

THE FORMATION, FATE, AND EFFECTS OF “FLOC” FROM ACID MINE DRAINAGE IN STREAM WATERS

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ABSTRACT

The neutralising process associated with buffering of waters when acid mine drainage (AMD) is mixed with natural waters of higher pH (e.g. pH 7 or above) results in the formation of precipitated material that is described as floc due to its characteristic finely dispersed and fluffy nature. Flocs have high specific surface areas and can promote sorption of heavy metals and other contaminants present in the acid mine drainage. When floc is extracted with solutions of decreasing pH the release of occluded metals will be restricted because of the excess base that is present until completely consumed by the reconstituting acid. Floc materials are demonstrated to be highly stable, and unlikely to remobilize metals in the down gradient streams in the tested pH range down to pH 4. The likely effects of sediment containing floc on species of aquatic biota can be predicted by extraction with 1M hydrochloric acid and comparison of metal concentrations with ANZECC sediment guidelines. A case study involving floc dispersion that showed some guideline values were exceeded for metals in sediment was able to demonstrate that there was no sustained effect downstream of a mine by comparing sediment toxicity with both upstream and downstream sites.

1.0 INTRODUCTION

The neutralising process associated with buffering of waters when acid mine drainage (AMD) is mixed with natural waters of higher pH (e.g. pH 7 or above) results in the formation of precipitated material. This material is termed floc due to its characteristic finely dispersed and fluffy nature. The colloidal precipitation of flocs can range in colour from yellow and red, to white and green forms when the acidic effluents enriched in dissolved aluminium and iron mix with near neutral surface water. Flocs have high specific surface areas and can promote sorption of heavy metals and other contaminants present in the acid mine drainage. The formation of floc is also an integral part of active AMD treatment (Jang et al., 2010).

The aim of the current study is to examine metal sequestration by aluminium flocs by understanding processes that form and neutralise acid mine drainage and to assess the effect of floc on aquatic biota in downstream sediment.

2.0 THE FORMATION, NATURE AND EFFECTS OF FLOC

The flocs in the current case study are mainly aluminium-rich precipitates from neutralisation of more acidic water. Aluminium hydroxide floc has been found to usually consist of 3 components: suspended solids hydrolysed poly-metal ions, and water trapped within the floc during floc growth (Tambo and Watanabe, 1979). The formation

of colloidal $\text{Al}(\text{OH})_3$ during the neutralization of acidic solutions has been, to some extent, described in previous field and laboratory studies (Nordstrom and Ball, 1986; Kimball et al., 1995). When metal-rich acidic runoff from mining sites travels through more alkaline streams or river water, fluffy flocs of suspended solids form because the solubilities of Al^{3+} , and other metal ions such as Fe^{3+} , are greatly reduced (Stumm and Morgan, 1996). With large changes in pH, hydrolysis of aluminium is a rapid process that produces predominantly amorphous colloids, which slowly aggregate and eventually form precipitates (Lydersen et al., 1991). The aluminium precipitates from solution at $4.2 < \text{pH} < 4.9$ as either x-ray amorphous $\text{Al}(\text{OH})_3$ or microcrystalline gibbsite.

The colloidal aluminium precipitates and other metals that coprecipitate or adsorb to them, such as copper, lead, and zinc, can be transported long distances before they are lost from the water column to the stream bed (Kimball et al., 1995). The stability of surface complexes is highest for Pb^{2+} , followed by Cu^{2+} , Zn^{2+} and Ca^{2+} (Hochella et al., 1999). When colloids aggregate, they may fill interstices in the stream bed and reduce the quality of habitat for benthic invertebrates and aquatic plants (McKnight and Feder, 1984; Malmqvist and Hoffsten, 1999; Niyogi et al., 1999). Colloidal metals that accumulate on the stream bed can enter the food chain through grazing by benthic organisms, which can subsequently be taken up through the food chain and produce toxic effects when consumed by fish (Woodward et al., 1995; Mayer et al., 1996). In the water column, colloidal aluminium can be more toxic to fish than the dissolved metal (Witters et al., 1996).

