

Executive Summary

1. The ecotoxicological and environmental risk of releases of residual coagulants and flocculants is reviewed. Two broad groups of flocculants are considered. These are polyelectrolytes and inorganic aluminium salts.
2. The overall conclusion is that there appears to be a small risk to the natural aquatic environment arising from potential losses of unbound residual flocculants from treatment ponds on construction sites. Impacts are likely to be low level and also likely to not be significant in relation to other factors which govern the health of aquatic communities. The benefit of reduced sediment levels in discharges is considered to outweigh the risk of any low level impacts attributable to residual flocculants.
3. Management focus should remain on best management practices, including preliminary bench testing where necessary, to ensure that the most appropriate product is used in a particular application and that water treatment chemicals are applied in accordance with product specifications to achieve the target dosage range.
4. It is considered that there is not a sufficient level of environmental risk to justify a programme of field testing of residual flocculants. In any event, such a programme is not achievable in respect of polyelectrolytes because these cannot usually be reliably measured in the field (ANZECC 2000). Furthermore there are no guideline trigger levels for polyelectrolytes (ANZECC 2000) that might enable field data to be interpreted in relation to acceptable or non-acceptable concentrations.
5. Other key findings of the review can be summarised as follows:
 - Polyelectrolytes are reported to have low mammalian toxicity and are generally considered to be innocuous in field situations. Aluminium coagulants also generally pose a small environmental risk at normal field pH.
 - The potential toxicity of cationic polymers is well recognised but is seldom realised in the field. There is a large body of evidence indicating that these polymers are inactivated by sorption to naturally occurring dissolved and suspended organic matter and clays and their potential toxicity thereby greatly diminished, effectively to non significant levels.
 - Polyelectrolytes do not bioaccumulate, are highly biodegradable, and so are not persistent in the environment. Bound residues pose no hazard to sediment biota and do not break down into toxic residuals.

- Aluminium in flocculated sludges is tightly bound under a wide range of redox conditions and is stable other than in severely acidified situations. The latter conditions are unlikely to occur naturally or be induced by the use of aluminium flocculants which themselves reduce pH.

Table of Contents

1	INTRODUCTION	1
1.1	BACKGROUND	1
1.2	AUCKLAND REGIONAL COUNCIL OBJECTIVES	2
2.	METHODOLOGY	3
3	PRODUCTS IN USE	4
3.1	POLYELECTROLYTES	4
3.2	ALUMINIUM COAGULANTS	5
4	POTENTIAL TOXICITY OF COAGULANTS AND FLOCCULANTS	6
4.1	POLYELECTROLYTES	6
4.2	ALUMINIUM COAGULANTS	10
4.3	PH.....	11
5	RESIDUAL CONCENTRATIONS, ECOTOXICITY INDICATORS AND ACTION LEVELS	13
5.1	ALUM.....	13
5.2	PAC.....	13
5.3	PAM.....	14
5.4	SUMMARY	14
6	OTHER CONSIDERATIONS	16
7	CONCLUSIONS	17
	REFERENCES	20

1 Introduction

1.1 Background

This report provides an overview of the ecotoxicological and environmental effects of residual coagulants and flocculants on natural waters. This overview is based on recent publications and scientific literature that has reviewed the environmental effects of the use of these chemicals. The report has been commissioned by the Auckland Regional Council (ARC) and has been prepared by Boffa Miskell Ltd. Beca Carter Hollings and Ferner Ltd have undertaken a review of the draft findings and completed the compilation of this report.

The report is part of a two-stage study. Broadly, the first stage is a review of available information, the findings of which may lead to a second stage which would be more field orientated. Boffa Miskell Ltd was commissioned to undertake only the first stage at this point.

Coagulants and flocculants can include polyelectrolytes and conventional inorganic coagulants such as aluminium and iron salts. They are used to remove particulate matter from a variety of waters. Polyelectrolytes are water-soluble polymers based on either synthetic or naturally occurring chemicals. Synthetic polyelectrolytes include polyacrylamides which can be in several charge states (cationic, anionic and non-ionic) and various cationic products, mainly polyamines.

These chemicals have uses other than water clarification, such as dewatering of sludges and dispersants to stabilise suspensions (Murgatroyd et al. 1996). However, in the context of the current review, their use for water clarification is of primary interest. Specifically, it is the effects of their use as an aid in the removal of suspended sediment in earthworks runoff that is of interest. Their discharge in site effluents and clarified waters, to drains, creeks, streams and marine zones are issues of concern to the ARC.

While some of the specific uses of flocculants (e.g. as process chemicals in industrial applications) are of little direct relevance to the present review, many of these chemicals have multiple applications and generic qualities. The studies of potential toxicity of these chemicals allow an informed view to be developed of the risk to the receiving environment as it applies within the Auckland region.

The Polyelectrolyte Suppliers Group, which is a subcommittee of the chemical sector of the Plastics and Chemical Industries Association (PACIA), have produced a Responsible Care Guideline for use of Polyelectrolytes Guidelines (PACIA 1998). Those Guidelines provide a code of practice for the use of polyelectrolytes and the

assessment of environmental risks. It comments that polyelectrolytes are reported in the literature to have a very low mammalian toxicity and are generally considered to be innocuous materials (PACIA 1998).

However, in some circumstances (such as overdosing with chemical flocculants and otherwise inappropriate use which can potentially lead to the release of unbound flocculants), there is a potential and perceived environmental risk. It is this aspect that this review addresses.

