

ASSESSMENT OF THE EFFECTS OF COMPLEX MIXTURED MIXTURES IN SEDIMENTS AND PROBLEMS FOR BENEFICIAL USE

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Introduction

As dredging activity continues to increase, the UK Government is actively pursuing alternatives to traditional methods of disposal of dredged material (Figure 1). Although disposal at sea remains the most cost-effective means of disposing dredged material, beneficial uses are being developed for the management of foreshore erosion and for positive intervention in coastal and estuarine sediment budgets (Bolam *et al.*, 2002) (e.g. Figure 2). In encouraging such uses, the risk assessment of the effects on saltmarsh communities of contaminant concentrations in dredged sediments will need to consider complex chemical mixtures. This study assesses experimentally the antagonistic and synergistic effects of mixtures of contaminants in sediments. The concentrations chosen for the experiments are typical of those found in sediments used for beneficial use.



Figure 1: Typical dredger and disposal at sea



Figure 2: Potential recharge site for the beneficial use of dredged material

Aims

- Develop an appropriate testing regime to evaluate the effects of contaminant mixtures from dredged materials with similar physico-chemical properties and different contaminant regimes.
- Identify synergy, additivity or antagonistic behaviour in model systems.
- Identify reasons for deviation from the model test regimes.

Model

- Initial range finding test conducted for individual metals to determine EC₅₀ values for selected test species. Range based on published sediment quality guidelines and EC/LC₅₀ values (from a variety of test organisms and endpoints) (e.g. Figure 3).
- Theoretical model based on combinations of individual EC₅₀ values (see Table 1) for test species below (Figure 4).
- Table 2 shows measured metal concentrations.

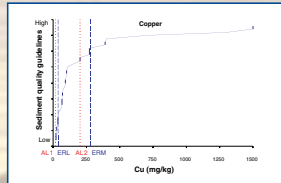


Figure 3: Example of effects ranges for copper based on SQGs and ECLC₅₀ values.

Table 1: Additivity Model (Mix 1-5) based on EC₅₀ values

	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5	Mix 6	Mix 7	Mix 8	Mix 9
Model	1/12	1/8	1/3	EC ₅₀	EC ₅₀	Action	Action	ERL	ERM
	EC ₅₀	EC ₅₀	EC ₅₀	value	value	Level 1	Level 2		
As	5.4	10.8	21.5	65	130	10	25	8.2	70
Cd	1.3	2.5	5	15.3	30.6	0.2	2.5	1.2	9.6
Cu	24.5	49	97	294	588	20	200	34	270
Hg	0.2	0.4	0.7	2.2	4.4	0.15	1.5	0.15	0.71
Pb	40.4	80.8	160.1	480	970	25	250	46.7	218
Zn	33.3	66.6	132	400	800	65	400	150	410

Table 2: Actual concentrations of mixtures in spiked sediments (mg/kg dw)

	Control	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5	Mix 6	Mix 7	Mix 8	Mix 9
As	5.9	6.8	10	20	25	8.9	18	7.2	31	
Cd	0.05	0.44	1	1.8	6.2	7.3	1.7	1.2	0.41	3.5
Cu	7.6	13	25	30	102	144	13	80	14	23
Hg	0.05	0.12	0.23	0.25	0.16	0.18	0.12	0.79	0.1	0.30
Pb	13	24	47	66	75	106	22	128	28	102
Zn	38	43	70	75	210	271	59	231	75	205

Sediment Preparation and Spiking

- Clean reference sediment identified
- Individual metals dissolved in deionised water and mixed into sediment separately.
- Seawater added to increase salinity of mixture before biological testing.
- After shaking for 3 h spiked sediment is left to equilibrate for 3 weeks.

Test Species and Test Methods

- 10-d acute sediment standard protocol using the surface deposit feeding polychaete *Arenicola marina* (ICES, 2002). Endpoints: survival and casting.



