Antarctic Science Ltd
International Bursary Project Report

Does sediment contamination explain spatial changes in the Antarctic benthic ecosystem?

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Antarctica has areas of contamination localised around current or historical anthropogenic activity (such as active or abandoned research stations, see Figure 1). Most contamination comes from emissions related to station activity (wastewater and the burning of fossil fuels for energy), accidental spills (particularly of diesel), or historical waste from abandoned tip sites, camps, and stations. Of these, metal contaminants accumulate in sediments and may pose a long-term contamination threat to coastal ecosystems. Whether or not these contaminants cause harm, however, depends on their ability to interact with organisms (their bioavailability). This in turn is controlled by the chemistry of the contaminant and the environment (their lability). It is possible that contaminants may be immobile, posing very little risk to ecosystems, because they are insoluble or bound to sediment phases such as iron and manganese oxides or particulate organic matter. However, the environment is dynamic, and conditions can change, such as when ice melts and streams are formed. These changes can lead to the increased lability and bioavailability. These types of changes are not generally considered in risk assessments of contaminants. Most national programs assess the risk of metal contaminants by taking a sample of soils or sediments, digesting them in acids, and measuring the total metal content. These approaches may over- or underestimate the risk of metals because they don't fully account for environmental controls on bioavailability and lability.

Figure 1. Historical contamination at the abandoned Wilkes Station in East Antarctica.

Techniques to better assess the risk of contaminants in Antarctica are needed to better understand our impact to local ecosystems, guide clean-up and remediation activities and demonstrate compliance with requirements under the Protocol on Environmental Protection to the Antarctic Treaty System.

My previous work validated a passive sampling technique known as diffusive gradients in thin-films (DGT) for Antarctic conditions. The DGT technique measures the flux of contaminants in pore waters that are released from sediments. This DGT-labile fraction of metals has been shown to better explain contaminant toxicity to organisms than total metal concentrations (measured by acid digests). Other benefits of the DGT technique include:

- *In-situ* deployment so contaminant speciation is preserved
- The pre-concentration of contaminants to a binding resin and removal of the environmental matrix (such as sediment or seawater) which provides sensitive detection limits
- DGT measure the average contaminant concentrations across their deployment times so are not biased by short term contaminant pulses
- The measurements reflect only contaminants that can dissociate from their binding site and bind to the DGT resin, which is considered a more biologically available fraction

I used this Antarctic Science International Bursary to measure DGT-samplers deployed in Antarctica and compare the labile metal concentrations with measures of biodiversity to understand whether metal contaminants are affecting benthic communities in Antarctica. This was done for freshwater (melt stream) and seawater sediments.

Freshwater sediments

The metal content of sediments in melt streams around Australia's Casey Station were analysed using acid digestion methods (the traditional approach) and DGT-samplers. The traditional sediment measuring showed that lead, chromium, copper, iron, and zinc contaminations were above environmental quality standards for some melt streams; however, when using the DGT-technique we found that only copper, zinc, and iron were labile and thus likely to cause harm. What was more interesting is that copper was only present in overlying stream waters, meaning that the sediments themselves were acting as an adsorbent and reducing the water concentrations. This was not the case for zinc which had similar labile concentrations above and below the sediment-water interface (Figure 2).

Another interesting finding was the presence of a strong reduction gradient leading to the dissolution of iron and manganese minerals. One stream's sediment had a reduced particle size (more silty texture) which we believe is creating anoxic conditions in the sediment because of reduced porosity and oxygen-rich water penetration. This is quite common in streams found in temperate and tropical regions but less so in Antarctica where the gravelly/sandy soils typically remain oxic. This is an important finding because non-chemical stressors such as changes to particle size in melt stream ecosystems can lead to a change in physicochemistry and thus microbial communities. These geochemical reactions may also lead to increased or decreased contaminant exposures. See the labile metal concentration measurements above and below the sediment water interface in Figure 2 for one of the deployment sites.

Alongside our measurements of sediment metal lability, we also investigated the diatom communities. This collaboration with Dr Jordan Bishop and Dr Kateřina Kopalová from Charles University in the Czech Republic and was only possible because of the funding provided by the Antarctic Science International Bursary. We found that changes in diatom richness between the melt streams were best explained by the DGT-labile copper concentration at the sediment-water interface (Figure 3). Using the traditional acid extractions resulted in no correlation. These correlations do not necessarily state causation and more work is needed to understand whether labile metals are causing toxicity; however, previous work with endemic Antarctic organisms has shown that copper is one of the most toxic metals in these ecosystems.