1.2 Auckland Regional Council Objectives

The ARC has identified the following objectives (paraphrased) in the overall project description as a guide to issues that needed to be addressed:

- Identify whether flocculated ponds are discharging significant amounts of residual flocculant.
- Identify effects on stream life arising from such discharges.
- Investigate the effects of cumulative discharges of flocculants.
- Evaluate other factors that may affect the performance of flocculant systems (e.g. soil pH, rainfall and lime stabilisation).
- Identify aquatic species sensitive to flocculants.
- Comment on the effects of flocculant discharges to the marine environment.
- If necessary, undertake field trials to investigate residual flocculants and their effects.

2 Methodology

A search for information available on the Internet was undertaken. Water and wastewater treatment companies and local authorities were contacted regarding flocculant products used in their processes, however, their response was generally poor. Chemical supply companies were contacted directly and information obtained on flocculant products, including Material Safety Data Sheets (MSDS). A search of the library catalogues of the Auckland Regional Council library, Auckland City Libraries, and University of Auckland library system was undertaken. The Biological Sciences library was also searched for relevant information.

The specific tasks undertaken for this part of the study were:

- Compile a list of coagulant and flocculant products or product types in use. Compile a dossier of product information including Material Safety Data Sheets (MSDS), where available.
- Review ecotoxicological information and if applicable compare dosed and residual concentrations with ecotoxicity indicators or action levels.
- Provide conclusions on:
 - Environmental risk (low/moderate/high)
 - Identified at-risk animals/plants
 - Bioaccumulation and environmental persistence
 - Recommendations for further investigations.

3 Products in Use

3.1 Polyelectrolytes

Polyelectrolytes are water-soluble macromolecules used in polymer treatment systems on construction sites. They include both primary coagulants and flocculant aids. These are briefly discussed below although for the purposes of this review the distinction is not important.

3.1.1 Coagulants

These are usually cationic (positively charged) and are used in lieu of aluminium and iron salt coagulants. They act by destabilising suspensions by overcoming the repulsion between particles by neutralising the surface charges, allowing particles to adhere and subsequently be removed by settlement. Primary coagulants are mainly polyamines.

3.1.2 Flocculants

These are mainly polyacrylamides (PAMS). PAMS is a generic term. PAMS are made up of many subunits of the monomer acrylamide. Chemical and physical properties differ greatly depending on the specific characteristics of the polymer.

The current generation of PAMS are reported to be ultrahigh molecular weight and moderately anionic (negatively charged) although they can come in various charge states. They are used to cause stabilised particles or coagulated suspensions to form aggregates that can be removed by settlement or filtration.

Different polyelectrolytes have different uses, benefits and limitations. For example, in a draft technical publication prepared for the ARC which presents the findings of field trials on chemical removal of sediment from earthworks stormwater, Larcombe (1999) notes that cationic (positively charged) PAMS are commonly used in municipal wastewater treatment to improve solids removal during pre-settlement. They are also cited as being used in clarification of drinking water and industrial applications including waste and sludge clarification, thickening, dewatering, paper manufacture and mining (Goodrich et al 1991).

It is also noted that the use of groups of these products having different charge classes is not mutually exclusive. For example, an anionic flocculant can be used after a cationic coagulant and serves to neutralise any unreacted coagulant. The actual type and dosage of polymer needed to flocculate sediments is dependant on the types and

levels of sediment in the water. For example, cationic polymers are reported generally to create a more complete flocculation when removing colloidal clays from water (Gannon, undated).

Polyelectrolyte products, or representative product types available are listed in Attachment A.

3.2 Aluminium Coagulants

Aluminium coagulants include aluminium sulphate (alum) and polyaluminium chloride (PAC). Larcombe (1999) comments that inorganic aluminium coagulants have been extensively used in the United States for direct dosing of eutrophic lakes which has achieved significant reductions in suspended matter, nutrients, oxygen demand and turbidity.

Choice of coagulant is dependant on a range of factors that must be assessed on a case specific basis. For example Larcombe (1999) found that alum treatment achieved good sediment removal during storm conditions when the hydraulic capacity of a trial retention pond was exceeded. Thus it could be considered a fairly robust product in that application. PAC is a less acidic product and may be preferred in naturally acidic locations. Larcombe found in field trials that PAC had consistently less effect in terms of pH reduction and concluded that it would have a lesser pH influence in sensitive receiving waters. Floc blocs suffered a number of limitations, but were determined to be effective in small catchments when flow balancing could be achieved before treatment and stormwater runoff was of a consistent quality.

Thus, choice of coagulant is determined partly by the capability of the chemical but also by extrinsic factors such as catchment size, receiving environment sensitivity, stormwater quality, etc.

Larcombe (1999) describes the general action of these coagulants as follows. Addition of the aluminium coagulant to water results in dissolved aluminium ions being incorporated into aluminium hydroxide and aluminium phosphate precipitates. These precipitates combine with phosphorus, suspended solids, metals and other dissolved and suspended matter. The insoluble precipitates are stable and as particle size increases so does density and the aggregates sink.

Aluminium products or representative product types are listed in Attachment B.

4 Potential Toxicity of Coagulants and Flocculants

4.1 Polyelectrolytes

4.1.1 Toxic Action

Despite 30 years of use there are few public and peer reviewed data on the toxicity of polymeric flocculants (ANZECC 2000). Toxicity varies with charge type and flocculant chemistry. The cationic polymers are recognized to pose a potentially significant hazard to aquatic life, particularly fish, but this varies with crustaceans (ANZECC 2000).