Figure 4: a) Test organism *A. marina* and b) test system

Results

Mortality of *Arenicola marina*

- Acute mortality was expected in mixtures 3-5 based on the assumption of additivity. Only mixture 5 was acutely toxic (see Figure 5). Statistical analyses (ANOVA) showed there were no significant differences between mean mortality and mixtures 1-4 and 6-9 ($p < 0.05$).
- Apart from mixture 5, highest mortality was observed in mixtures 4 and 9 which was expected based on actual measured concentrations.
- Observed biological response in all mixtures was as expected from actual measured metal concentrations in the sediment except for mixtures 1 and 7. Results from these mixtures were unexpected and further tests are being conducted to confirm these findings.

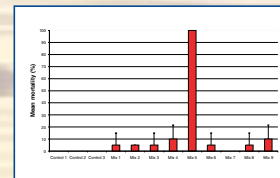


Figure 5: *Arenicola marina* 10 Day mean mortality

Casting rate of *A. marina*

- No significant difference between the control mean casting rate and mixtures 1-4 and 6-9 ($p < 0.05$).
- Decreasing casting rate from mixtures 2-5 as expected from model, but not significantly different from the control (Figure 6). Again, results from mixture 1 were unexpected and further tests are being conducted.
- Actual observed cast rate expressed as (% of expected cast rate as measured from single metal toxicity tests) for the total metal load is shown in Table 3.
- Observed responses for mixtures 6-9 are as expected from measured individual metal concentrations except for the ERM (mix 9) treatment (Figure 7). This mixture showed the lowest casting rate even though mix 7 contained the highest measured total metal load.

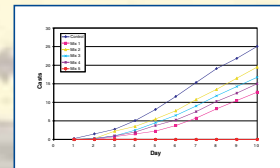


Figure 6: *Arenicola marina* 10 day accumulative cast rate mixtures 1-5

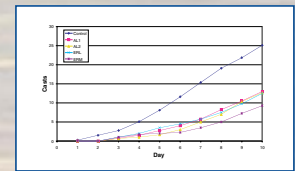


Figure 7: *Arenicola marina* 10 day accumulative cast rate of SQGs and ALS

Table 3: Observed cast rate expressed as (% of expected cast rate (as measured from single metal toxicity tests) for total metal load

	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5	Mix 6	Mix 7	Mix 8	Mix 9
Ratio of observed vs predicted	43	67	58	55	0	44	47	42	51
Stdev	1.2	2.6	1.5	3.1	0	1.6	3.9	1.5	3.9

Discussion

Although several studies have focused on the effects of contaminants on marine species, most have used single elements or compounds. Where studies on mixtures have been undertaken, these have often been carried out in simple matrices e.g. water and only a few have considered complex media such as sediments.

In this study, observed biological responses in mixtures 1-5 were as expected from the model, but the biological effects were reduced suggesting that the metals mixtures tested appeared to be less than additive. There are a number of possible explanations for this: (1) metal behaviour within the sediment is not as anticipated; (2) metals are reacting with each other in the mixture; (3) bioavailability of metals when present as a mixture differs from single metals and (4) the ability of animals to regulate metal mixtures may be different to single metals on their own. Statistical and experimental relationships between the six metals are currently being investigated.

Conclusion

- Behaviour of complex mixtures is complicated and this study is a first step at investigating mixtures of metals. Initial results suggest that mixtures of metals tested appear to be less than additive
- Possible detoxification/regulation mechanisms
- Action level 1 appears to be sufficiently precautionary but further investigation is required.

Future Work

- Conduct further statistical and experimental tests on metals.
- Expand model system to other contaminant mixtures.
- Investigate other bioassays/biomarkers to evaluate contaminant mixtures relevant to sensitive receiving environments.

Acknowledgements

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References

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- ICES. 2002. Biological effects of contaminants: sediment bioassay using the polychaete *Arenicola marina*. ICES CEM. No. 29, pp.17