

# **ANTA502: Literature Review**

## **Heavy metals: A heavy burden on the icy continent**

Phil Emmet

58212711

*Antarctica has for a long time been viewed as a pristine and isolated environment mostly untouched by human activity. During the early years of southern exploration Antarctica's worth to science and humanity was dismissed as a waste of time, but as our understanding of the earth's various environmental systems increased it showed Antarctica influences much of the way the earth works. With increasing amounts of research taking place it is becoming clear that Antarctica not only profoundly influences us, but that we are globally linked and are having an influence on it too through pollution produced locally and from all over the globe.*

*Most human activity and its associated pollution in Antarctica is highly localized, and waste disposal in the early years was in the form of snow pits, waste dumps, open pit burning, and release of untreated sewage into the oceans. This was the mindset in those times, but has now changed to a more environmentally aware regime. Antarctica is now facing a more serious threat from pollution which began at the time of the industrial revolution. Heavy metals such as Pb, Cd, As, and Hg, and volatile organic compounds (VOCs) such as chlorofluorocarbons, pesticides, and industrial compounds can now be found in places humans have never been before. These pollutants are transported to the poles via the atmosphere in the form of aerosols and global distillation of volatile compounds, and are accumulating in snow and wildlife.*

### *Introduction:*

VOCs are manmade compounds, and are mainly responsible for the ozone hole. Their arrival at the poles is a fairly recent phenomenon as they were manufactured only in the 20<sup>th</sup> century. In the case of heavy metals the picture is less clear. Trace levels of heavy metals have been found in ice cores dating back as far as 672 kyr BP<sup>1</sup>, and studies have now shown there are trace levels of Cu, Pb, Hg, Bi, Zn, As, Cd, Al, Ag, V, Mn, Fe, Ba, and U in snow pack in Antarctica<sup>1-3</sup>, most of which have natural sources (rock and soil dust and volcanism<sup>1</sup>, sea spray<sup>3</sup>, and atmospheric aerosols<sup>4</sup>). Hg is somewhat unique in its transport mechanism due to its high volatility and long atmospheric residence time<sup>4</sup>, and arrives at the poles via global distillation. Its main natural source is thought to be gaseous emissions from the oceans<sup>5</sup>. Another natural source of Cd, Pb, and Hg in the polar environments is the methylation of these metals carried out by marine bacteria. These new compounds are highly volatile and are transported by global distillation to the polar regions<sup>2</sup>.

These natural background levels are now being disturbed by anthropogenic influences. The natural composition of aerosols is being changed and now contains raised levels of heavy metals<sup>3</sup> (eg raised levels of lead in road dust). Isotope ratios of lead in Antarctic sea waters shows significant anthropogenic inputs, but luckily levels remain low due to biological scavenging<sup>6</sup>. Cr, Cu, Zn, Ag, Pb, Bi, and U show enhanced levels associated with mining and smelting in South America, Southern Africa, and Australia<sup>7</sup>, and Hg

emissions into the atmosphere are increased by factories and waste dumps. Antarctic spring time depletion events (mercury sunrise events) quickly release Hg that accumulated on the ice surface over winter months into the ecosystem each year<sup>4</sup>, which now makes it one of the most serious pollutants of polar ecosystems<sup>8</sup>. This process is analogous to the processes leading up to the accumulation and production of chlorine during the winter and spring months, and subsequent ozone depletion.

On top of the general increases in heavy metal concentrations through atmospheric processes is the input of pollution from scientific stations based around the continent. Some bases used to operate waste dumps that have left a legacy of extreme pollution<sup>9-11</sup>, and bases continue to leave a pollution footprint from waste incineration<sup>12</sup>, release of sewage<sup>13</sup>, and other human activities.

This poses an interesting question. What impact have bases had on the concentrations of heavy metals in their surroundings, and which activities have had the most significant impact?