In a breakthrough study on the nature of floc, Furrer et al. (2002) showed that the aluminium floc commonly found in polluted streams originates mainly from condensation of Al_{13} molecules that forms rapidly and then aggregated as pH of the effluent increased to more than 5. Al_{13} is an aqueous polyoxycation $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$ (aq). It is thought that the flocs form by aggregation of monomeric aluminium complexes into an $\text{Al}_6(\text{OH})_{12}(\text{H}_2\text{O})_{12}^{6+}$ multimer that is structurally similar to dioctahedral sheets of gibbsite" (Furrer et al., 2002). Although equilibrium calculations give no information about disequilibrium pathways, they showed by field sampling and experimental work that aluminium-rich acidic waters pass through the Al_{13} metastability field during mixing with pristine surface water. At the typical conditions of AMD decomposition of Al_{13} molecules takes hundreds of hours. Previously it was thought that Al_{13} was quite rare. This is important because Al_{13} is ecotoxic and is probably responsible for the decline of fish populations in streams (Furrer et al., 2002).

3.0 EXPERIMENTAL TECHNIQUES

3.1 Sediment sample collection and analysis

A case study was undertaken to assess the presence, dispersion characteristics and effect of heavy metals in floc from mining activity in sediment at a sub-tropical location in northern Australia. The key approaches of comparison chemical guidelines and ecotoxicity following the decision tree of ANZECC (2000) for sediment were used to assess the effect of floc in downstream sediment.

Sampling locations were located on the main streams draining a rehabilitated mine site, at and down-gradient of the mine lease boundary, and included 6 sites on the main downstream rivers and 9 sites on creeks below the mine lease (Figure 1). The pH of creek and river water was consistently high (> 7.0) and associated with higher

conductivity at the mine lease boundary compared with upstream and downstream sites. Dissolved Oxygen concentration was low when water had limited or no flow.

Total digestion metal concentrations (USEPA aqua regia method) and acid leaching of sediment was determined in the < 63 µm fraction by ICP-AES and analysed by ALS Laboratory Group. In the case of exceedance of the ISQG-low guideline value (Table 1), the next step in the decision tree approach given in Figure 1 is to undertake acute toxicity assessment. Ecotoxicity testing was undertaken on sediment samples by Ecotox Services Australasia Pty Ltd, Lane Cove, N.S.W. as described below. Floc samples were collected at downstream Creek 2 and Creek 3 for the floc pH leaching experiment using hydrochloric acid solutions of fixed pH 6.5, 5.5, 4.5 to leach floc in sequence.

3.2 ANZECC guideline approach for sediment

The Australian Government has developed guidelines for the protection of aquatic ecosystems for both water and sediment. The objective adopted by ANZECC (2000) for the protection of aquatic ecosystems, and clearly of relevance to the case study, is to maintain and enhance the ecological integrity of freshwater ecosystems, including biological diversity, relative abundance and ecological processes. A procedure for the development of appropriate sediment quality assessments is given as a decision tree in the ANZECC (2000) guidelines (Figure 2). Interim Sediment Quality Guidelines (ISQGs) (Table 1) are trigger values that, if exceeded, prompt further action as defined by the decision tree. The two kinds of trigger levels that are indicated are: (i) ISQG-High which is defined as the probable-effects concentrations below which biological effects in sediment would possibly occur; and above which effects in sediment would be expected to frequently occur; and (ii) ISQG-Low which is defined as the probable-effects concentration below which biological effects in sediment would rarely occur.

As a first step, the total contaminant concentrations are compared with the ISQG-High and ISQG-Low trigger values (Table 1). If the low trigger value is exceeded and the concentration is greater than background levels, then management/remedial action or further investigation is required. Further investigation should consider the fraction of the contaminant that is bioavailable or can be transformed and mobilized into a bioavailable form allowing comparison of contaminant concentrations adjusted for bioavailability with the ISQG-Low trigger value (Figure 2). In the case of metals and metalloids, the estimate of the bioavailable concentration by extraction with dilute acid, e.g. 1M hydrochloric acid (HCl), (ANZECC 2000) is likely to be a more meaningful measure than the total contaminant concentration. When the ISQG-Low trigger value is exceeded by the concentration once adjusted for predicted bioavailability, acute and chronic toxicity testing can be undertaken (Figure 2). Toxicity testing then enables the response of the test organism to the bioavailable fraction to be assessed.