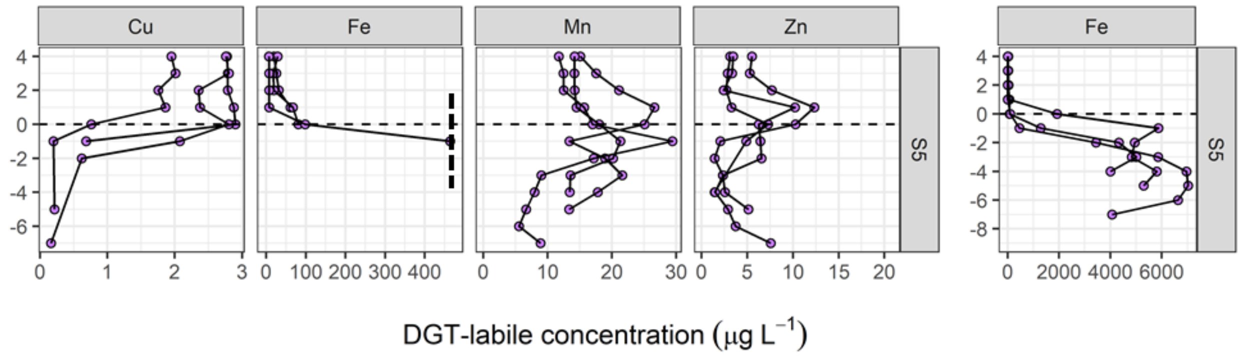

Figure 2. DGT-labile copper (Cu), iron (Fe), manganese (Mn), and zinc (Zn) concentrations along a depth profile in melt-stream sediments around Casey and Wilkes stations, Windmill Islands, East Antarctica. The sediment-water interface is defined as a height of 0 cm on the y-axis. Each line represents an individual DGT sampler. Iron concentrations are plotted twice on different x-axes, 0-500 μg L^{-1} in the main figure and 0-7000 μg L^{-1} in the figure on the right.

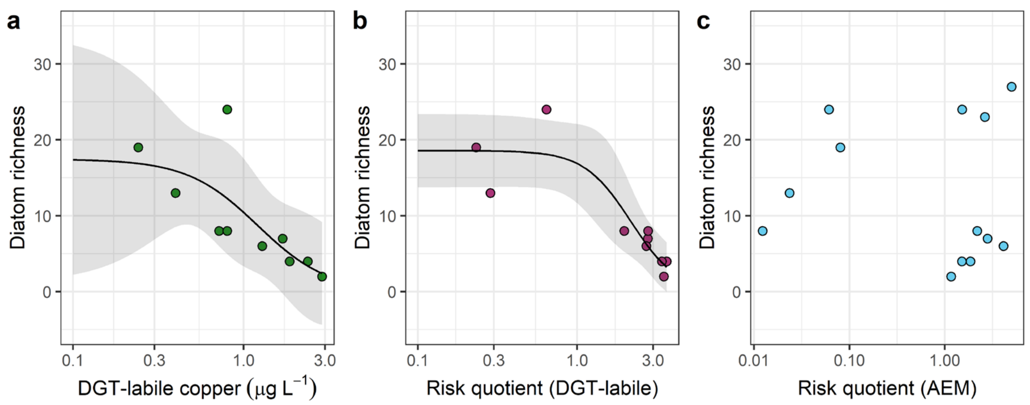

Figure 3. Concentration-response relationships between the diatom richness and measures of metal contaminants in corresponding sediments: (a) the DGT-labile copper concentration 1 cm above the sediment-water interface, (b) the risk quotient of DGT-labile metal concentrations 1 cm above the sediment-water interface and their respective water quality guideline value, and (c) a risk quotient of dilute-acid extractable metal concentrations in the sediment and their respective default sediment quality guideline values.