Not all bases listed in the official COMNAP files<sup>14</sup> have carried out studies on environmental pollution, and so the picture remains unclear as to the total impact of human activities on heavy metal concentrations. Also, not all bases listed in this review have specifically investigated their heavy metal input, but rather measured natural background concentrations to be used as reference values for future studies<sup>15</sup>. Another drawback to this review is each station has carried out their experiments in vastly different years with different sampling and analytical procedures. Less recent papers may be out of date and may not fully reflect the present heavy metal concentrations. In fact, comparing results of different studies is difficult because of too much variability due to seasonal variability and chemical composition and amount of aerosols, coastal vs. inland sites, and different sampling and analysis procedures for each study<sup>8</sup>. Therefore quoting numerical results will simply not form an adequate picture of the issue, and so it seems appropriate to approach this via a more qualitative rather than quantitative manner.

#### *Pollution sources and pathways:*

The major pathways of pollution are atmospheric inputs from incineration and distribution of aerosols from around the world, sewage, machinery, and the leeching of pollutants from old waste dumps. Atmospheric inputs other than incineration smoke from a base cannot be controlled, and have been shown to be highly variable depending on the metal, geographical location, altitude, and other factors<sup>3</sup>. Leeching from waste dumps can be remediated by removal of the soil or capping and sealing it off from the environment. This is difficult however as the potential for release of pollutants during the remediation process is high and may lead to more severe pollution than would have occurred if the site remained undisturbed. Sources of pollution vary between stations and their location (inland vs. coastal), and the magnitude of pollution depends on factors such as size of the station. The most common types of pollution are waste dumps, litter, motor vehicles with associated fuel spills, and release of sewage into the oceans. Harbours and areas of high ship traffic also show an increased risk of pollution associated with fuel spills and from hull coatings.

#### *Marine sediment:*

All of this comes together in the case of McMurdo station (USA) which has severe pollution problems due to its size, harbour, and history of poor environmental

management. McMurdo is by far the largest station operating in the Antarctic, with a summer capacity of over a thousand people. Pollution is a major problem at the station, and before clean up operations began in the late 1980's McMurdo harbour was more polluted than harbours found in the US<sup>16</sup>. Cu, Pb, Ag, and Zn exceeded the acute toxicity levels on several occasions, with Cu frequently being detected 100-1000 times above this level<sup>13</sup>. Waste used to be piled up in Winter Quarters Bay (WQB) near the station, doused with fuel and ignited<sup>9</sup>. While this has stopped in 1980 it has left a legacy of highly contaminated land and a sea bed still covered with litter. Benthic organisms have high mortality rates when exposed to WQB sediments, and a highly changed structure of benthic organism communities<sup>17</sup>. Adding to this, tributyltin (TBT), which is highly toxic and was used as a biocide in antifouling paint on ship hulls, was for the first time discovered in Antarctic marine sediments around McMurdo Bay<sup>18</sup>.

McMurdo still operates a waste water discharge pipeline out to sea with regular monitoring taking place, and a special wastewater impact study was carried out in 1996<sup>13</sup>. The study found elevated levels of Cu, Pb, Zn, and Ag in sediments near the outfall, but no raised levels of Cd and Ni.

Casey station (UK) has also had a significant impact because of its use of waste dumps. Casey station used to operate a waste disposal site in the Thala valley, and the area is still heavily contaminated with fuel hydrocarbons and heavy metals. Since then site remediation was conducted in the austral summer of 2003/2004<sup>19</sup>, and extensive monitoring has taken place to determine the pollution levels in the adjacent Brown Bay waters and sediments<sup>10, 19-21</sup>. Amongst the analysed metals were Cr, Pb, Cd, Cu, Zn, and As. Another study looked at pollution output from waste incineration where As was found in the gaseous emissions. Above average levels of As, Cr, Cu, Pb, Mn, and Ni were found in some ash samples, which indicated the use of chemically treated timber at the station<sup>12</sup>.