The surface of fish gills carries a negative charge to which cationic polyelectrolytes will readily bind due to electrostatic attraction (Murgatroyd et al. 1996). It is likely that sublethal effects and mortality of fish is the result of mechanical suffocation, reduction in oxygen transfer and mucous production on gill surfaces. Impacts on invertebrates are likely to derive from a similar mechanism (that is, interactions with the surfaces of aquatic organisms).

Freshwater Impacts

The toxicity of polyelectrolytes to freshwater organisms varies widely, with reported EC50/LC50 values between 0.04->4,000 mg/l, depending upon ionic state and the particular organisms concerned (e.g.. algae, invertebrates or fish). Cationic polymers are more toxic to aquatic life than anionic or non-ionic polyelectrolytes. For example the median EC50/LC50 values cited by Murgatroyd et al (1996) for invertebrates and fish were 3.9 and 0.89 mg/l respectively. The varying toxicity from cationic polyelectrolytes is explained by differences in charge density, with toxicity increasing as charge density increases.

The non-ionic polymers are considered to be the least toxic. Non-ionic polymers and anionic (i.e. negatively charged) polymers are considered to be the safest and easiest to use (often being in solid form) in environmentally sensitive situations because of their low toxicity.

Marine Impacts

Murgatroyd et al. (1996) in a review, provide a summary of polyelectrolyte toxicity to marine organisms based on very few studies. The data is cited as laboratory based acute studies in which no 'natural substances' such as humic or fluvic acids and clays were added. Therefore the results were considered to represent worse case estimates with respect to aquatic toxicity. That is, much higher field concentrations

could be required to generate a toxic effect but it is likely such concentrations would occur in natural waters.

Notwithstanding these limitations, the EC50/LC50 range for cationic products is cited as 1000-2370 mg/l for fish and for anionic products for fish is cited as >1000 mg/l. No data is presented for non-ionic products. Although the marine studies are so few as to negate valid comparison with the freshwater data, it is noted that the marine values are 1-2 orders of magnitude greater than comparable values for freshwater fish presented by the same authors, which showed median EC50/LC50 of 0.89 and 37.2 mg/l for cationic and anionic products respectively.

The literature accessed in the current review provides no other data or peer reviewed published studies on the effect of residual flocculants in the marine environment. Apart from the study cited above, the toxicological and bioassay studies cited have focused on freshwater species or non-marine species of alga and bacteria. These studies confirm a low level of biological risk in field situations.

Notwithstanding this, there is a strong basis upon which to extrapolate the findings of the non-marine studies in general to the marine environment. Of particular relevance are the generic characteristics of flocculants and their propensity for toxicity to be lessened by particulate and dissolved organic matter including humic substances, and by neutral range pH. Saline water carries a strong signature of these characteristics and it is therefore likely that residual flocculants would be rapidly inactivated. Such bound residuals are stable and do not release or breakdown into toxic components.

Additional to this is the reality that any discharges of residual flocculants are likely to be highly infrequent and of a very small volume relative to the dilution potential of the receiving waters (especially in the coastal marine area).

All in all, notwithstanding the lack of empirical information, there is no reasonable basis upon which to speculate that residual unbound flocculant is likely to cause adverse effects in the marine receiving environment.

4.1.2 Bioaccumulation

Polyelectrolytes are generally of high molecular weights that do not pass across biological membranes. Therefore bioaccumulation does not occur.

4.1.3 Persistence

Polyelectrolytes are highly biodegradable. Biodegradation and abiotic hydrolysis are important processes contributing to the removal and deactivation of polyelectrolytes, especially in alkaline conditions. In a natural water body complete degradation of cationic polymers can be expected to occur within a few weeks. There is little data available on degradation of non-ionic and anionic polymers but the potential toxicity of these is low and is not of concern.

Sorption of the potentially more hazardous cationic polyelectrolytes to dissolved and suspended organic matter and clays is recognized as a particularly important mechanism for the removal of cationic polymers from the water column and for a greatly diminished toxicity risk. Furthermore such binding is thought to be irreversible and bound residues pose no hazard to sediment dwelling biota.

In summary, cationic polyelectrolytes are considered to have a low persistence.

4.1.4 Residual Acrylamide

Polyacrylamides contain residual acrylamide that may be released into the surface waters. Acrylamide monomer (AMD) is a neurotoxin. Murgatroyd et al. (1996) noted that polyacrylamide appeared to be significantly more toxic to invertebrates in the field than would be indicated by laboratory studies of acute exposure. The cause of the toxicity in this case was considered to probably be via a sub-lethal mechanism such as a neurotoxicological effect. Murgatroyd et al. (1996) concluded that the environmental risk of acrylamide is unclear because of lack of data.

However Larcombe (1999) comments that although acrylamide is toxic in field situations, it is present in low concentrations and is completely degraded by bacteria in surface waters. Sojka and Surapaneni (2001) comment that it is considered to be environmentally safe at levels present in polyacrylamide products. Guidelines for PAM use in the United States recommend products with <0.05% AMD. AMD is easily metabolised by micro-organisms in soil and biologically active waters and has a half-life of tens of hours (Lande et al., 1979; Shanker et al., 1990)

4.1.5 Other Relevant Comments on Toxicity

Polyacrylamide (PAM) is described by Sojka and Lentz (1996) as “an environmentally safe industrial flocculant widely used in municipal water treatment, paper manufacturing, food processing and other sensitive applications”.

PAM is used extensively in agriculture in the United States to reduce soil erosion (Sojka and Sudapaneni, 2001). Research in Idaho described by Yonts and Benham (1998) found that less than 5 percent of PAM applied in furrow irrigation left the field in runoff water, and this quickly fell below detection limits (at distances of >1500 yards). These authors state that there was no indication of any adverse impact on soil, plant or aquatic systems when anionic PAM was used for erosion control in this application.

