Polychlorinated Biphenyls and Trace Metals in Matanuska Glacier and Exit Glacier, Alaska

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09/30/2011

Abstract and Specific Aims:

As a result of increased temperatures, Alaska's glaciers are swiftly melting and releasing unknown amounts of possible contaminants into the state's waterways. Two of Alaska's easily accessible glaciers –Exit Glacier and Matanuska Glacier – will be sampled and compared. Trace metals and Polychlorinated Biphenyls (PCBs) will analyzed at the University of Alaska Anchorage's Applied Science, Engineering, and Technology (ASET) Laboratory in the fall of 2011. This study seeks to gain an understanding of the types of glacial contaminants, if any, and if the release of such contaminants contributes to the 21st century climate change.

Specific Aim #1: To properly collect and analyze glacier runoff samples.

Specific Aim #2: To develop a working method for the analysis of trace metals and PCBs at low concentrations in glacier runoff.

Specific Aim#3: Determine the concentrations of trace metals and PCBs and the risks they pose to the environment.

Introduction:

A study of eight glacier forefields in the western Prince William Sound region determined that the Little Ice Age (LIA) greatly impacted the growth of Alaska's glaciers. This study used the technique of tree-ring analysis of trees overrun by ice and is so effective that in many cases a calendar date could be assigned to a glacier advance (Wiles 1999). The end of the LIA marked the beginning of glacier retreat around the globe. Between the 1950s and the mid-1990s, Alaska's glaciers have decreased an average of 0.02% per year (Barry 2006).

Alaska is home to over 100,000 glaciers covering roughly five percent of the state. The magnitude of these glaciers arise from the geographical controls involving the latitude, elevation, and proximity to an upwind moisture source, that allows for some of the largest glaciers to be found in southern Alaska (Barry *et al.* 2006). The glaciers to be sampled in this study include Exit Glacier and Matanuska Glacier.

The amount of pollutants released from a glacier is not entirely dependent upon the rate at which the glacier is melting. Glaciers undergo a flow of ice from their upper altitudinal zone to their lower part, resulting in a delayed release of contaminants (Bogdal 2009). Hence, a comparatively small amount ice formed when pollutants were high will release more than a large amount of ice formed when environmental levels of pollutants were low.

Global warming is a major global issue. Glaciers are predicted to undergo massive melting in the future; which would have many social, economic, environmental, and health-related impacts (Bogdal et al. 2009). Even though Alaska's glaciers have been extensively studied, the full composition is still unknown. There is a high possibility that copious amounts of contaminants are entrapped in these ice bodies. The use of glacial meltwater for things such as drinking water, irrigation facilities, artificial snow production, and fishing in mountain lakes may result in increased exposure of humans and wildlife to hazardous compounds (Bogdal et al. 2009).

A study of the Palisade Glacier in California by McIntyre (2007) revealed the existence of ten volatile organic compounds and seventeen trace dissolved metals in the parts per billion range. He postulated that the metals were trapped in the glaciers from fires, volcanoes, and a nearby dry lake bed which uncovered a large amount of briny silt and minute amounts of trace metals (McIntyre *et al.* 2007). Another recent study analyzed sediment for Persistent Organic Pollutants in Lake Iseo in Northern Italy. Here they found that the melting Alpine ice was a secondary source of contamination for DDT and PCBs. The analysts correlated the times of maximum PCB concentration in the 1970s when the use of these compounds were common in Italy. The concentration of DDT was at its highest in the early 1990s, long after its use was banned, providing support that the pesticides were preserved in the ice during the time of their use (Bettinetti 2011). A study of the glacier-fed lake in Switzerland, Lake Oberaar, used dated sediment cores to investigate the fluxes of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs),

dichlorodiphenyl trichloroethane (DDT) and its main transformation products, as well as other organochlorine pesticides, and synthetic nitro and polycyclic musk fragrances (Bogdal et al. 2009). This study concluded that large amounts of persistent organic chemicals were released since the late 1990s, and considering the lower usage of these organochlorides, signifies that the pollutants came from melting glaciers rather than atmospheric disposition. A study of the inorganic material in the Rasass See in the European Alps found that the electrical conductivity increased 18-fold and that the nickel concentration was more than an order of magnitude greater than the limit allowed in drinking water over the past two decades (Thies 2007).

By studying glacial contamination, we will get a better understanding of the types of pollutants trapped in two of Alaska's glaciers and the extent of their presence. Understanding these problems now will allow us to be prepared for the problems that will result due to increased climate warming that is projected in the future.

Experimental Design:

Sampling: To determine the level of pollutants, runoff samples will be taken from Exit Glacier and Matanuska Glacier. Runoff samples are representative over the entire surface of the glacier and will be taken directly from the glacier's terminus. The sampling method will be similar to the USGS Collection of Water Samples using the clean hands, dirty hands (ch/dh) technique. Samples will be taken using a 1 L low-density polyethylene (LDPE) bottle, rinsed several times in the runoff and then filled. Sample collection bottles will be soaked in Fisher trace metal grade HNO3 (10%) for one week then rinsed five times and filled with ultrapure 18 megohm water. The bottle will then be double bagged with clean polyethylene plastic bags to be used within five days. Strict adherence to these principles will result in low concentrations measured in method blanks.

If possible, samples will also be taken along a glacier fed stream. The water will be collected by placing the jar, with its cap still in place, in the deepest part of the stream. The cap will slowly be twisted off to allow the jar to fill with minimum disturbance. No water will be filtered prior to analysis. Between the collections of each sample, all equipment will be rinsed with 18 megohm water and a new pair of nitrile-rubber gloves will be worn. The samples will then be placed in a cooler maintained at a temperature of 2-6° C until they are delivered to the ASET lab. Field duplicate samples will be collocated grab samples at a frequency of approximately one for every ten primary samples. Method blanks will be DI water transported to the field for each sampling event.