#### *Air:*

Global atmospheric processes can also transport heavy metals to the Antarctic. In the 2000-2001 season at Neumayer station (Germany) the mercury sunrise phenomena was for the first time observed in the Antarctic<sup>4,22</sup>. Up until that time it has only been observed in the Arctic, and emphasised the global reaches human activities are having on pollution. Since Hg concentrations are mainly atmospherically controlled it can be speculated Hg pollution is present all over the continent, and Hg has been reported at Great Wall (China) and Zhongshan (China) station<sup>23</sup>.

Aerosols are also transported to the poles via the atmosphere, and are a natural source of heavy metals<sup>1-3</sup>. However through human activities the heavy metal content of aerosols is increased, and aerosols (PM10) collected at Mario Zucchelli station (Italy) showed increased levels of Cd, Pb, and Cu<sup>24</sup>. Low level contributions of Cd and Pb (10% and 5% respectively) from volcanism were identified, and a marine source for Cd and Pb is speculated, as has been proposed by Pongratz<sup>2</sup>. However the majority of the heavy metals come from long range transport of pollution. Aerosols enriched in Pb reach as far south as the South Pole, where it accumulates into the snow layers<sup>25</sup>. Snow layers from 1928-1977 were analysed for Pb, Cd, Cu, Zn, Ag, and other non-heavy metals. The study showed no increase in concentration over the years apart from Pb, which showed a 4-fold increase after 1960. This increase can be explained either by long range aerosols, or may in fact come from Amundsen-Scott Base (USA) that has been established there in 1957.

### *Soil:*

Apart from waters, ocean sediments, and air, soil is another medium of life that is being contaminated at stations around Antarctica. Elevated levels of Ag, As, Pb, Cd, Cu, and Zn were detected in soils around Scott Base (Ross Island)<sup>26</sup>. Raised levels were found across most of the station but are highest at sites where materials are dumped or stored. The metals are transported over the site via surface water flow, water percolation through soils, and via wind action. These transport effects appear to be seasonal and occur during summer when water can melt in localised areas. Topsoil (0-10cm) around Marambio station (Argentina) was analysed for Zn, Pb, Cr, Cu, and Ni, and Zn and Pb showed a 14 to 23 fold concentration increase respectively compared to the reference sites<sup>27</sup>. Pollution sources are thought to be motor vehicle traffic, planes and helicopters, power plant operations, fuel residues, solid waste disposal, paints, construction materials, galvanised material, and incineration of wastes. Cr and Cu showed moderately high concentrations compared to the reference sites. Cr was linked to the early use of Cr based paints, and Cu is believed to come from electrical wiring. Ni concentrations showed only slight elevations, and may be due to diesel discharges.

While research on WQB near McMurdo has been extensive and ongoing, little work could be found on metal contamination in soils around the station. Background levels of Ag, Al, As, Ba, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Se, Sn, and Zn were established in the mid 90s for various soil types<sup>15</sup> for future studies, and contamination from point sources such as cans, batteries, and fires around Marble Point near the station were investigated in another study<sup>28</sup>. Pb, Zn, and Cu were detected but the pollution showed little lateral and vertical movement away from the source. The metal concentrations are considered minor, but are still indicators of the impacts of human activities.

Paints, sewage, and petroleum are the main source of contamination of soils near Comandante Ferrara station (Brazil), which showed increased levels of Pb, Cu, and Zn, along with B, Mo, V, Ni, Mg, and Mn that could not be explained by natural enrichment<sup>29</sup>. However the metals are believed to not be readily bioavailable, and so are of low environmental risk. Up until 1994 NZ operated a mainland station in the Dry Valleys, near Scott Base and McMurdo, and the station has since been removed. But residual levels of Pb, Zn, Ag, and Cd have been detected in soils, and Cu, Ni, Co, and phosphate have been detected in suprapermanfrost fluids<sup>11</sup>. There is believed to be little risk of adverse impacts to the environment, though enhanced growth of cyanobacteria due to increased levels of phosphate is possible during flood events.