Tobiason et al. (2001) note that effective doses for water and soil treatment are generally an order of magnitude or more below toxic concentrations. Bioassays using daphnids exposed to test-plot runoff treated with 80 mg/l wet-applied PAM solution found no acute or chronic effects attributable to PAM.

In a report on potential use of PAM in Australian agriculture, Sojka and Surapaneni (2001) state that environmental and safety considerations of anionic PAM's have been

thoroughly reviewed by Barvenik (1994), Bologna et al. (1999), and Seybold (1994), and conclude that no significant negative impacts have been reported for aquatic macrofauna, edaphic micro-organisms or crop species when used for erosion control at recommended concentrations and rates. Even in high dose applications effects on biota are greatly buffered due to adsorption and deactivation associated with suspended particles.

Cary *et al.* (1987) in bioassay experiments on the freshwater daphnid (*Daphnia magna*) and the freshwater fish fathead minnow (*Pimophales promelas*) reported bentonite and all of the dissolved organic carbon compounds tested (humic, fulvic, and tannic acids, lignin and lignosite) reduced the toxicities of cationic polymers by one to two orders of magnitude. In that study levels of suspended solids and dissolved organic carbon were representative of environmental conditions. The authors concluded that the results of acute toxicity tests conducted in standard reconstituted laboratory water may be too stringent for estimating the effects of cationic polyelectrolytes in receiving waters. In other words, they suggested that laboratory studies generally overestimate toxicity effects likely to be experienced in the field.

Goodrich et al. (1991) in laboratory bioassay experiments of rainbow trout (*Onchorhynchus mykiss*) similarly found that a strong negative correlation existed between toxicity of cationic polyelectrolytes and humic acid, whereby as humic acid concentration increased toxicity greatly decreased. Residual concentrations tend to quickly adhere to particles in the receiving waters or to channel surfaces. These authors concluded that the physical nature of the receiving waters would determine the actual acute response, in that case for trout. They emphasised that toxicity should be evaluated not only in standardised tests but also under conditions of actual use to obtain reasonable estimates of hazard. Any such studies of toxicity in field situations have not been reported.

Despite good suspended solids removal rates in bench tests, Larcombe (1999) reported major difficulties with the practical use of PAM in field studies of the Albany to Puhoi State Highway 1 motorway extension project (ALPURT) earthworks stormwater. Larcombe commented that because of the high affinity for solids of both anionic and cationic polymers, the remaining concentration in treated waters is very low in all but serious overdose situations. Such low concentrations would effectively avoid a toxicological risk.

Murgatroyd et al. (1996) make a pertinent comment with respect to analysis, to the effect that analytical methods have limits of detection typically in the order of 1mg/l but methods are not specific and are prone to interference from other substances. The implication is that measurement of field concentrations of residual polyelectrolyte is difficult and this situation makes equally difficult controlled toxicity evaluations in the field.

4.2 Aluminium Coagulants

4.2.1 Toxic Action

Aluminium coagulants contain high concentrations of ionic aluminium, the toxic form. Toxicity is very dependant on pH and increases at lower pH. At high pH, most aluminium is present in solid form and is not bio-available. Below pH 6 it is mostly in the dissolved, bio-available form. The bioavailability and toxicity of aluminium is generally greatest in acid solutions and generally most toxic over the pH range 4.4 -5.4 with a maximum toxicity around 5.0-5.2 (ANZECC 2000). However, at pH of 6.5–8.0, which is the normal range for natural waters, there is generally considered to be little threat of toxicity. Where pH of natural waters is outside this range, instream values including fish and invertebrate diversity would tend to be limited in any event, and environmental sensitivity reduced.

In fish the toxic effect is manifest as an accumulation of mucous on gill surfaces, which impairs their function. Aluminium has been implicated in fish mortalities in acidified waters (Baker, 1982). A review by Spry and Weiner (1991) concluded that in low-pH water (i.e. 6-6.5 or less): “both sub-lethal and lethal toxicity of aluminium has been clearly demonstrated in both laboratory and field studies at environmental concentrations”.

Complexing agents including humic substances reduce the bioavailability of aluminium to organisms resulting in lower toxicity.

Larcombe (1999) reported that even at doses in excess of requirements, the dissolved toxic aluminium is reduced in the receiving environment very rapidly to a very low concentration with no serious toxicity implications. Larcombe concluded from dosing trials that the risk of significant adverse effects from discharges associated with aluminium based flocculant materials is low.

While no studies have reported the effect of salinity on the uptake and toxicity of aluminium to estuarine and marine animals, aluminium is relatively insoluble in seawater, where pH normally ranges from 6.5 to 8. Under these conditions insoluble $Al(OH)_3$ is the predominant species and the dissolved aluminium species concentrations, which are responsible for both toxicity and bioavailability, are likely to be low. Discharges containing high concentrations of potentially toxic dissolved aluminium, as might be associated with acidified runoff, should be rapidly rendered non-toxic on entering the marine zone provided dilutions are significant and mixing is relatively rapid.

4.2.2 Bioaccumulation

Conflicting results have been reported on the effect of pH and uptake of aluminium, and hence its bioavailability, in freshwater organisms (ANZECC 2000). Aluminium

forms stable complexes with natural dissolved organic matter (DOM) and this greatly ameliorates its bioavailability. Under a normal pH range of 6.5 to 9 for freshwaters and 6.5 to 8 for marine waters, aluminium can be considered to carry a low risk of bioaccumulation. Runoff from acid soils will tend to enhance bioaccumulation risk if the effect is to reduce pH to below 6.5. Conversely, runoff from alkaline soils will tend to increase pH and thereby reduce such risk. However, in addition to mediating influences such as DOM, other factors need to be taken into account on a site specific basis. For example in an 'acid catchment' the biota may already be limited by or at least robust, in relation to exposure to dissolved metals. It seems unlikely that small scale episodic releases of aluminium based residual flocculant diluted with general catchment runoff would significantly alter the bioaccumulation risk.