All information pertinent to a field activity will be recorded in a logbook. Things such as date and time of sampling, description of sample location, climatic conditions, detailed field observations, and GPS coordinates will be included.

Trace Metals: Samples will be preconcentrated using a sub-boiling evaporation procedure and then ran through an Inductively Coupled Plasma- Mass Spectrometry (ICMPS), which provides a higher sensitivity for the samples. Samples will be acidified and carried along by argon gas into a plasma torch where it is ionized and atomized.

PCBs: Samples tested for PCBs will be analyzed using the Extraction, Cleanup, and Analysis of Polychlorinated Biphenyl Congeners and Aroclors in Lyphilized Tissue by ASE and Gas Chromatography/Electron Capture Detector Method (Applegate). As the samples pass through the GC column, an electron capture detector (ECD) will detect up to 18 different PCB congeners.

The GC/ECD coupled to two capillary columns should detect chlorinated hydrocarbons in the parts per billion (ppb) range. The capillary columns are Vh-5MS (30m x 0.25mm ID and 0.25 μ m film thickness). A continuing calibration verification (CCV) will be run at a frequency of one to every twenty samples analyzed and should fall within 20% of its actual value. This CCV will contain 10.0 ng/mL for each of the PCB congeners in hexane and then fortified to a concentration of 20 ng/mL using Decachlorobiphenyl internal standard.

Anticipated Results:

This study expects to see all of the target contaminants in minute amounts. Arsenic and chromium are commonly high in Alaska and are believed to be present at higher concentrations in the glacier runoff. Alaska is generally a clean state. Emissions testing and lack of having many industrial companies have helped to keep the pollutant levels in the air down. However things such as volcanoes, past military efforts, mines, and coal plants produce harmful effects to the environment.

Project Budget:

Item	Cost per Item	Quantity	Cost
ICP-MS Method			0.450
Omnitrace Nitric Acid. Trace Metal grade.	\$450	1	\$450
Maintenance and Supplies	\$125	1	\$125
GC/ECD			
Hexane. Pesticide Residue Analysis grade.	\$200	1	\$200
	\$400	1	\$400
Florisil. Pesticide Residue grade, 60-100 mesh.	\$400	•	4.00
Silica Gel. Pesticide Residue grade, 60-100 mesh.	\$200	1	\$200
	0250	1	\$350
Primary Secondary Amine (PSA). Sepelclean TM (Sigma-Aldrich 52738-U)	\$350	1	Ψ330
PCB Congener Mix Standard (Restek, 32416)	\$125	1	\$125
PCB Congener with Standard (Rester, 32 110)	4.		
Decachlorobiphenyl (Ultra Scientific, PPS-150-1)	\$25	1	\$25
	\$125	1	\$125
Maintenance and Supplies	Φ123	1	Ψ125
Total Cost			\$2000.00

Budget Justification:

Trace Metals Analysis: Due to the low amounts of contaminants expected it is important to use pure Nitric Acid. This will ensure that low concentrations in the blank samples.

PCBs Analysis: The chemicals listed above are needed to analyze the target contaminants for this project. Maintenance and supplies include such things as the gas to run the instruments.

Timeline:

October 2011 - Start sampling. Begin to develop a method.

November 2011 – Sampling completed. Present current findings at undergraduate seminar.

December 2011 – Have a working method.

February 2012 – All instrumental analysis completed. Continue data analysis.

April 2012 – Poster presentation completed.

May 2012 - Final written report completed and submitted.

References:

- Applegate, B.L. Extraction, Cleanup, and Analysis of Polychlorinated Biphenyl Congeners and Aroclors in Lyphilized Tissue by ASE and Gas Chromatogrphy/Electron Capture Detector.
- Barry, R.G. (2006). The Status of Research On Glaciers and Global Glacier Recession: A Review. Progress in Physical Geography 30, 3 (2006), 285-306.
- Bettinette, R., Galassi, S., Guilizzoni, P., & Quadroni, S. (2011). Sediment Analysis to Support the Recent Glacial Origin of DDT Pollution in Lake Iseo (Northern Italy) [Abstract]. Chemosphere. doi:10.1016/j.chemosphere.2011.06.037 Key: citeulike: 9531549
- Bogdal, C., Schmid, P., Zennegg, M., Anselmetti, F.S., Scheringer, M., Hungerbuhler, K. (2009). Blast From the Past: Melting Glaciers as a Relevant Source for Persistent Organic Pollutants. Environmental Science and Technology (2009), 43, 8173-8177.
- Brown, J., Harper, J., & Humphrey, N. (2010). Cirque Glacier Sensitivity to 21st Century Warming: Sperry Glacier, Rocky Mountains, USA. Elseuier Global and Planetary Change, 74 (2010), 91-98. doi:10.1016/j.gloplacha2010.09.001
- McIntyre, E. (2007). Water Quality Analysis of the North Palisade Glacier Sierra Nevada Mountains, California.
- National Snow and Ice Data Center. (n.d.). All About Glaciers. Retrieved September 20, 2011, from http://nsidc.org/glaciers/quickfacts.html.
- Thies, H., Nickus, U., Mair., Tessadri, R., Tait, D., Thaler, B., & Psenner, R. (2007).

Unexpected Response of High Alpine Lake Waters to Climate Warming [Abstract]. Environmental Science and Technology. 41 (2007), 7424-7429. doi: 10.1021/es0708060

Wiles, G.C., Barclay, D.J, Calkin, P.E. (1999). Tree-Ring-Dated 'Little Ice Age' Histories

of Maritime Glaciers From Western Prince William Sound, Alaska. The Holocene 9,2 (1999), 163-173.