelas	96	9.47	LC50	-	Biesinger & Stokes 1986
kation.	gel	a12	Fish	Ictalurus punctatus	96	10-100	LC50	-	Supplier a
kation.	2%	Aetac CE6	Fish	Pimephales promelas	96	11.6	LC50	-	Hall & Mirenda 1991
kation.	6%	Aetac CE7	Fish	Pimephales promelas	96	13.49	LC50	-	Hall & Mirenda 1991
kation.	-	Polymer B	Fish	Pimephales promelas	96	>100	LC50	-	Biesinger & Stokes 1986
kation.	-	Polymer C	Fish	Pimephales promelas	96	>100	LC50	-	Biesinger & Stokes 1986
kation.	-	Polymer A	Fish	Pimephales promelas	96	>100	LC50	-	Biesinger & Stokes 1986
kation.	75%	MF CS5	Fish	Pimephales promelas	96	>170	LC50	-	Hall & Mirenda 1991
kation.		Gendriv 162	Fish	Salmo gairdneri	96	218	LC50	-	Biesinger, 1976
kation.	50%	a19	Fish	Salmo gairdneri	96	226	LC50	-	Supplier a
kation.	gel	a13	Fish	Leuciscus idus	48	280	LC50	-	Supplier a
kation.	bead	a13	Fish	Ictalurus punctatus	96	>1000	LC50	-	Supplier a
kation.		Purifloc C31	Fish	Salmo gairdneri	36	1	LC100	still water	Biesinger, 1976
kation.	bead	a11	Fish	Leuciscus idus	48	20	LC100	-	Supplier a
kation.		Zetag 74	Fish	Salmo gairdneri	130min	54	LC100	130 min. survive	Criddle, 1990
KATIONIC P.E. EXTENDED WITH ORGANIC SUBSTANCES									
kation.	15.4% a	poly(dimethyldiallylammonium)chloride D	Crustacea	Daphnia magna	48	0.14	LC50	+ 50 mg/l silica	Cary, 1987
kation.	8.3% a	poly(dimethylvinylpyridinium)chloride B	Crustacea	Daphnia magna	48	0.24	LC50	+ 50 mg/l kaoline	Cary, 1987
kation.	45.7% a	quaternized polyalkanolamine A	Crustacea	Daphnia magna	48	0.26	LC50	+ 50 mg/l silica	Cary, 1987
kation.	8.3% a	poly(dimethylvinylpyridinium)chloride B	Crustacea	Daphnia magna	48	0.37	LC50	+ 50 mg/l silica	Cary, 1987
kation.	45.7% a	quaternized polyalkanolamine A	Crustacea	Daphnia magna	48	0.91	LC50	+ 50 mg/l kaoline	Cary, 1987
kation.	45.7% a	quaternized polyalkanolamine A	Crustacea	Daphnia magna	48	1	LC50	+ 50 mg/l illite	Cary, 1987
kation.	15.4% a	poly(dimethyldiallylammonium)chloride D	Crustacea	Daphnia magna	48	1.1	LC50	+ 50 mg/l kaoline	Cary, 1987
kation.	15.4% a	poly(dimethyldiallylammonium)chloride D	Crustacea	Daphnia magna	48	1.2	LC50	+ 50 mg/l illite	Cary, 1987
kation.	15.4% a	poly(dimethyldiallylammonium)chloride D	Crustacea	Daphnia magna	48	2.2	LC50	+ 50 mg/l fulvic acid	Cary, 1987
kation.	8.3% a	poly(dimethylvinylpyridinium)chloride B	Crustacea	Daphnia magna	48	3.6	LC50	+ 50 mg/l illite	Cary, 1987
kation.	8.3% a	poly(dimethylvinylpyridinium)chloride B	Crustacea	Daphnia magna	48	4.3	LC50	+ 50 mg/l fulvic acid	Cary, 1987
kation.	45.7% a	quaternized polyalkanolamine A	Crustacea	Daphnia magna	48	5.9	LC50	+ 50 mg/l lignosite	Cary, 1987
kation.	15.4% a	poly(dimethyldiallylammonium)chloride D	Crustacea	Daphnia magna	48	7.1	LC50	+ 50 mg/l bentonite	Cary, 1987

Overview from literature of the toxicity of various polyelectrolytes (continued)

