Ecotoxicity and Biogeochemical assessment of deep-sea mine sediments

1. National Institute of Water and Atmospheric Research
   Hamilton, New Zealand
2. NIWA, Wellington
3. University of Waikato, Hamilton
4. Victoria University, Wellington

SETAC Australasia, Darwin, July 2019

Chris Hickey
Grace Frontin-Rollet
Chris Eager
Monica Handler
Richard Wysoczanski

Climate, Freshwater & Ocean Science
Guidance documents

Toxicity and chemistry

- Standard elutriate procedures
- Laboratory based
- Initial screening assessments

Too simplistic...
An example of phosphorite nodule (adapted from von Rad and Rösch 1984).

I: Weakly phosphatised nanno chalk core;
II: Outer phosphatised chalk zone;
III: Goethite zone;
IV: Collophane zone (amorphous phosphatic apatities);
V: glauconite outer rim.

Chatham Rise phosphorites occur at about 500 m depth.
Contaminants of concern
- Trace metals (including rare earths) and other elements (???) – primarily dissolved fractions for toxicity and bioaccumulation
- Sulphide, ammonia
- pH
- Modifiers (pH, dissolved organic carbon, iron/manganese, calcium, sediment)

Dilution and dispersion (near-field, far-field)

Elutriate and sediment toxicity

Food-chain bioaccumulation

Bioturbation/recovery processes

Standard assessment methods

Practical approaches
Objectives

1. To develop standardised approaches for chemical and ecotoxic characterisation of deep sea mining sediment
2. To field test assessment tools for potential deep sea mining activity
3. To establish critical effects thresholds for deep sea sponges and corals for suspended sediments (another project)
4. To provide updated guidelines for deep sea management
Background: Phosphorites
Biomonitoring: Crustacea

Decapods - *Munida gracilis*

Amphipod - *Ampelisca chiltoni*
Trace element abundances in sediments collected from the Chatham Rise (2012 survey).

Notes: All units mg/kg dry wt.; <2 mm fraction. All results are mean values ± standard error. * n = 19. ** n = 12. *** n = 7. **** n = 5. Kingett Mitchell (2005).

| Element       | Non-chalk | Chalk**** | Phosphorite | Pegasus Bay 
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>All samples*</td>
<td>Surface**</td>
<td>Sub-surface***</td>
<td></td>
</tr>
<tr>
<td>Arsenic</td>
<td>6.1 ± 0.6</td>
<td>5.9 ± 0.7</td>
<td>6.5 ± 1.1</td>
<td>&lt;4</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.22 ± 0.02</td>
<td>0.18 ± 0.01</td>
<td>0.30 ± 0.03</td>
<td>0.29 ± 0.05</td>
</tr>
<tr>
<td>Chromium</td>
<td>39 ± 3</td>
<td>41 ± 3</td>
<td>36 ± 6</td>
<td>20 ± 4</td>
</tr>
<tr>
<td>Copper</td>
<td>6.2 ± 0.2</td>
<td>6.2 ± 0.2</td>
<td>6.2 ± 0.5</td>
<td>4.0 ± 0.8</td>
</tr>
<tr>
<td>Lead</td>
<td>3.4 ± 0.2</td>
<td>3.6 ± 0.2</td>
<td>3.2 ± 0.4</td>
<td>2.3 ± 0.4</td>
</tr>
<tr>
<td>Manganese</td>
<td>83 ± 2</td>
<td>82 ± 3</td>
<td>84 ± 4</td>
<td>81 ± 10</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>0.46 ± 0.05</td>
<td>0.40 ± 0.05</td>
<td>0.57 ± 0.11</td>
<td>0.36 ± 0.07</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.062 ± 0.004</td>
<td>0.066 ± 0.005</td>
<td>0.054 ± 0.005</td>
<td>0.038 ± 0.008</td>
</tr>
<tr>
<td>Nickel</td>
<td>20 ± 0.4</td>
<td>19 ± 0.5</td>
<td>21 ± 1</td>
<td>18 ± 1</td>
</tr>
<tr>
<td>Strontium</td>
<td>630 ± 40</td>
<td>570 ± 30</td>
<td>720 ± 80</td>
<td>1,100 ± 50</td>
</tr>
<tr>
<td>Uranium</td>
<td>8.6 ± 1.2</td>
<td>8.6 ± 1.5</td>
<td>8.6 ± 2.1</td>
<td>9.9 ± 1.8</td>
</tr>
<tr>
<td>Zinc</td>
<td>27 ± 0.8</td>
<td>27 ± 1</td>
<td>26 ± 2</td>
<td>17 ± 3</td>
</tr>
</tbody>
</table>
Laboratory: Elutriation and Toxicity