### *Biomonitoring:*

As little of the life found in Antarctica is land based, heavy metal contamination is not a very serious issue when it comes to soils. However as described earlier there is significant pollution occurring in bays and marine sediments near coastal stations, and most of the continents life resides in the ocean. Measuring levels of pollution in the environment is one thing, but the more important factor to consider is whether that pollution can bioaccumulate and cause adverse effects on wildlife. To study this biomonitoring is often carried out around the world to assess the severity of a pollution event. Antarctica is no different, and several studies have been carried out to identify species that are good biomontiors for detecting pollution and bioaccumulation.

A species of clam was used to investigate metal pollution at Rothera station (UK)<sup>30</sup>. Molluscs are known to tolerate metal concentrations several orders magnitude higher than environmental levels, and so make them good candidates for biomonitoring<sup>31</sup>. Elevated concentrations of Cu were found in clams sampled near the runway, but found no elevated levels of any other metals in clams sampled throughout the area.

Above ground the candidates for biomonitoring are somewhat limited, but researchers at Jubany station (Argentina) have successfully used lichen to monitor the atmospheric distribution of heavy metals on King George Island<sup>32</sup>. The lichen were analysed for Pb, Zb, Cu, Cd, Fe, and Mn, and all but Cd were present in the samples. Fuel combustion and weathering of metallic structures were identified as potential anthropogenic sources for the metals apart from Cd. The findings suggest atmospheric Cd circulation is negligible at least around King George Island.

A recent study has used animal excrement to investigate bioaccumulation of Hg, Pb, Cu, and Zn around Great Wall station (China) and other stations around the world<sup>23</sup>. Enrichment up the trophic levels was seen for Hg and Cu, and pollution from the northern hemisphere was attributed as a source of Hg. The high background concentrations of Cu are believed to be due to natural geographical factors.

#### *Conclusions:*

With bases now trying to stay as clean as possible, major pollution events such as waste dumps are now a thing of the past. However bases will continue to remain a source of continuous, and at best low level pollution that is unavoidable. Natural background levels of trace metals and organic compounds have been elevated since the establishment of bases on the continent, and some heavy metals such as Pb and Hg have shown increases due to atmospheric processes that humans have started to influence before permanent bases were established. Some increases are minor, and some areas show natural elevations of trace metals. But some other areas show significant pollution levels to the extent that biological activity has been compromised. Waste dumps, machinery, and litter seem to be of most importance. Litter is a very preventable source of pollution, and it seems odd that cans and batteries have been left exposed to the elements leeching heavy metals for a long period of time before being removed. The use of waste dumps has seized but has left a legacy of contaminated land that is unlikely to be remediated in the near future. Even stations that have long since been removed continue to leave a pollution footprint. The use of machinery will continue to have fuel spills and heavy metals associated with it, and spare parts can be left exposed to the elements without realizing, adding to the problem of litter. The picture is still not complete as to the whole extent of human effects and more research on other bases needs to be carried out to complete this. However with environmental awareness high we are on our way to keeping waste and pollution to a minimum to keep Antarctica as pristine as possible for the future.

#### **References:**

1. Marteel, A.; Boutron, C. F.; Barbante, C.; Gabrielli, P.; Cozzi, G.; Gaspari, V.; Cescon, P.; Ferrari, C. P.; Dommergue, A.; Rosman, K.; Hong, S.; Hur, S. D., Changes in atmospheric heavy metals and metalloids in Dome C (East Antarctica) ice back to 672.0 kyr BP (Marine Isotope Stages 16.2). *Earth and Planetary Science Letters* **2008**, 272, 579-590.

