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# Control of Denitrification in a Permanently Ice Covered Antarctic Lake: Potential for Regulation By Bioactive Metals

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**Final Report for Period:** 01/2000 - 09/2002**Submitted on:** 02/20/2003**Principal Investigator:** Wells, Mark L.**Award ID:** 0096146**Organization:** University of Maine**Title:**

Control of Denitrification in a Permanently Ice Covered Antarctic Lake: Potential for Regulation By Bioactive Metals

**Project Participants****Senior Personnel****Name:** Wells, Mark**Worked for more than 160 Hours:** Yes**Contribution to Project:****Post-doc****Name:** Maldonado, Maria**Worked for more than 160 Hours:** Yes**Contribution to Project:**

Shared responsibilities for metal determinations of Lake Bonney waters, digestions of cell concentrates from culture experiments, and in method development.

**Graduate Student****Undergraduate Student****Technician, Programmer****Other Participant****Research Experience for Undergraduates****Organizational Partners****Other Collaborators or Contacts**

Continuing collaboration with Dr. Bess Ward, Princeton, on this joint project

**Activities and Findings****Research and Education Activities:**

Lake Bonney is a permanently ice-covered lake in the Dry Valley's region of Antarctica separated into two deep lobes by a shallow (12 m) sill.

Denitrification occurs in the sub-oxic, saline waters of the west lobe but not in that of the east lobe for reasons unknown. Previous work has established this disparity cannot be attributed to temperature or salinity limitations, nor by the comparative availability of organic carbon substrates. Our research objective is to determine if trace metal limitation or toxicity may be responsible for this unusual feature. The broader objective is to assess the likelihood that denitrification in the oceans may have been at times similarly affected, thereby complicating the use of nitrogen isotope data in paleoproductivity reconstructions.

Dissolved (< 0.4  $\mu\text{m}$ ) and particulate (> 0.4  $\mu\text{m}$ ) samples were obtained from vertical profiles taken at two sites central in each lobe during the first field season (year two of the project). Dissolved metal concentrations (Mo, Cd, Pb, Fe, Co, Ni, Cu, and Zn) were measured in the freshwater samples collected above the pycnocline after direct nebulization on a Finnigan high resolution ICP-MS. Samples from within and below the pycnocline were diluted 10x with acidic deionized water and measured by high resolution ICP-MS after desolvation. A subset of samples near the pycnocline had very low concentrations of one or more metals. These samples were preconcentrated by solid phase extraction and the metal concentrations analyzed by direct nebulization ICP-MS. Particulate samples, deemed to be of lower priority, have not yet been digested and analyzed.

In addition to the collection and measurement of dissolved metal concentrations, we have been developing a new method for determining the chemical speciation of metals by solid phase extraction. This work builds upon the solvent extraction method developed by K. Bruland and J. Moffett for determining Cu speciation in seawater. Briefly, the competitive ligand exchange method uses the non-specific metal chelator hydroxyethanol dithiocarbamate (HEDC) to compete with natural organic ligand classes in solution as increasing concentrations of the metal of interest are added. The HEDC:metal complex is then extracted and analyzed by ICP-MS. Linear transformations of the resultant titration curves allow calculation of conditional stability constants of ligand classes present along with their respective concentrations. Although we have explored only single metal titrations to date, the goal is to use the power of high resolution ICP-MS to determine the chemical speciation of several metals simultaneously.

In our second and final field season (2000 - 2001), we expanded the suite of metals analyzed to include 34 metals. New ICP-MS methods were developed to enable these multiple analyses and verified with laboratory testing. In addition, terrestrial soil samples were collected from site believed to be representative sources of dust to the lake surface.

As in the first season, the trace metal clean sampling system was used to collect lake waters for the experimental incubation treatments. Longer incubations were used requiring large (10L) samples free of both metal and O<sub>2</sub> contamination. An extensive series of manipulation experiments was performed on lake water, in which both the rate of thymidine incorporation and denitrification were measured. Oxygen concentration in the trilaminar gas impermeable incubation bags was monitored with the microcolorimetric method. The concentration of cultivated denitrifying cells (strains previously isolated from Lake Bonney) was monitored in the incubations using immunofluorescence.

### **Findings:**

Dissolved trace metal concentrations are comparatively low in the near surface freshwater layer but increase sharply at the pycnocline and deeper in both lobes of Lake Bonney. All the bioactive metals appear to be in excess of that expected to be required for bacterial growth and denitrification. In fact, the concentrations of some metals (e.g. Cu, Zn and Cd) are so high near the base of the freshwater layer that organic complexation is likely required to permit the growth of bacteria that is measured. While there are clear differences in the concentrations of total dissolved metals in the two profiles, no single element stands out as a likely candidate of a causative factor for explaining why denitrification does not occur in the East Lobe of Lake Bonney. Metals are known to act synergistically, so that one metal interferes

in the uptake of another. The Mn/Cu and Zn/Cu ratios in the East Lobe are 10x higher than in the West Lobe, perhaps suggesting that Cu availability may be significantly different at the depths where denitrification should occur. However, preliminary field incubations studies indicate that denitrification may be stimulated in East Lobe waters by diluting the water with deionized water or by adding organic chelators. While both of these results are consistent with trace metals being responsible for the absence of denitrification in the East Lobe, they suggest that metal toxicity may be to blame rather than metal limitation. This toxicity could be due to differences in the degree of metal complexation between the two lobes, or be due to another non-nutrient metal not quantified in these analyses (e.g., Hg, As, Ag).

In the second field season we analyzed a wider suite of metals in the vertical profiles. Silver and iron were the only metals that showed dramatic distribution differences between the two lobes of the lake. Silver concentrations were up to 150-fold higher in the East than in the West. Concentrations of Cd, Pb, Cr, Ni and Zn in suboxic East Lobe waters were a factor of 2-5-fold higher than in the West Lobe and Fe concentration was 200 times lower in the East Lobe.

Low Fe concentrations may exacerbate the potential toxicity of the other metals, so a general metal toxicity is a possibility for the inhibition of denitrification. Silver, on the other hand, has the potential to specifically inhibit denitrification because of its ability to interfere with Cu binding in redox proteins, such as nitrite reductase and nitrous oxide reductase. High Ag concentrations might prevent the functioning of nitrous oxide reductase in the same way that simple Cu limitation does, therefor causing the buildup of nitrous oxide and a nonfunctional N cycle. These determinations of Ag need to be verified by alternate analytical methods.

#### **Training and Development:**

Dr. Maria Maldonado has received training in ultraclean methods of sampling and sample processing. She has become proficient at the use of solid phase metal extractions and in the use of microwave digestion methods. She also has gained experience in the use of gamma emitting radioisotope tracers.

#### **Outreach Activities:**

An elementary school teacher participated in the field sampling season as a team member. This person was sponsored by the Teachers Experiencing Antarctica (TEA) program.

#### **Journal Publications**

#### **Books or Other One-time Publications**

#### **Web/Internet Site**

**URL(s):**

**Description:**

#### **Other Specific Products**

#### **Contributions**

**Contributions within Discipline:**

**Contributions to Other Disciplines:**

**Contributions to Human Resource Development:**

**Contributions to Resources for Research and Education:**

**Contributions Beyond Science and Engineering:**

**Categories for which nothing is reported:**

Organizational Partners

Any Journal

Any Book

Any Product

Contributions: To Any within Discipline

Contributions: To Any Other Disciplines

Contributions: To Any Human Resource Development

Contributions: To Any Resources for Research and Education

Contributions: To Any Beyond Science and Engineering