4.2.3 Persistence

The biogeochemical cycle of aluminium is complex, yet poorly understood (ANZECC 2000). Research into effects of alum sludge discharged from wastewater treatment plants indicates that dissolved aluminium can be released from sludge under highly acidic conditions (George et. al., 1991). However overseas research indicates that alum sludge is stable under normal pH conditions and pollutants have little or no affinity for release.

Furthermore, aluminium is reported to be tightly bound in alum treated sediment under both reduced and oxidized conditions and at pH ranges between 5-7 (Larcombe, 1999). Larcombe (1999) reports that alum floc is not toxic to benthic organisms and small planktonic crustaceans present in sediment pond water showed no toxicity during coagulation and settlement periods.

Aluminium toxicity is reduced by calcium and dissolved organic carbon. The use of lime for soil stabilisation would have the effect of increasing water pH and thereby decrease aluminium toxicity. There is also evidence of acclimation (i.e. increase in resistance or tolerance) of fish to aluminium (Spry and Weiner, 1991). Fish in waters with high background concentrations of aluminium may therefore have enhanced resistance to episodic increases.

4.3 pH

Both polyacrylamides and aluminium flocculants can lower water pH, which can have direct pH effects and also potentially increase the toxicity of metals through making them more bio-available. The mechanism for this bio-availability is of some interest because it emphasises that the alkalinity of the receiving waters has an important bearing on toxicity potential.

In a study of metal bio-availability and toxicity to fish in low alkalinity lakes, Spry and Weiner (1991) commented that the greater bioaccumulation potential comes not only

from the greater aqueous abundance of metals in such waters but also as a result of low concentrations of aqueous calcium increasing the permeability of biological membranes to metals. This emphasises that the quality and character of the receiving water (e.g. its hardness) can have an important influence on toxicity potential.

The responses to pH of nine fish species and one shrimp native to New Zealand freshwaters were investigated by West *et al.* (1997). Most of the species preferred pH values between 6.5 to 9.5, although shortfinned eiders (*Anguilla australis*), koaro (*Galaxias brevipinnis*), and banded kokopu (*G. fasciatus*) did not avoid water of low pH. The response of most fish to pH within the normal range for streams appears to be weak.

Where potentially toxic concentrations of heavy metals are present, low pH could potentially facilitate adverse effects on biota by increasing the dissolved, bioavailable fraction of metals and therefore increasing the toxicity of metals. Where metal concentrations are below guideline concentrations in the receiving environment, toxic effects would be unlikely irrespective of the pH. In other words, for pH to be a potentially important factor, the environment into which the residual flocculant is to be discharged would have to be heavily polluted in the first instance.

Effects of pH are also discussed by Harding *et al.* (2000). They note that New Zealand invertebrates appear to be relatively tolerant, but that molluscs are likely to be a relatively sensitive group. Changes in pH can also reduce or increase periphyton biomass, but such effects are poorly understood. Notwithstanding this, because few streams in the Auckland Region are stony-bottomed and primarily periphyton driven, such effects are unlikely to be significant.

The concentration of dissolved aluminium increases as pH lowers below 6.5. Larcombe (1999) observed that concentrations did not increase rapidly until pH decreased below 5. Larcombe (1999) recommended that discharges from treatment devices such as settlement ponds, having a pH below 5.5 should be avoided. However, Larcombe (1999) concluded that even in relatively acidic clay soils, flocculant dosing is unlikely to reduce pH to such levels. There is a risk associated with overdosing, and appropriate management or quality assurance procedures should be instituted to minimise such risks.

5 Residual Concentrations, Ecotoxicity Indicators and Action Levels

ANZECC (2000) reports that there are insufficient data to develop guideline trigger levels for polyelectrolytes, particularly given the range of polymer types. ANZECC (2000) recommended that because polyelectrolytes cannot usually be measured in water (particularly in field situations), discharges are best controlled by best management practices and other appropriate source controls.

At a local level, a series of trials of several aluminium based flocculant products was undertaken by Larcombe (1999), to determine practicality of application, optimal doses, effectiveness of sediment removal, effects on pH, and concentrations of dissolved aluminium in bench tests and discharges from stormwater treatment ponds. Relevant results are summarised below.

5.1 Alum

Alum was tested in a catchment with major cut and fill in limestone (Onerahi chaos) soils. The aluminium dose rate was 5.5 mg/l. Dissolved aluminium in the discharge from the retention pond averaged about 0.1mg/l, and was often lower than the dissolved aluminium concentration at the inflow to the pond from the site. The runoff pH at the site was between 7.9 and 8.2, and the treatment reduced the pH by about 0.5 pH units (Larcombe, 1999).

Bench testing undertaken by Larcombe (1999) showed that the addition of aluminium at up to 12.6 mg/l did not result in any increase in the dissolved aluminium concentration in the reacted sample after a 1 hour settlement period.

5.2 PAC

Because of the presence of clay soils with high natural acidity in the ALPURT highway project the use of polyaluminium chloride was investigated (PAC is less acidic than alum).