Type	Activity	Name of substance	Org.Group	Species	Time in h	Conc. in mg/l	Crit.	Effect/Remarks	Reference
KATIONIC P.E. EXTENDED WITH ORGANIC SUBSTANCES (cont'd)									
kation.	15.4% a	poly(dimethyldiallylammonium)chloride D	Crustacea	Daphnia magna	48	7.4	LC50	+ 50 mg/l humic acid	Cary, 1987
kation.	8.3% a	poly(dimethylvinylpyridinium)chloride B	Crustacea	Daphnia magna	48	7.7	LC50	+ 50 mg/l humic acid	Cary, 1987
kation.	15.4% a	poly(dimethyldiallylammonium)chloride D	Crustacea	Daphnia magna	48	7.9	LC50	+ 50 mg/l lignosite	Cary, 1987
kation.	8.3% a	poly(dimethylvinylpyridinium)chloride B	Crustacea	Daphnia magna	48	>8.3	LC50	+ 50 mg/l bentonite	Cary, 1987
kation.	8.3% a	poly(dimethylvinylpyridinium)chloride B	Crustacea	Daphnia magna	48	>8.3	LC50	+ 50 mg/l tannic acid	Cary, 1987
kation.	8.3% a	poly(dimethylvinylpyridinium)chloride B	Crustacea	Daphnia magna	48	>8.3	LC50	+ 50 mg/l lignosite	Cary, 1987
kation.	8.3% a	poly(dimethylvinylpyridinium)chloride B	Crustacea	Daphnia magna	48	>8.3	LC50	+ 50 mg/l lignine	Cary, 1987
kation.	45.7% a	quaternized polyalkanolamine A	Crustacea	Daphnia magna	48	10.5	LC50	+ 50 mg/l humic acid	Cary, 1987
kation.	15.4% a	poly(dimethyldiallylammonium)chloride D	Crustacea	Daphnia magna	48	11.9	LC50	+ 50 mg/l tannic acid	Cary, 1987
kation.	45.7% a	quaternized polyalkanolamine A	Crustacea	Daphnia magna	48	14.6	LC50	+ 50 mg/l fulvic acid	Cary, 1987
kation.	15.4% a	poly(dimethyldiallylammonium)chloride D	Crustacea	Daphnia magna	48	>15.4	LC50	+ 50 mg/l lignine	Cary, 1987
kation.	45.7% a	quaternized polyalkanolamine A	Crustacea	Daphnia magna	48	17.4	LC50	+ 50 mg/l tannic acid	Cary, 1987
kation.	45.7% a	quaternized polyalkanolamine A	Crustacea	Daphnia magna	48	20.1	LC50	+ 50 mg/l bentonite	Cary, 1987
kation.	45.7% a	quaternized polyalkanolamine A	Crustacea	Daphnia magna	48	28.8	LC50	+ 50 mg/l lignine	Cary, 1987
kation.		Purifloc C31	Fish	Salmo gairdneri	72	30	NOEC	+ 33 mg/l solid matter	Biesinger, 1976
kation.	8.3% a	poly(dimethylvinylpyridinium)chloride B	Fish	Lepomis macrochirus	96	0.26	LC50	+ 50 mg/l kaoline	Cary, 1987
kation.	8.3% a	poly(dimethylvinylpyridinium)chloride B	Fish	Lepomis macrochirus	96	0.27	LC50	+ 50 mg/l illite	Cary, 1987