The Australian (ANZECC 2000) guidelines identify the need to protect species that have special significance in the aquatic ecosystem and recommend that a suite of organisms be used for aquatic testing purposes. Use of a minimum of 5 taxa is required for water comprising an invertebrate, a fish and an alga. For sediment the identification of suitable end or test species is not clear. Selection of suitable test aquatic organisms for toxicity testing is governed by the available test species and fully-validated test methods that conform to USEPA, OECD and ASTM guidelines. For aquatic toxicity testing purposes, it is normally accepted that sensitive end-point species are identified that occupy key steps in the trophic chain (USEPA, 1998).

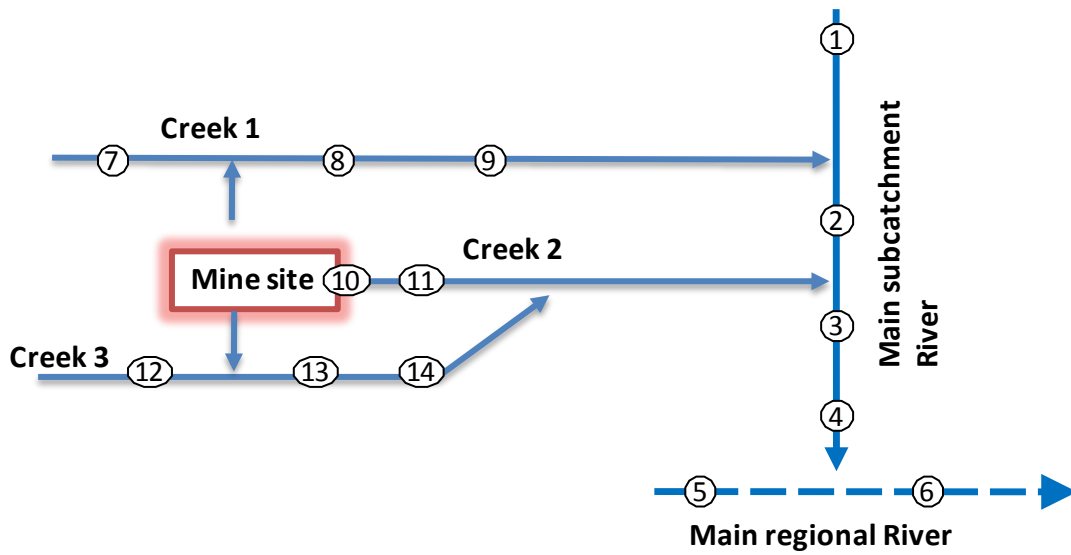


Fig. 1. Schematic of sampling locations

Table 1. ANZECC (2000) ISQG-Low and ISQG-High trigger values for sediments

Metal/ Metalloid	Sediment ISQG-Low	Sediment ISQG-High
Antimony (Sb)	2	25
Arsenic (As)	20	70
Cadmium (Cd)	1.5	10
Cobalt (Co)	NA	NA
Copper (Cu)	65	270
Lead (Pb)	50	220
Manganese (Mn)	NA	NA
Nickel (Ni)	21	52
Zinc (Zn)	200	410