The dissolved aluminium concentrations in the outflows from treated ponds ranged from 0.010 – 0.084 mg/l, and were lower in most of the pond outflows than in the inflows. Concentrations were lower than the applicable USEPA criteria. The dissolved aluminium concentration in an untreated control pond was much higher.

Bench tests confirmed that PAC had consistently less effect in reducing pH than alum. Trials for stormwater ponds showed an obvious reduction in three of the four treated ponds. Inflow concentrations ranged from 6.81 to 9.97, and outflow concentrations from 5.47 to 7.62 mg/l.

5.3 PAM

Bench testing of a number of liquid polyacrylamide (PAM) formulations achieved good removal of suspended solids from ALPURT sector B1 stormwater but major difficulties were identified with the use of liquid PAM for dosing of stormwater on remote sites. These problems arose primarily due to the highly viscous form of liquid PAM concentrates. This required pre-dilution of the concentrates, which generated the need for special mixing equipment, storage tanks and electric power. Pre-diluted PAM still retained a high viscosity and had a limited storage life.

A solid form (the Floc Bloc) was tested but problems were also encountered. These problems included blocs deteriorating, flow channels in which the blocs were deployed becoming clogged, and difficulty in achieving effective dosing under storm flows.

Sokja and Lentz (1996) carried out studies, which also emphasised the inherent difficulties but importance of achieving uniform PAM dissolution and distribution. They focused on the use of PAM as a conservation measure mitigating irrigation induced erosion, reporting on PAM use where small amounts of PAM were dissolved in irrigation water used in furrow irrigation in the U.S.A. In that case the PAM copolymer utilised was a dry granulate which was used to prepare a liquid stock solution. The authors noted that similar products are available worldwide. The PAM's were metered into the irrigation supply ditches either as a concentrated stock solution, or as dry granules.

The authors emphasised that if dry granules were used then methods needed to also be used to promote the uniform dissolution and distribution of PAM. They emphasised that no untreated water should wet the furrows ahead of the flows treated with PAM, as this greatly reduced the PAM's effect. While the findings of Sokja and Lentz (1996) confirm the effectiveness of PAM's in that particular application they also emphasise the general situation that effectiveness is very much a function of the ability to control dosage and delivery systems.

5.4 Summary

In conclusion, the bench tests and field trials reported by Larcombe (1999) showed that alum had a greater effect on pH than PAC. Outflow concentrations of aluminium for the PAC trials were generally lower than the inflows and lower than USEPA chronic toxicity criteria (0.087 mg/l, 4 day average not to be exceeded in waters with pH 6.5-9.0).

Sensitivity of native biota to pH and heavy metals is discussed by Harding et al. (2000) and Hickey (2000). New Zealand biota generally appear to be tolerant to these stressors although there is some evidence of effects in streams receiving mine drainage. Molluscs are identified as potentially sensitive to low pH. The most sensitive organisms to metals were the cladoceran *Ceriodaphnia dubia* and amphipod *Paracalliope fluviatilis*, while the mayfly *Deleatidium* sp. was fairly sensitive. Sensitivity of New Zealand aquatic insect species has not been assessed in specific relation to aluminium.

However, from the limited available studies on other metal species, it appears unlikely that any species or groups of key ecological significance will be sensitive to potential toxicants released from treated ponds.

Lime stabilisation works would tend to increase pH and therefore buffer the effects of flocculants on pH, and also reduce aluminium toxicity.

6 Other Considerations

In addition to the complexities of the variable chemistry associated with the wide range of flocculants, the factors governing the potential for effects are themselves complex. Such effects include: soil type; the spatio/temporal proximity of discharges; natural discharge and dilution scenarios; the specific ecological characteristics of local receiving environments; the natural mitigative chemistry of the receiving environment that would deactivate flocculants (e.g. total organic carbon, suspended and colloidal material and clay surfaces), and the value placed on those waters by the community.

Where there are concerns regarding multiple and perhaps cumulative discharges, further investigations or monitoring might at first glance seem warranted. However, given the problematic analysis of polyelectrolytes and the general absence of any strong body of evidence establishing significant adverse effects in the field, best management practice and source controls would still seem the most cost effective way of ensuring that chemical treatment avoids adverse off-site water quality effects.

7 Conclusions

In light of their low toxicity, anionic and non-ionic polymers are recognised as the safest to use and would be the most appropriate where a particular receiving environment was regarded as a sensitive location. Sensitivity could be based on a variety of values including ecological (e.g. important native fish stocks); chemical (e.g. high natural acidity); cultural; or perceptual.

Cationic polymers are widely recognised as having a high toxicity under laboratory conditions in pure waters. However there is a large body of evidence verifying that under natural conditions this toxicity is greatly mitigated by natural organic compounds and natural surfaces.

In relation to the ARC Objectives outlined in Section 1.2 of this report, the following summary comments can be made at this point.

- *Identify whether flocculated ponds are discharging significant amounts of residual flocculant.*

This has not been empirically determined for polyelectrolytes at this point. Based on the review of the literature including the Larcombe (1999) work, it is unlikely that significant quantities of unattached (residual) flocculant are released from treatment ponds, provided that organic polymer treatment chemicals or aluminium based flocculants are being used as prescribed for the particular product in use.

In so far as polyelectrolytes are concerned, there are in any event insufficiently well developed analytical techniques to enable levels of discharged flocculant to be reliably identified let alone measured.

In laboratory studies, acute effects have been shown to be the main response. However, in relation to dissolved aluminium, Larcombe (1999) found that concentrations in the outflow of treated ponds were below the USEPA chronic criterion and therefore also well below the acute threshold.