kation.	8.3% a	poly(dimethylvinylpyridinium)chloride B	Fish	Lepomis macrochirus	96	0.28	LC50	+ 50 mg/l silica	Cary, 1987
kation.	45.7% a	quaternized polyalkanolamine A	Fish	Lepomis macrochirus	96	0.35	LC50	+ 50 mg/l silica	Cary, 1987
kation.	15.4% a	poly(dimethyldiallylammonium)chloride D	Fish	Lepomis macrochirus	96	0.39	LC50	+ 50 mg/l silica	Cary, 1987
kation.	15.4% a	poly(dimethyldiallylammonium)chloride D	Fish	Lepomis macrochirus	96	0.4	LC50	+ 50 mg/l kaoline	Cary, 1987
kation.	45.7% a	quaternized polyalkanolamine A	Fish	Lepomis macrochirus	96	0.41	LC50	+ 50 mg/l kaoline	Cary, 1987
kation.	15.4% a	poly(dimethyldiallylammonium)chloride D	Fish	Lepomis macrochirus	96	0.55	LC50	+ 50 mg/l illite	Cary, 1987
kation.	45.7% a	quaternized polyalkanolamine A	Fish	Lepomis macrochirus	96	1.1	LC50	+ 50 mg/l illite	Cary, 1987
kation.	45.7% a	quaternized polyalkanolamine A	Fish	Lepomis macrochirus	96	2.2	LC50	+ 50 mg/l fulvic acid	Cary, 1987
kation.	45.7% a	quaternized polyalkanolamine A	Fish	Lepomis macrochirus	96	2.9	LC50	+ 50 mg/l lignosite	Cary, 1987
kation.	8.3% a	poly(dimethylvinylpyridinium)chloride B	Fish	Lepomis macrochirus	96	3.2	LC50	+ 50 mg/l lignine	Cary, 1987
kation.	8.3% a	poly(dimethylvinylpyridinium)chloride B	Fish	Lepomis macrochirus	96	3.3	LC50	+ 50 mg/l fulvic acid	Cary, 1987
kation.	8.3% a	poly(dimethylvinylpyridinium)chloride B	Fish	Lepomis macrochirus	96	3.5	LC50	+ 50 mg/l lignosite	Cary, 1987
kation.	15.4% a	poly(dimethyldiallylammonium)chloride D	Fish	Lepomis macrochirus	96	3.7	LC50	+ 50 mg/l lignine	Cary, 1987
kation.	15.4% a	poly(dimethyldiallylammonium)chloride D	Fish	Lepomis macrochirus	96	3.7	LC50	+ 50 mg/l lignosite	Cary, 1987
kation.	45.7% a	quaternized polyalkanolamine A	Fish	Lepomis macrochirus	96	3.8	LC50	+ 50 mg/l lignine	Cary, 1987
kation.	15.4% a	poly(dimethyldiallylammonium)chloride D	Fish	Lepomis macrochirus	96	4.2	LC50	+ 50 mg/l fulvic acid	Cary, 1987
kation.	45.7% a	quaternized polyalkanolamine A	Fish	Lepomis macrochirus	96	4.6	LC50	+ 50 mg/l tannic acid	Cary, 1987
kation.	8.3% a	poly(dimethylvinylpyridinium)chloride B	Fish	Lepomis macrochirus	96	6.2	LC50	+ 50 mg/l humic acid	Cary, 1987
kation.	8.3% a	poly(dimethylvinylpyridinium)chloride B	Fish	Lepomis macrochirus	96	6.2	LC50	+ 50 mg/l tannic acid	Cary, 1987