**Elutriate testing:**
- Standardised test (EPA, ASTM)
- Developed to assess point of dredging/far-field/confined disposal scenarios
- Defines key factors including sediment/water ratio, dark, temperature

- Sediment to water ratio of 1:4
- Standard 30 minute agitation (tumbling)
- Extended 24 hour agitation
- Seawater (offshore)
- No sieving (retaining phosphorite nodules)
- Room temperature (~20°C)
- Elutriates checked for pH, DO
Chatham Rise Elutriates

- 30 minute elutriate
- 24 hour elutriate
Chatham Rise Elutriate Results

- Results compared with ANZECC (2000) guidelines for 99% species protection and the relative increase in background concentrations.
- The elutriate exceeded guidelines for dissolved copper and total ammoniacal-N. For the 30 min elutriate the maximum dilution to meet the copper guideline was 22x and ammoniacal-N 1.4x (vanadium maximally 64% of the guideline value).

Parameters with concentrations 5x over the offshore seawater were:
- For 30 min elutriates - manganese (maximally 6.2x), ammoniacal-N (120x), vanadium (11x) and DOC (maximally 8.3x)
- For 24 hour elutriates - uranium (maximally 8.2x), ammoniacal-N (68x), vanadium (15x) and DOC (maximally 7.6x).
- The relative elevations in concentration of uranium, molybdenum and fluoride were low (<4.3x, <1.4x and <1.5x respectively) in the 30 min elutriates.
Chatham Rise Toxicity tests

<table>
<thead>
<tr>
<th>Organism</th>
<th>Test type</th>
<th>End-point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marine amphipod</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chaetocorophium c.f. lucasi</td>
<td>Acute</td>
<td>96 h morbidity and survival</td>
</tr>
<tr>
<td>Blue-mussel</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mytilus galloprovincialis</td>
<td>Chronic</td>
<td>48 h embryo-larval development</td>
</tr>
<tr>
<td>Microtox™</td>
<td></td>
<td></td>
</tr>
<tr>
<td>bacterium</td>
<td>Chronic</td>
<td>bioluminescence</td>
</tr>
<tr>
<td>Vibrio fisheri</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3-1: Toxicity results for 30 min elutriate procedure.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Test Organism</th>
<th>EC$_{50}^a$ (95% CI)</th>
<th>EC$_{10}$</th>
<th>Chronic NOEC$^b$</th>
<th>Dilution for no toxicity$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB1</td>
<td>Amphipod</td>
<td>&gt;57.1%</td>
<td>57.1%</td>
<td>5.7%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Blue Mussels</td>
<td>&gt;100%</td>
<td>&gt;100%</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Microtox™</td>
<td>&gt;100%</td>
<td>c.90%</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>17.5</td>
</tr>
<tr>
<td>PB2</td>
<td>Amphipod</td>
<td>&gt;57.1%</td>
<td>&gt;57.1%</td>
<td>57.1%</td>
<td>&lt;2</td>
</tr>
<tr>
<td></td>
<td>Blue Mussels</td>
<td>&gt;100%</td>
<td>&gt;100%</td>
<td>100</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Microtox™</td>
<td>&gt;100%</td>
<td>&gt;100%</td>
<td>100</td>
<td>1</td>
</tr>
<tr>
<td>PB3</td>
<td>Amphipod</td>
<td>&gt;57.1%</td>
<td>&gt;57.1%</td>
<td>57.1%</td>
<td>&lt;2</td>
</tr>
<tr>
<td></td>
<td>Blue Mussels</td>
<td>&gt;100%</td>
<td>&gt;100%</td>
<td>100</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Microtox™</td>
<td>&gt;100%</td>
<td>100%</td>
<td>100</td>
<td>1</td>
</tr>
</tbody>
</table>

$^a$ EC$_N$: The sample concentration causing an N% response relative to the control.