2. Pongratz, R.; Heumann, K. G., Production of methylated mercury, lead, and cadmium by marine bacteria as a significant natural source for atmospheric heavy metals in polar regions. *Chemosphere* **1999**, 39, (1), 89-102.
3. Hur, S. D.; Cunde, X.; Hong, S.; Barbante, C.; Gabrielli, P.; Lee, K.; Boutron, C. F.; Ming, Y., Seasonal patterns of heavy metal deposition to the snow on Lambert Glacier basin, East Antarctica. *Atmospheric Environment* **2007**, 41, 8567-8578.
4. Ebinghaus, R.; Kock, H. H.; Einax, C. T. J. W.; Loewe, A. G.; Richter, A.; Burrows, J. P.; Schroeder, W. H., Antarctic springtime depletion of atmospheric mercury. *Environmental Science and Technology* **2002**, 36, 1238-1244.
5. Vandal, G. M.; Fitzgerald, W. F.; Boutron, C. F.; Candelone, J.-P., Variations in mercury deposition to Antarctica over the past 34,000 years. *Nature* **1993**, 362, (6421), 621-623.
6. Flegal, A. R.; Maring, H.; Nlemeyer, S., Anthropogenic lead in Antarctic sea water. *Letters to Nature* **1993**, 365, 242-244.
7. Planchon, F. A. M.; Boutron, C. F.; Barbante, C.; Cozzi, G.; Gaspari, V.; Wolff, E. W.; Ferrari, C. P.; Cescon, P., Changes in heavy metals in Antarctic snow from Coats Land since the mid-19th to late-20th century. *Earth and Planetary Science Letters* **2002**, 200, (1-2), 207-222.
8. Bargagli, R., Environmental contamination in Antarctic ecosystems. *Science of the Total Environment* **2008**, 400, (1-3), 212-226.
9. Crockett, A. B.; White, G. J., Mapping sediment contamination and toxicity in Winter Quarters Bay, McMurdo Station, Antarctica. *Environmental Monitoring and Assessment* **2003**, 85, 257-275.
10. Stark, J. S.; Johnstone, G. J.; Palmer, A. S.; Snape, I.; Larner, B. L.; Riddle, M. J., Monitoring the remediation of a near shore waste disposal site in Antarctica using the amphipod *Paramoera walkeri* and diffusive gradients in thin films (DGTs). *Marine Pollution Bulletin* **2006**, 52, 1595-1610.
11. Webster, J.; Webster, K.; Nelson, P.; Waterhouse, E., The behaviour of residual contaminants at a former station site, Antarctica. *Environmental Pollution* **2003**, 123, 163-179.
12. O'Brien, J. S.; Todd, J. J.; Kriwoken, L. K., Incineration of waste at Casey Station, Australian Antarctic Territory. *Polar Record* **2004**, 40, (214), 221-234.
13. Crockett, A. B., Water and wastewater quality monitoring, McMurdo Station, Antarctica. *Environmental Monitoring and Assessment* **1996**, 47, 39-57.
14. COMNAP <https://www.comnap.aq/>, accessed December 2<sup>nd</sup> 2008
15. Crockett, A. B., Background levels of metals in soils, McMurdo Station, Antarctica. *Environmental Monitoring and Assessment* **1998**, 50, 289-296.
16. Lenihan, H. S.; Oliver, J. S.; Oarden, J. M.; Stephenson, M. D., Intense and localized benthic marine pollution around McMurdo Station, Antarctica. *Marine Pollution Bulletin* **1990**, 21, (9), 422-430.
17. Lenihan, H. S.; Oliver, J. S., Anthropogenic and natural disturbances to marine benthic communities in Antarctica. *Journal of Applied Ecology* **1995**, 5, 311-326.
18. Negri, A. P.; Hales, L. T.; Battershill, C.; Wolff, C.; Webster, N. S., TBT contamination identified in Antarctic marine sediments. *Marine Pollution Bulletin* **2004**, 48, 1142-1144.