Overview from literature of the toxicity of various polyelectrolytes (continued)

Type	Activity	Name of substance	Org.Group	Species	Time in h	Conc. in mg/l	Crit.	Effect/Remarks	Reference
kation.	8.3% a	poly(dimethylvinylpyridinium)chloride B	Fish	Lepomis macrochirus	96	6.2	LC50	+ 50 mg/l bentonite	Cary, 1987
kation.	45.7% a	quaternized polyalkanolamine A	Fish	Lepomis macrochirus	96	6.4	LC50	+ 50 mg/l humic acid	Cary, 1987
kation.	15.4% a	poly(dimethyldiallylammonium)chloride D	Fish	Lepomis macrochirus	96	6.5	LC50	+ 50 mg/l bentonite	Cary, 1987
kation.	15.4% a	poly(dimethyldiallylammonium)chloride D	Fish	Lepomis macrochirus	96	6.5	LC50	+ 50 mg/l humic acid	Cary, 1987
kation.	15.4% a	poly(dimethyldiallylammonium)chloride D	Fish	Lepomis macrochirus	96	6.5	LC50	+ 50 mg/l tannic acid	Cary, 1987
kation.	45.7% a	quaternized polyalkanolamine A	Fish	Lepomis macrochirus	96	7.3	LC50	+ 50 mg/l bentonite	Cary, 1987
kation.		b1	Fish	Salmo gairdneri	96	42	LC50	with humic acid	Supplier b
NONIONIC P.E.									
nonion.	15%	a22	Crustacea	Daphnia magna	96	>1000	NOEC	immobility	Supplier a
nonion.	0%	PA NE1	Crustacea	Daphnia pulex	48	0.08	LC50	-	Hall & Mirenda 1991
nonion.	-4%	PA NE2	Crustacea	Daphnia pulex	48	0.15	LC50	-	Hall & Mirenda 1991
nonion.	25%	a20	Crustacea	Daphnia magna	48	15.3	EC50	-	Supplier a
nonion.		Magnifloc 905N	Crustacea	Daphnia magna	96	16.5	LC50	-	Biesinger, 1976
nonion.		Magnifloc 905N	Crustacea	Daphnia magna	48	>50	LC50	static	Biesinger, 1976
nonion.	50%	a21	Crustacea	Crangon crangon	96	53	LC50	-	Supplier a
nonion.	15%	a22	Fish	Brachydanio rerio	96	>1000	NOEC	mortality	Supplier a
nonion.	25%	a20	Fish	Salmo gairdneri	96	7.97	LC50	-	Supplier a
nonion.		Magnifloc 905N	Fish	Salmo gairdneri	96	>8	LC50	static	Biesinger, 1976
nonion.	-4%	PA NE2	Fish	Pimephales promelas	96	63.63	LC50	-	Hall & Mirenda 1991
nonion.	0%	PA NE1	Fish	Pimephales promelas	96	63.63	LC50	-	Hall & Mirenda 1991
nonion.+anion.		a16	Fish	Fish	-	500	LC50	-	Supplier a
nonion.	gel	a23	Fish	Salmo gairdneri	96	3500	LC50	-	Supplier a
MONOMER ACRYLAMIDE									
monomer		acrylamide	Algae	Selenastrum capricornutum		72	EC50	inhibition	Spraggs, 1982
monomer		acrylamide	Bacteria	Microtox		13500	EC50		Spraggs, 1982
monomer		acrylamide	Fish	-	9 d	56	LOEC	feeding behaviour	Criddle, 1990
monomer		acrylamide	Fish	Salmo gairdneri		8	LC50		Spraggs, 1982
monomer		acrylamide	Fish	Salmo gairdneri		140	EC50	evasive behaviour	Spraggs, 1982
monomer		DMDAAC monomer	Algae	Selenastrum capricornutum		220	EC50	inhibition	Spraggs, 1982
monomer		DMDAAC monomer	Bacteria	Microtox		22500	EC50		Spraggs, 1982
monomer		DMDAAC monomer	Fish	Salmo gairdneri		>4	LC50		Spraggs, 1982
monomer		DMDAAC monomer	Fish	Salmo gairdneri		900	EC50	evasive behaviour	Spraggs, 1982

Appendix 3

Adsorption and hydrolysis of p.e.

Adsorption and hydrolysis of p.e.

The adsorption behaviour of p.e. in the water line has been calculated with the aid of the SIMPLETREAT model. In this model it is assumed that there is a linear relation between the adsorbed and dissolved fraction according to:

$$Kp \quad = \quad Xs/Cw [l/kg]$$

In practice the adsorption behaviour is described better by the Langmuir isotherm:

$$qe \quad = \quad bQCw/(1+bCw)$$

The starting point of the langmuir isotherm can be linearised. Linearisation with qe << Qc yields:

$$qe \quad = \quad bQ * C = Xs/1{,}000 = Kp * Cw/1{,}000$$

By Gehr (1982) the Langmuir isotherms were derived for three different cationic p.e. (Fig. 6). With the b and Q derived from these isotherms an average Kp can be derived of 18.700 l/kg. Figure 6 shows that up to 1/10 of the maximum adsorption capacity, this line is followed. Above this an increasingly underrating of the concentration in the water phase is made. From Figure 6 it may be concluded that only at 1/3 of the adsorption capacity the isotherm diverts substantially. Regression of the data up to 1/3 of the adsorption yields a constant of 13.65 with a high regression co-efficient (R^2=0.975). Consequently, up to 1/3 of the maximum adsorption capacity a linear relation can be assumed with a Kp of 13,650 l/kg. The maximum adsorption capacity found by Gehr was 7 mg p.e./g d.s. on an average, so a linear relation may be assumed up to 2.3 mg p.e./g d.s.

From the experiments by Schumann (1991) a Kp of 12,250 l/kg can be calculated.