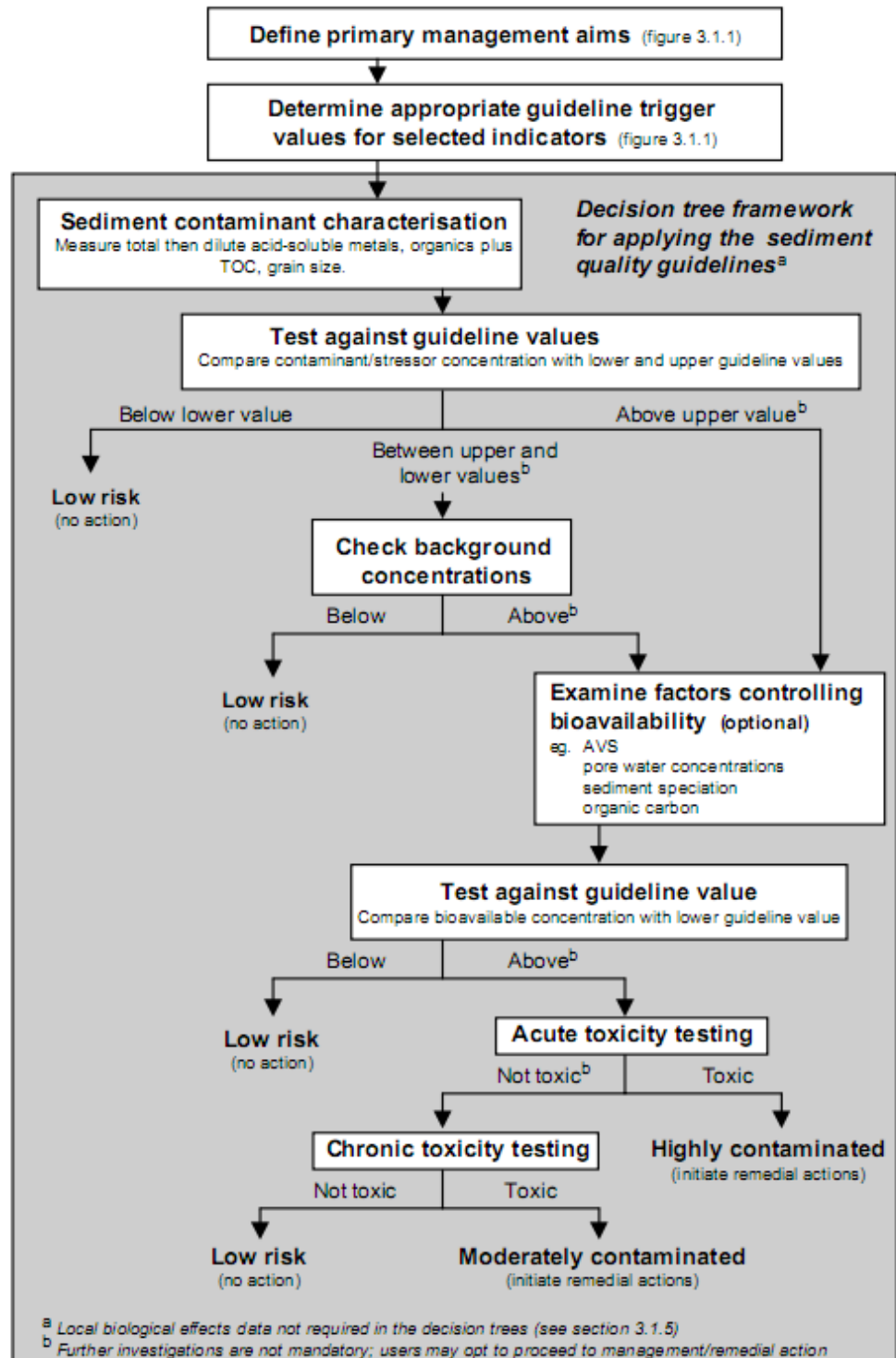


Fig. 2. Decision tree for the assessment of contaminated sediments (ANZECC, 2000)

There is a current lack of fully-validated test methods for tropical aquatic sediment macroinvertebrates in Australia that conform to USEPA (1994), ASTM (1994) and OECD (2004) for sediment toxicity. The 10-day whole sediment survival toxicity test using the estuarine amphipod *Corophium* spp., based on the method described by Surtikanti and Hyne (2000) and USEPA (1996). *Corophium* spp. is a burrowing organism that is compatible with the high pH found in sub-tropical north Australian inland river waters.

An alternative method is the 48-hour acute (survival) toxicity test using the freshwater cladoceran *Ceriodaphnia cf dubia* and/or 72 hr IC50 % concentration of cells for the green alga *Selenastrum capricornutum* based on USEPA (1993). This species exists and emerges in water and can be a food source to higher species including fish. Tests can be conducted on elutriate prepared from the dry sediment according to the US EPA procedure (US EPA, 1991), where sediment is mixed with dilution water at a ratio of 1:4, stirred and allowed to settle for two hours prior to preparation of a dilution series and seeding with test organisms.