$^b$ NOEC = No observed effect concentration; LOEC = Lowest observed effect concentration.

$^c$ Estimated by acute LC$_{50}$/10 to allow for chronic effects.

$^d$ No toxicity dilution = (1/Chronic NOEC) x 100.
Field: Survey Region
Field: The Benthic Disturber
Extent of disturbance....

- Limited fluidisation of sediment (5 cm vs expected 15 cm-silty sediments under thin layer of muds)
- Sediment plume generated was less than expected
- Plus extensive benthic boundary layer height in water column (50-100 m above bottom)
- High levels of natural sedimentation

Before

After
Field: Benthic landers and Glider “Betty”
**Field: Sediment coring**

**Ship-board lab work**

- Elutriates (metals, nutrients, DOC, settling rates of fines)
- Biogeochemistry of sediments (DO, pH, redox profiles)
- Sediment capping by fine sediments-incubation
- Core fluxes-incubations (metals, nutrients, DOC)
- Sediment community oxygen consumption (SCOC)
- Sediment erosion measurement system (EROMES) - sediment transport parameters related to seabed shear stress
Elutriate trials

Elutriate test with natural reference sediment suspension (200x v/v dilution) and time series of measurements of turbidity and dissolved organic matter (fDOM).
Cores and apparatus for dissolved oxygen (DO) and pH micro-profiling with results for DO profiles for natural sediment (left) and sediment capped with fine material generated by the Benthic Disturber (right).
Cores showing addition of fine sediment capping layer and generation of black anoxic (smells sulphurous) sediments at about 10 cm sub-surface after 6 days incubation.
Sediment capping & elutriates – DGT metals

Cores (triplicate exposures)

Elutriates

Plus: marked DOC, nitrate and ammonia flux changes → key nitrogen cycle effects
Conclusions:

- Elutriate process need to be site-specific to best represent conditions/process (Issues: temperature, pH, time)
- Understand dredging/pumping/processing/dispersal/times involved (short but strong mechanical agitation)
- Spatial scale of physical changes (e.g., fine sediment deposition) are large
- Response times will be slow in the deep sea environment (potentially weeks to months) – new tools such as DGTs useful
- Field experimental work necessary to define biogeochemical process and effects (e.g., benthic nitrogen cycling – flux & eDNA techniques)
- Understand what can change geochemistry (especially if sediment/material being mined is sulfidic or organic – role of DOC)
- Interdisciplinary team and robust assessment tools needed for investigations
Questions?

References:


Acknowledgements:
The crew of the Tangaroa; team at Chatham Rock Phosphate; Crew and Cruise Teams on Dorado Discovery (and other cruise vessels) for sampling; Tineke Stewart, GNS Science for providing the sediment samples; NIWA Hamilton Ecotox staff for testing; Graham Corban, Hill Laboratories, for collection of the offshore seawater from Alderman Islands.

Contact: chris.hickey@niwa.co.nz
Future:

- To further develop standardised approaches for chemical and ecotoxic characterisation of deep sea mining sediments
- Establish effects of ocean pH on chemical equilibria
- Conduct reference toxicant tests with major ecotoxic metals which are released during elutriation of deep sea sediments (e.g., vanadium, cobalt)
- Establish baseline metals levels and other physiological measures (e.g., lipids content, stable isotope composition) for selected species in deep sea mining areas
- Develop standard methods with representative deep sea species (e.g., corals, amphipods)
- Investigate and potentially develop standardised toxicity tests for whole sediment and sediment elutriates using selected infaunal species
- Conduct chemical and ecotoxic characterisation on additional marine mineral sediments (e.g., manganese nodules)
- Characterise bioturbation and sediment recovery process