Calculation of the adsorption

In Figures 6 and 7 an empirical correlation is represented between the equilibrium concentration in water and a certain degree of charge of the sludge. This proves that Kp decreases at a higher degree of charge. Since the correlation is not linear, this empirical line is particularly to be preferred over a constant Kp at a higher loading rate. On the line a point can be looked for at which it holds that the adsorbed fraction (*f*) yields a degree of charge corresponding to the rest fraction (1-*f*) in the solution. The degree of charge is calculated on the amount of p.e. per population equivalent (p.eq.) and the amount of sludge per p.eq. Per p.eq. the quantity of waste water amounts to 150 l/day, the quantities of primary and secondary sludge amount to 40 and 13 g d.s./day, respectively. For instance for the pre-settlement it holds:

$$\frac{f_i * 150 * C_i}{40} = Kp * (1-f_i) * Ci$$

In an installation which uses pre-settlement, the adsorption passes in two steps. At the highest dosage, resulting in 1 mg p.e./l in the influent, 150 mg p.e./p.eq. is distributed over the water and 40 g d.s. primary sludge per p.eq. in the pre-settlement. The graph shows that herewith approximately 75% is bound to the sludge (f_1). The dissolved fraction (25%) enters the aeration reservoir and is distributed over the water and 13 g d.s. secondary sludge/p.eq./day.

With T = 32 hours 60% is bound in the secondary sludge (f_2).
If the aeration time is shorter, also more secondary sludge is formed. Based on 20 g d.s. secondary sludge/p.eq./day at T = 10 h, 70% is bound in the secondary sludge (f_2).
Using a dosage in the sludge line at which 0.2 mg p.e. enters the effluent, the adsorption percentages are different. In the pre-settlement 83% is bound (f_1) and in secondary sludge with a low or high loading rate approximately 50% and 60% are bound (f_2), respectively.

The rest concentration in solution is subject to hydrolysis during liquid residence time in the aeration reservoir.

Calculation of the hydrolysis

According to the specification of the manufacturer the cationic polyelectrolytes based on polyacrylamide and polyacrylate copolymer are very sensitive to hydrolysis. At neutral pH and a temperature of 20° C, the half-life would amount to approximately 8 hours (further data Maroni SNF).
The first-order hydrolysis speed constant follows from:

$$\text{Ln } 2 = K_h * 8$$

$$K_h = 0.086/\text{h}$$

In a fully homogeneously mixed system the decrease as a result of hydrolysis is a function of the equilibrium concentration in the reactor, which is also equal to the effluent concentration (C_e).

$$- dC/dt = K_h * C_e$$

From a mass balance across the reactor with volume V and flow debit Q follows:

$$Q * C_i = Q * C_e + K_h * V * C_e$$

$$C_i/C_e = 1 + K_h * T$$

where T is the average hydraulic residence time (T = V/Q).

In this respect, the description of waste water treatment plant in accordance with a fully homogeneously mixed system is a "worst case" approach. If the system is conceived as a complete plug flow reactor the conversion with a first-order progressing reaction is more complete. The conversion then follows from:

$$\frac{C_i}{C_e} = e\, K_h * T$$

The real conversion in a waste water treatment plant is best to be approached as the average between the conversion which occurs in a fully homogeneously mixed system and that which occurs in a plug flow reactor.

At a residence time (T) of 32 h, as in the default adjustment of Simple Treat, the degradation by *hydrolysis in a homogenous mixer becomes 73% and in a plug flow 94%.*

Thus, the average hydrolysis in installations with a low loading rate amounts to 83% (f_3).

The default value for T of 32 h seems rather extreme. Based on data from CBS the value varies between 10 and 32 h.

At a residence time of 10 h, the conversion by hydrolysis amounts to 46% in a homogenous mixer and 58% in a plug flow. Thus, the average hydrolysis in installations with a high loading rate is 52% (f_3).