Both methods appear to be good for application of model organisms to assess sediment toxicity. However, lack of the minimum recommended number of species by ANZECC (2000) indicates that the additional test species are required to assess potential toxicity of sediments. Since fish are not applicable to aquatic toxicity testing of dried river sediment, alternative species are needed.

Sediment toxicity testing using 2 test species in creek sediments (10 day whole sediment survival toxicity test using the amphipod *Corophium* spp. and 48 hour acute survival test on water elutriate of sediment using the freshwater Cladoceran (*Ceriodaphnia cf dubia*), collected from all 14 sites is described in Table 3.

Samples were received chilled in Sydney and water quality was consistent with field sample measurements and analyses. Dissolved oxygen remained high in test waters during trials.

4.0 RESULTS

Table 2 gives result for total concentrations of heavy metals and arsenic in the < 63 µm fraction of sediment from some of the sites. Some results for heavy metals and arsenic had higher concentrations than the ISQG-low (Table 1) and led to following further steps in the decision tree for sediment (Figure 2).

The results for the floc pH leaching experiment are given in Table 3 together with total concentrations of metals and metalloids in floc. These extracts show that the proportions of heavy metals and arsenic that are removed from sediment / floc by dilute acid are very low. This simulates the process of natural pH of creek water decreasing from the summer transition to winter and spring and provides predictive information about likely effects in the aquatic system. The metal and arsenic leaching results also indicate that the concentrations when compared against the ISQG-low as estimates of bioavailable concentrations are not likely to exceed the guideline values.

The results for the 10-day whole sediment survival toxicity using the estuarine amphipod *Corophium* spp. are given in Table 4 and show no toxicity effects when compared with the variability of the laboratory control (>85%). All samples

Table 2. Mean metal and arsenic concentrations in sediment (< 63 µm fraction, total digestion)

Location	Arsenic (mg/kg)	Cadmium (mg/kg)	Copper (mg/kg)	Lead (mg/kg)	Zinc (mg/kg)	Mercury (mg/kg)
Upper main sub-catchment river n=1	<5	<1	<5	<5	<5	<0.1
Creeks above mine Mean± se	<5	<1	12.8±10.3	15.3±12.8	25.3±22.8	<0.1
Creeks at Mine Lease Mean± se	7.8±5.3	0.8±0.3	40±22	22.3±19.8	168±72	<0.1
Creeks below Mine Lease Mean± se	11.5±6	1.2±0.4	110±72.8	27.5±13.8	362.3±183.9	<0.1

tested for 48 hour acute survival test on water elutriate of sediment using the freshwater Cladoceran (*Ceriodaphnia cf dubia*) showed 48 hr EC50 > 100 % (NOEC = 100% and LOEC = > 100%) indicating no toxicity.

5.0 DISCUSSION

The whole of sediment data geochemistry in Tables 2 and 3 can be compare against the results of the toxicity tests for sediment and elutriate. A comparison with the sediment toxicity results (Table 4) with the data in Table 2 shows that the predicted sediment toxicity that can be associated with the presence of zinc and copper was not apparent. The leaching study results for floc provide support for the hypothesis that metals in floc associated with sediment will be less toxic to aquatic biota due to minimal release of metals at the prevailing pH.

When floc is extracted with solutions of decreasing pH the release of occluded metals will be restricted because of the excess base that is present until completely consume by the reconstituting acid. Floc materials are demonstrated to be highly stable, and unlikely to remobilize metals in the down gradient streams in the tested pH range down to pH 4. The likely effects of sediment containing floc on species of aquatic biota can be predicted by extraction with 1M hydrochloric acid (Figure 2; ANZECC 2000). However confirmation of a predicted toxicity response from floc in sediment would be more fully confirmed via a dose response estimation of the effects on test aquatic species.

Aquatic toxicity testing upstream and downstream of the mine can significantly improve the capacity to assess environmental impacts from mine water releases involving floc formation following a release and in demonstrating long term recovery.