Marine sediments

Our aim was to assess sediments impacted by the now abandoned Wilkes Station or the currently operating Casey Station. We chose sites downstream of former tip sites or where melt water would be running through known contaminated sites. What we didn't expect was how difficult it was to find sediments in shallow waters! Many coastal areas were inaccessible because of sea ice and the bathymetry of the area means that sediments are quickly exported to deeper basins. After many attempts we eventually found 8 sites with collectable sediments (shown in Figure 4).

After assessing the metal content, we found that there was little to no metal contamination. One replicate at site 1 had a small flux of lead to overlying waters and site 6 had a flux of cadmium released to sediment porewaters. However, the concentrations of both were low and the cadmium is likely from naturally occurring geological sources. These results were unexpected because we were close to known sites of anthropogenic disturbance. However, our sampling was opportunistic around each site and not designed to be a widespread survey, so hotspots could have been missed. Nonetheless, this does suggest that even after 50 years, pollution is not leaching or mobilising to any great extent from where it was dumped. Great news for the environment!

The DGT method also measures fluxes of reduced iron, Fe^{2+}, and manganese, Mn^{2+}, so give an understanding of metal geochemistry. All sediments showed similar patterns. Manganese and iron oxides were being reduced below the sediment water interface, as would be expected for anoxic sediments with active microbial communities. These provide great estimates of important trace metals inputs to coastal Antarctic waters.

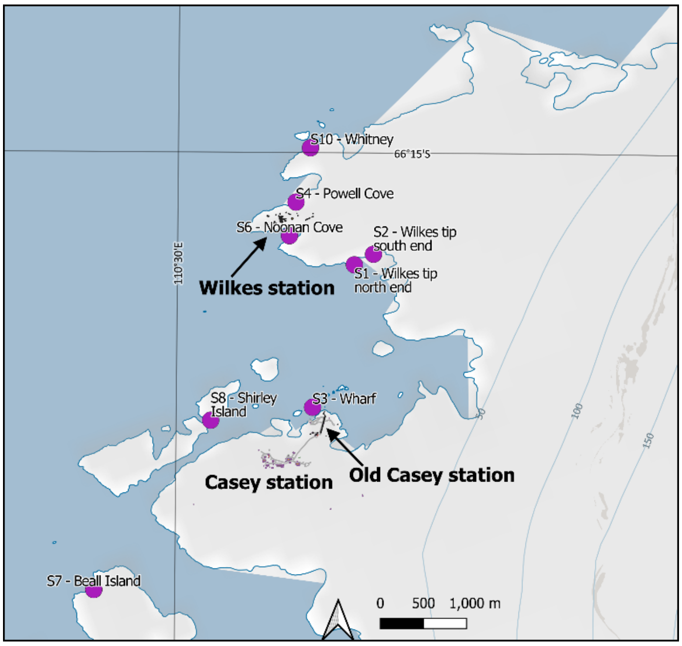

Figure 4. Map of marine sediment sampling locations. All samples were collected at depths of approximately 5 m using a Van Veen grab sampler.

We extracted environmental DNA (eDNA) from the marine sediments and used eDNA metabarcoding to profile the eukaryotic and prokaryotic communities at each site. There were significant differences between sites. Sites nearer research stations were more like each other than control sites further away (such as at Beall Island to the south and Whitney Cove to the north). We're still investigating what is driving these differences. A running theory is that phosphate enrichment (say from penguin poo) may play a role, another theory is it's just proximity to one another, but other ecological drivers need to be explored. One finding is clear though, each site has a diverse and rich benthic eukaryotic and prokaryotic community despite their proximity to research stations. These results are being written up for publication.

Findings from the Bursary

The Antarctic Science International Bursary gave me the opportunity to investigate the sediment geochemistry of metal contaminants in coastal Antarctic marine and freshwater sediments to better understand whether they were driving changes to the local biodiversity. We found that the labile metal concentration of overlying melt streams was correlated to reduced diatom diversity but that marine sediments were generally uncontaminated. Freshwater melt stream sediments that had altered physical properties (such as a reduced particle size distribution) were also found to have altered chemical properties – such as being anoxic. This is not widely recognised as an anthropogenic impact but may be particularly important to consider for future construction activities.

Thank you to Antarctic Science Ltd for the bursary and their support of early career researchers. It truly helped bridge the PhD-Postdoc gap for me!

If you are interested, you can keep a lookout for updates from this project at the hashtag #polartox on twitter.