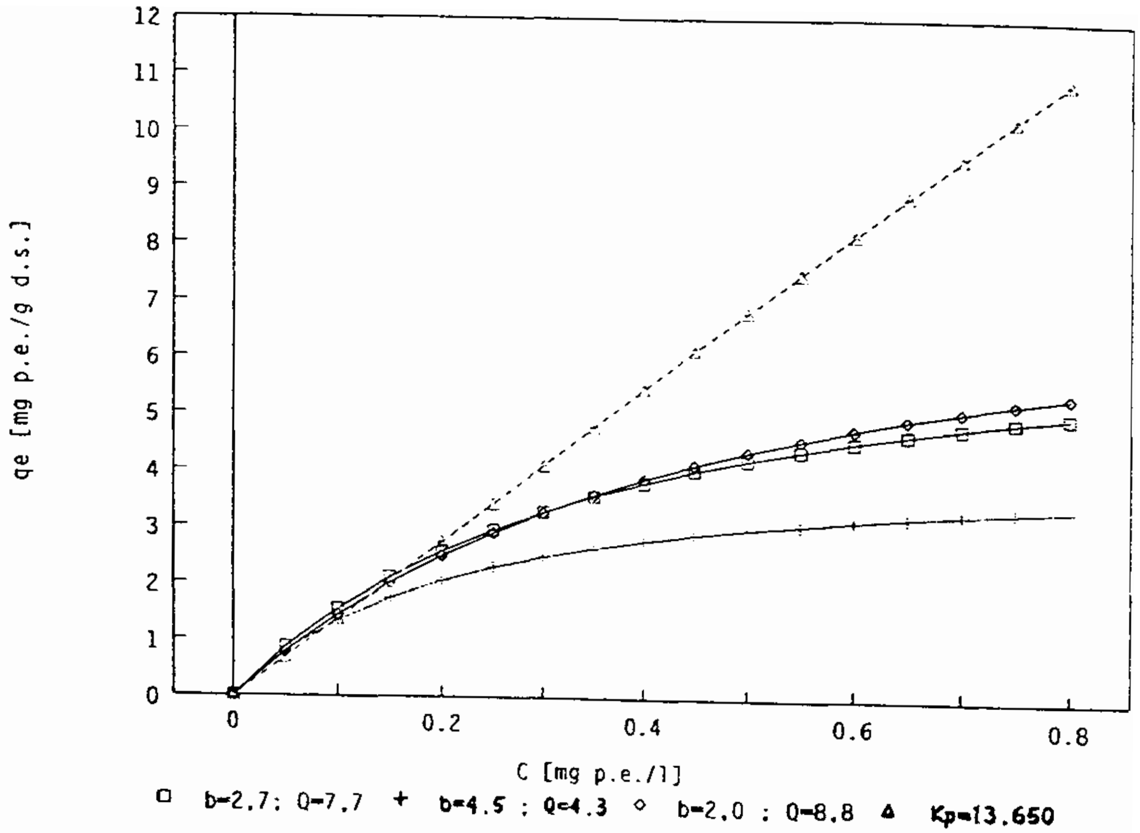

Figure 6 *Adsorbed fraction p.e. (qe) as a function of the p.e. concentration in the water phase (C) according to 3 derived Langmuir isotherms for different cationic p.e. to active sludge and according to a rectilinear adsorption behaviour having a Kp of 13,650 l/kg.*