At ephemeral sub-tropical locations, many aquatic invertebrates have developed strategies to survive by burrowing down to the saturated sediment in permanent interstitial water and contaminants. This is a key detail for selection of suitable sub-

Table 3. Sequential leaching of metals at decreasing pH from floc collected at Creek 2 and Creek 3

Metal or metalloid	Total Digestion (mg/kg)	Sequential leaching with decreasing pH			Detection Limit (mg/L)
		pH 6.5	pH 5.5	pH 4.5	
(% Removal)					
Creek 2– At Mine Lease (Site 10, Figure1)					
Al	52300	0.026	0.031	0.025	0.01
As	11	nd	nd	nd	0.001
Be	50	nd	nd	nd	0.001
Ba	9	nd	nd	nd	0.001
Cd	5	1.2	0.3	0.7	0.0001
Cr	12	nd	nd	nd	0.001
Co	12	nd	nd	nd	0.001
Cu	239	0.01	nd	nd	0.001
Pb	18	nd	nd	nd	0.001
Mn	1470	0.22	0.03	0.29	0.001
Mo	<2	nd	nd	nd	0.001
Ni	12	nd	nd	nd	0.001
Se	<5	nd	nd	nd	0.010
Zn	32	nd	nd	nd	0.005
Creek 3– Downstream of Mine Lease (Site14, Figure1)					
Al	129000	0.002	0.003	0.003	0.05
As	5	0.500	nd	nd	0.005
Be	30	nd [†]	nd	nd	0.01
Ba	42	0.83	nd	nd	0.001
Cd	3	11	11	11	0.001
Cr	8	nd	nd	nd	0.002
Co	2	5	5	5	0.002
Cu	4900	0.10	0.09	0.09	0.005
Pb	12	nd	nd	nd	0.005
Mn	38	18	17	18	0.005
Mo	<2	nd	nd	nd	0.005
Ni	6	1.3	0.4	0.8	0.002
Se	<5	nd	nd	nd	0.005
Zn	4910	1.62	1.48	1.45	0.005

[†] nd: under detection limit of the ICP-MS

tropical invertebrate species for aquatic test species. Identification of a suitable range of end species for aquatic toxicity testing of sediment at tropical locations is not yet achieved meaning investigators are unable to undertake a comprehensive assessment of impact to aquatic sediment species in ephemeral streams. The current lack of fully validated test methods for tropical aquatic sediment macro-invertebrates means that an alternative approach to local species is required. The combination of using chemical guidelines and ecotoxicity and biomonitoring approaches to assess the degree of sediment contamination is demonstrated to be a practical option until a full suite of tropical test species including the chironomid (Diptera) (Burton 1991; Cranston et al.,1997; Peck et al., 2002; Smith et al., 1999).

Table 4. 10-day whole sediment survival toxicity using the estuarine amphipod *Corophium* spp. and 48 hour acute survival test (EC 50) on water elutriate of sediment using the freshwater Cladoceran (*Ceriodaphnia cf dubia*)

Site	% Survival (at 10 days) using <i>Corophium</i> spp. (Sediment Control 85.0 ± 5.6)	48 hour acute survival test (EC 50) on water elutriate of sediment using the freshwater Cladoceran (<i>Ceriodaphnia cf dubia</i>)
1.	85.0±12.9	>100%
2.	92.5±9.6	>100%
3.	85.0±12.9	>100%
4.	90.0±8.2	>100%
5.	85.0±10.0	>100%
6.	100±0.0	>100%
7.	90.0±8.2	>100%
8.	87.5±12.9	>100%
9.	90.0±8.2	>100%
10.	90.0±14.2	>100%
11.	90.0±14.2	>100%
12.	90.0±20.0	>100%
13.	95.0±5.6	>100%
14.	90.0±14.2	>100%

5.0 CONCLUSIONS

Floc formation as a result of water impacted by minesite discharges and then mixing with higher pH catchment water can create significant aesthetic and perceptual impacts in the locations where they form. The case study is able to demonstrate that there is no sustained effect downstream of the mine and compares favourably with both upstream sites from the mine and to main river downstream. There appears to be no demonstrated effect on the various species of aquatic biota, from metals and metalloids in creek and river water downstream of the mine. The development of more area specific test using sediment dwelling species would provide greater confidence in such circumstances in the future.

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