- *Identify effects on stream life arising from such discharges.*

It follows from the above that this cannot be done directly for polyelectrolytes. The literature provides no strong body of evidence documenting adverse effects in the field or data that would suggest such effects are likely. Significant effects are unlikely to be occurring and therefore are not a significant issue.

- *Investigate the effects of cumulative discharges of flocculants.*

The same comments apply.

➤ *Evaluate other factors that may affect the performance of flocculant systems (e.g. soil pH, rainfall and lime stabilisation).*

Many factors can affect the performance of flocculants. These need to be assessed on a case by case basis in relation to the particular capabilities and applications of individual products, of which there are many. Most importantly the type and dose of polyelectrolyte required for a particular application needs to be determined by either laboratory tests (e.g. jar tests) or site-specific field trials or both. These would take into account the ability to deliver the flocculant to the target water body under the expected range of hydraulic and water quality conditions. Lime stabilisation works would tend to increase pH and therefore buffer the effects of flocculants on pH, and also reduce aluminium toxicity in relation to the particular characteristics of the particulates to be settled. No general conclusions can be offered that would be of assistance in the context of the present review.

➤ *Identify aquatic species sensitive to flocculants.*

There has been no specific systematic comparative study of New Zealand species. Overseas laboratory based research suggests that fish are the most potentially sensitive group and cationic polymers are the flocculant group of most concern. Crustaceans have also been shown to be sensitive but like fish only under laboratory conditions.

➤ *Comment on the effects of flocculant discharges to the marine environment.*

In the ARC region, stormwater treatment ponds may frequently be close to estuarine and marine receiving environments.

Murgatroyd et al. (1996) in a review, provide a summary of polyelectrolyte toxicity to marine organisms based on very few studies. The data is cited as laboratory based acute studies in which no 'natural substances' such as humic or fulvic acids and clays were added. Therefore the results were considered to represent worse case estimates with respect to aquatic toxicity. That is, much higher field concentrations could be required to generate a toxic effect but it is likely such concentrations would occur in natural waters.

Notwithstanding these limitations, the EC50/LC50 range for cationic products is cited as 1000-2370 mg/l for fish and for anionic products for fish is cited as >1000mg/l. No data is presented for non-ionic products. Although the marine studies are so few as to negate valid comparison with the freshwater data, it is noted that the marine values are 1-2 orders of magnitude greater than comparable values for freshwater fish presented by the same authors, which showed median EC50/LC50 of 0.89 and 37.2 mg/l for cationic and anionic products respectively.

The literature accessed in the current review provides no other data or peer reviewed published studies on the effect of residual flocculants in the marine environment. Apart from the study cited above the toxicological and bioassay studies that have been cited have focused on freshwater species or non-marine species of alga and bacteria. These studies confirm a low level of biological risk in field situations.

Notwithstanding this, there is a strong basis upon which to extrapolate the findings of the non-marine studies in general to the marine environment. Of particular relevance are the generic characteristics of flocculants and their propensity for toxicity to be lessened by particulate and dissolved organic matter including humic substances, and by neutral range pH. Saline water carries a strong signature of these characteristics and it is therefore likely that residual flocculants would be rapidly inactivated. Such bound residuals are stable and do not release or breakdown into toxic components. Additional to this is the reality that any discharges of residual flocculants are likely to be highly infrequent and of a very small volume relative to the dilution potential of the receiving waters (especially in the coastal marine area).

All in all, notwithstanding the lack of empirical information, there is no reasonable basis upon which to speculate that residual unbound flocculant is likely to cause adverse effects in the marine receiving environment.

- *If necessary, undertake field trials to investigate residual flocculants and their effects.*

Field trials to determine concentrations of unbound residual flocculant and/or to assess toxicity response are not recommended and are considered unwarranted based on the low level of environmental risk associated with residual flocculant releases.

References

- ANZECC (2000) Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Volume 2. Aquatic Ecosystems. Rational and Background Information.
- Baker, J.P. (1982) Effects on Fish of metals Associated with acidification. In: Acid Rain/Fisheries: Proceedings of an International Symposium on acidic precipitation and fishery impacts in north-eastern North America ed. R.E. Johnson, America Fisheries Society, Bethesda, Maryland, pp. 165-76.
- Barvenik, F.W. (1994) Polyacrylamide characteristics related to soil application. Soil. Sci. 58: 235-243.
- Biesinger, K E, Lemke, A E, Smith, W E and Tyo, R M (1976) Comparative Toxicity of Polyelectrolytes to Selected Aquatic Animals. Jnl. Water Pollution Control Fed 48: 183-187
- Biesinger, K E and Stokes, G N (1986) Effects of Synthetic Polyelectrolytes on Selected Aquatic Organisms. Jnl. Water Pollution Control Fed 58: 207-213
- Bologna *et al.* (1999) Analysis of Residual Acrylamide in Field Crops. Journal of Chromatographic Science, 37: 240-244
- Cary, G A, McMahon, J A and Kuc, W J (1987) 'The Effect of Suspended Solids and Naturally Occurring Dissolved Organics In reducing The Acute Toxicities of Cationic Polyelectrolytes To Aquatic Organisms'. Environmental Toxicology and Chemistry, Vol 6, pp 469- 474
- Gannon, (undated) 'A Review of Sediment Control Measures'. [http://www.forester.net/ec-9911-review sediment.html](http://www.forester.net/ec-9911-review%20sediment.html)
- George *et al.* (1991) Alum Sludge in the Aquatic Environment. AwwaRF Research Project. <http://www.awwarf.com/exsums/90582.html>
- Goodrich, M S, Dulak, L H, Friedman, M A and Lech, J J. 'Acute Toxicity of Water Soluble Cationic Polymers to Rainbow Trout (*Oncorhynchus mykiss*) and the Modification of Toxicity By Humic-Acid.' Environmental Toxicology and Chemistry, 10, 509-515.