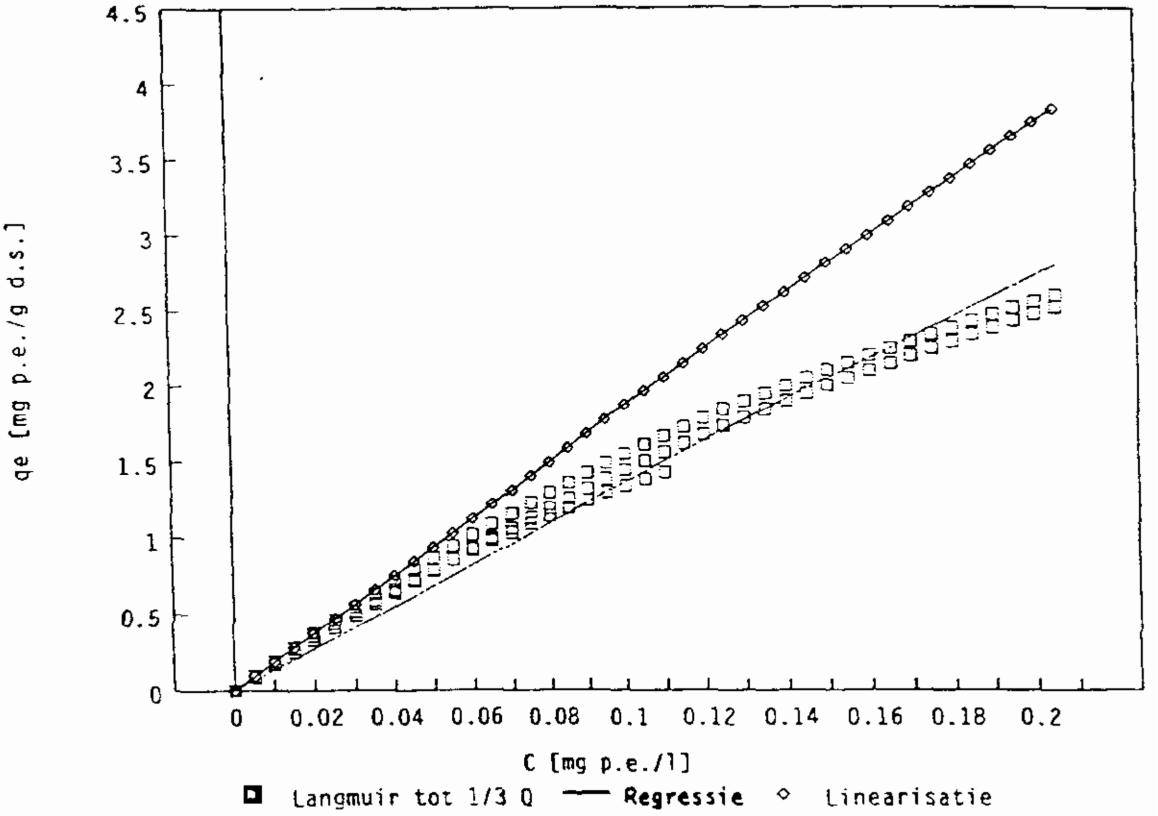

Figure 7 *Adsorbed fraction p.e. (qe) as a function of the p.e. concentration in the water phase (C) according to 3 derived Langmuir isotherms for different cationic p.e. till 1/3 of the maximum adsorption capacity (Q), de regression line of these points (agreeing with a Kp of 13,650) and linearisation of the Langmuir isotherm (agreeing with a Kp of 18,700).*

Appendix 4

Health effects of by-products

Health effects of by-products

Besides the active substance several by-products occur in p.e. In a number of cases these by-products are more dangerous to man that the active substances themselves.
Mineral oil, e.g. is carcinogenic to man. Petroleum distillate can cause irritation of the skin, the eyes and the bronchial tubes. Prolonged exposure to the vapour of petroleum distillate can harm the central nervous system.

Both liquid and solid products can contain small amounts of acrylamide. Acrylamide irritates the skin and the mucous membrane. It can cause blisters and peeling, particularly on the palms of the hand and the foot-soles.
Acrylamide can affect the nervous system. The effects on the central nervous system are characterised by extreme fatigue, drowsiness, memory disorders and dizziness. In severe cases confusion, disorientation and hallucinations can occur. Characteristic are co-ordination disorders in walking. Effects on the peripheral nervous system generally occur after prolonged exposure and are characterised by loss of tendon reflexes, decreased feeling and muscle weakness in the limbs. Effects on the autonomous nervous system are manifest among others in abundant perspiration. After stopping the exposure to acrylamide generally there is a full recovery.
Acrylamide is carcinogenic to test animals. In mice, skin and lung tumours have been found. There are not enough data available to be able to evaluate the carcinogenic properties for humans (IARC, 1986). In The Netherlands acrylamide is include on the Dutch list of carcinogenic substances.
There are no indications that acrylamide affects the foetus in humans. Probably the substance can be excreted by way of mother's milk. No judgement can be made on the effects of acrylamide on human fertility, however, the substance can accumulate in the male reproductive system. For substances harmful to reproduction an additional registration duty is compulsory. In addition to this, the Ministry Social Affairs and Employment advises a coupling to the registration of carcinogenic substances. Acrylamide is mentioned explicitly, because of the possible effects of mutagenous substances on the reproduction (SZW '95).
Acrylamide is absorbed in the body rapidly on ingestion, after exposure of the skin and on inhalation. On ingestion the greater part (66%) is excreted again by way of the kidneys and bile (half-life some hours). Part of it remains and can accumulate in the nervous system, the liver and the kidneys and in the male reproductive system. The remaining acrylamide has a half-life of 10 days (WHO/IPCS, 1985).

Other by-products concern, i.a., hydroxypropionitrile, isobutyronitrile, sorbitan mono-oleate and acrylonitrile.
Of hydroxypropionitrile it is known that it is toxic on ingestion or after skin contact. The effects after exposure are not specified further. In the presence of basic substances cyanide can arise, which is highly toxic. Isobutyronitrile also is toxic on ingestion or after skin contact. Also for this substance possible effects after exposure are not specified further. It is known that the substance can cause skin irritation.
Of sorbitan mono-oleate no toxicity data were found (SAX, 1989).
Acrylonitrile, which was detected in a liquid cationic quaternized polyacrylamide by Goppers (1976), is carcinogenic to man.