19. Palmer, A. S.; Snape, I.; Stark, J. S.; Johnstone, G. J.; Townsend, A. T., Baseline metal concentrations in *Paramoera walkeri* from East Antarctica. *Marine Pollution Bulletin* **2006**, 52, 1441-1449.
20. Snape, I.; Scouller, R. C.; Stark, S. C.; Stark, J.; Riddle, M. J.; Gore, D. B., Characterisation of the dilute HCl extraction method for the identification of metal contamination in Antarctic marine sediments. *Chemosphere* **2004**, 57, 491-504.
21. Cunningham, L.; Snape, I.; Stark, J. S.; Riddle, M. J., Benthic diatom community response to environmental variables and metal concentrations in a contaminated bay adjacent to Casey Station, Antarctica. *Marine Pollution Bulletin* **2005**, 50, 264-275.
22. Temme, C.; Einax, J. W.; Ebinghaus, R.; Schroeder, W. H., Measurements of atmospheric mercury species at a coastal site in the Antarctic and over the South Atlantic Ocean during polar summer. *Environmental Science and Technology* **2003**, 37, (1), 22-31.
23. Yin, X.; Xia, L.; Sun, L.; Luo, H.; Wang, Y., Animal excrement: A potential biomonitor of heavy metal contamination in the marine environment. *Science of the Total Environment* **2008**, 399, 179-185.
24. Annibaldi, A.; Truzzi, C.; Illuminati, S.; Bassotti, E.; Scarponi, G., Determination of water-soluble and insoluble (dilute-HCl-extractable) fractions of Cd, Pb, and Cu in Antarctic aerosol by square wave anodic stripping voltammetry: distribution and summer seasonal evolution at Terra Nova Bay (Victoria Land). *Analytical and Bioanalytical Chemistry* **2007**, 387, 977-998.
25. Boutron, C., Atmospheric trace metals in the snow layers deposited at the South Pole from 1928 to 1977. *Atmospheric Environment* **1982**, 16, (10), 2451-2459.
26. Sheppard, D. S.; Claridge, G. G. C.; Campbell, I. B., Metal contamination of soils at Scott Base, Antarctica. *Applied Geochemistry* **2000**, 15, 513-530.
27. Chaparro, M. A. E.; Nunez, H.; Lirio, J. M.; Gogorza, C. S. G.; Sinito, A. M., Magnetic screening and heavy metal pollution studies in soils from Marambio Station, Antarctica. *Antarctic Science* **2007**, 19, (3), 379-393.
28. Claridge, G. G. C.; Campbell, I. B.; Powell, H. K. J.; Amin, Z. H.; Balks, M. R., Heavy metal contamination in some soils of the McMurdo Sound region, Antarctica. *Antarctic Science* **1995**, 7, (1), 9-14.
29. Santos, I. R.; Silva-Filho, E. V.; Schaefer, C. E. G. R.; Albuquerque-Filho, M. R.; Campos, L. S., Heavy metal contamination in coastal sediments and soils near the Brazilian Antarctic Station, King George Island. *Marine Pollution Bulletin* **2006**, 50, 185-194.
30. Lohan, M. C.; Statham, P. J.; Peck, L., Trace metals in the Antarctic soft-shelled clam *Laternula elliptica*: implications for metal pollution from Antarctic research stations. *Polar Biology* **2001**, 24, 808-817.
31. Ahn, I. Y.; Lee, S. H.; Kim, K. T.; Shim, J. E.; Kim, D. Y., Baseline heavy metal concentrations in the Antarctic clam, *Laternula elliptica* in Maxwell bay, King George Island, Antarctica. *Marine Pollution Bulletin* **1996**, 32, 592-598.
32. Poblet, A.; Andrade, S.; Scagliola, M.; Vodopivec, C.; Curtosi, A.; Pucci, A.; Marcovecchio, J., The use of epilithic Antarctic lichens (*Usnea aurantiacoatra* and *U. antarctica*) to determine deposition patterns of heavy metals in the Shetland Islands, Antarctica. *Science of the total environment* **1997**, 207, 187-194.