- Harding, J.S., J.M. Quinn and C.W. Hickey (2000) Effects of Mining and Production Forestry. In: Collier, K.J. and Winterbourn, M.J. New Zealand Stream Invertebrates: Ecology and Implications for Management. New Zealand Limnological Society. 415pp.
- Hickey, C. (2000) Ecotoxicology: Laboratory and Field Approaches. In: Collier, K.J. and Winterbourn, M.J. New Zealand Stream Invertebrates: Ecology and Implications for Management. New Zealand Limnological Society. 415pp.
- Krautter, G R, Mast, R W, Alexander, H C, Wolf, C H and Thompson, C M (1986) Acute Aquatic Toxicity Tests with Acrylamide Monomer and Macroinvertebrates and Fish. *Env. Toxicology and Chemistry* 5 : 373-377
- Lande *et al.* (1979) Degradation and Leaching of Acrylamide in Soil. *J. Environ. Qual.* 8: 133-137.
- Larcombe, M.F. (1999) Technical Publication on Chemical Removal of Sediment from Earthworks Stormwater. Draft Auckland Regional Council Technical Publication, September 1999.
- Letterman, RD and Per, R W (1990) Contaminants in Polyelectrolytes Used in Water Treatment. *Jnl. Am. Water Works Assoc.* 82 : 87-97.
- Mallevalle, J, Bruchet, A and Fiessinger, F (1984) How Safe Are Organic Polymers in Water Treatment. *Jnl. Am. Water Works Assoc.* 76 : 87-93
- McDonald, R A (1971) Use of a Polyelectrolyte to Reduce Soil Turbidity in Two Fish Ponds and Effects on Plankton, Benthos and Fishery. Unpub – cited in Biesinger & Stokes (1986)
- Murgatroyd, C; Barry, M; Bailey, K and Whitehouse, P. A review of Polyelectrolytes To Identify Priorities for EQS Development. Environment Agency. Foundation for Water Research, Allen House. The Listons. R & D Technical report P21.
- Narkis, N and Rebhun, M (1975) The Mechanism of Flocculation Processes in the Presence of Humic Substances. *Jnl. Am. Water Works Assoc.* 67 : 101-108
- Responsible Care Guidelines For Use Of Polyelectrolytes, Polyelectrolyte Suppliers Group, Plastics and Chemical Industries Association (PACIA). (January 1998)
- Seybold, C.A. (1994) Polyacrylamide Review: Soil Conditioning and Environmental Fate. *Comm. Soil. Sci. Plant. Anal.* 25: 2171-2185.

- Shanker *et al.* (1990) Microbial degradation of acrylamide monomer. *Arch. Microbiol.* 154: 192-198.
- Sojka, R.E. and A. Surapaneni, (~2001) Potential Use of Polyacrylamide (PAM) in Australian Agriculture to Improve Off- and On-Site Environmental Impacts and Infiltration Management.
- Report to the Australian Land and Water Resource Research Development Council, the Institute for Sustainable Irrigated Agriculture, Goulburn-Murray Water, and USDA Agricultural Research Service. <http://kimberly.ars.usda.gov/Sojka/Oz/OzPAMUSA.htm>
- Sojka, R.E., R.D. Lentz, D.L. Bjorneberg, and J.K. Aase (1998) The PAMphlet: a concise guide for the safe and practical use of polyacrylamide (PAM) for irrigation-induced erosion control and infiltration enhancement. Northwest Irrigation and Soils Research Lab, USDA-Agricultural
- Sojka, R.E. and R.D. Lentz (1996) Polyacrylamide in Furrow Irrigation, an Erosion Control Breakthrough. Reproduced from article of same name in: *Proceedings of the First European Conference and Trade Exposition on Erosion Control. Lecture Book Vol.1*, pp 183-189. 29-31 May, 1996. <http://kimberly.ars.usda.gov/images/spain/spain.htm>
- Soponaporn, T and Gehr, R (1989) The Degradation of Polyelectrolytes in the Environment: Insights Provided by Size Exclusion Chromatography Measurements. *Water Science and Technology* 21 : 857-868
- Spraggs, L D, Gehr, R and Hadjinicolaou, J (1982) Polyelectrolyte Toxicity Tests by Fish Avoidance Studies. *Water Science and Technology* 14 : 1564-1567
- Spry D.J. and J.G. Wiener (1991) Metal Bioavailability and Toxicity to Fish in Low-Alkalinity Lakes: A Critical Review. *Environmental Pollution* Vol. 71: 243-304
- Yonts, C.D. and B. Benham (1998) Polyacrylamide – A Method to Reduce Soil Erosion. Published by University of Nebraska in cooperation with the United States Department of Agriculture. <http://www.ianr.unl.edu/pubs/water/g1356.htm>
- Tobiason, S., D. Jenkins, E. Molash, and S. Rush (2001) Polymer Use and Testing for Erosion and Sediment Control on Construction Sites. *Erosion Control*, January/February 2001. http://www.forester.net/ec_0101_polymer.html

West, D.W., J. A. T. Boubée, and R.F.G. Barrier (1997) Responses to pH of Nine Fish and One Shrimp native to New Zealand Freshwaters. *New Zealand Journal of Marine and Freshwater Research*, Vol 31: 461-468.

- Appendix A

Polyelectrolyte Product Types

- Appendix B

Representative Aluminium Product Types