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Biotransport of Marine-Derived Trace Elements to a Coastal Ecosystems in the Canadian High Arctic

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BIOTRANSPORT OF MARINE-DERIVED TRACE ELEMENTS TO A COASTAL ECOSYSTEM IN THE CANADIAN HIGH ARCTIC

Samantha Brimble

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Table of contents

Abstract

Seabirds are an important link between their marine feeding areas and their terrestrial breeding environments, transporting both marine-derived nutrients and contaminants to land via their excreta, feathers and carcasses. The importance of seabird-derived nutrients is particularly apparent in nutrient poor regions like the Canadian High Arctic, where biological oases form in the area surrounding a colony. While providing the nutrient subsidies that shape the terrestrial ecosystem of many Arctic sites, seabirds may focus contaminants into their nesting sites at potentially toxic levels. Here, we investigated the impact of a large northern fulmar (*Fulmarus glacialis*) colony on nearby ponds spanning a broad gradient of seabird influence at Cape Vera, Devon Island. Nutrient concentrations were significantly higher in ponds receiving guano than in reference ponds. The ponds closest to the cliffs, and thus receiving the highest seabird subsidies, were the most contaminated, and in some cases exceeded Canadian Sediment Quality Guidelines for the Protection of Aquatic Life for As, Cd and Zn. This study demonstrates that seabirds can transport contaminants bioaccumulated from the ocean and funnel them into receptor sites to potentially toxic levels thousands of kilometers from industrial centers.

Résumé

Les oiseaux de mer représentent un lien important entre les écosystèmes marins et terrestres, transportant des nutriments et des polluants en provenance de la mer à leurs sites de nidification via leurs excrétions, leurs plumes et leurs cadavres. Le rôle des oiseaux de mer dans le cycle des nutriments est évident dans des régions pauvres en nutriments, tel l'Arctique canadien. Grâce aux nutriments présents dans leurs excréments, des oasis biologiques forment autour d'une colonie. Même si ce guano est riche en nutriments, il contient aussi des contaminants bioaccumulés d'une diète marine. L'accumulation de guano aux sites de nidifications peut amplifier les concentrations des contaminants jusqu'à des niveaux toxiques. L'impact d'une colonie de fulmars boréaux (*Fulmarus glacialis*) sur une série d'étangs a été étudié à Cape Vera, Nunavut. Les concentrations de nutriments étaient significativement plus hautes dans les étangs recevant du guano que dans les sites de contrôle. Les étangs les plus proches des falaises, et recevant ainsi les plus hautes quantités de guano, étaient les plus contaminés. Dans quelques cas, les recommandations canadiennes pour la qualité des sédiments: protection de la vie aquatique, pour As, Cd et Zn, ont été dépassés. Cette étude démontre que les oiseaux de mer peuvent transporter des contaminants de l'océan et les concentrer dans leurs sites de nidification à des niveaux potentiellement toxiques.

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Introduction

Seabirds are keystone species in coastal ecosystems, greatly altering resource availability in the terrestrial environment (Polis et al. 1997). Annually, seabirds consume approximately 70 million tonnes of fish (Brooke 2004), transferring this biomass across ecosystem boundaries from the ocean to their terrestrial nesting sites via their guano, feathers, and mortality (Bildstein 1992; Anderson and Polis 1999). Guano, rich in marine-derived N and P (Hutchinson 1950), deposited at communal nesting sites focuses nutrients, enriching their concentrations above background levels and altering resource availability for terrestrial species (Polis et al. 1997; Ellis et al. 2005). The importance of seabirds to ecosystem function is especially apparent in polar regions, where nutrient poor soils limit plant growth (Muir, 1999). In the Arctic, the presence of seabird colonies is one of the main factors controlling the diversity and abundance of vegetation (Godzik 1991). Furthermore, nutrient enrichment via guano has a top-down effect, increasing plant quality, resulting in an elevated density of herbivores and predators (Polis et al. 1999), thus affecting the entire food web (Anderson and Polis 1999).

Seabirds feed high on the marine food web and tend to bioaccumulate high body burdens of certain pollutants (Buckman et al. 2005; Campbell et al. 2005). Elevated levels of trace elements are a concern in the Arctic marine food web, particularly those of Cd, Pb and Hg, which exceed Health Canada and World Health Organization guidelines for human consumption in many Arctic biota (Muir et al. 1999). While seabird guano nourishes the productivity of Arctic ecosystems, it has also been recognized as an important medium for the transport of contaminants accumulated from a marine diet. High inputs of seabird subsidies (*i.e.* guano, regurgitated stomach oils, carcasses) have been associated with elevated levels of organic pollutants (*i.e.* PCBs, organochlorine pesticides), metals and metalloids in vegetation, soils and sediments from seabird colonies (e.g. see, Headley 1996; Evenset et al. 2004; Sun et al. 2004; Liu et al. 2006a).

Communal nesting can significantly enrich nutrients and contaminants on a local scale, often to potentially toxic levels (Bildstein et al. 1992). Germination of vegetation was inhibited by extremely high concentration of ammonia at densely arranged cormorant (*Phalacrocorax auritus*) nesting sites (Ellis et al. 2006). Likewise, Sun et al. (2004) found that while vegetation surrounding a penguin rookery proliferated due to nutrient rich guano, plants within the colony were destroyed by over-fertilization and trampling. Heavy metal levels at many heavily affected seabird sites exceed environmental quality guidelines and toxicity thresholds. For example, Liu et al. (2006b) found that Cd concentrations in sediments at a red-footed booby (*Sula sula*) colony exceeded the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life. Furthermore, Blais et al. (2005) showed that biotransport increased pollutants 10- to 60-fold in freshwater sediments compared to nearby sites not influenced by the seabird colony. Still, the role of biovectors in the global cycling of nutrients and contaminants is generally ignored.

Seabirds may be the most globally relevant biovectors as they are often the dominant form of wildlife in coastal areas and nest in large colonies that can number in the millions of individuals (Michelutti et al. 2009). In the Canadian Arctic alone, it is estimated that there are more than 10 million seabirds (Mallory 2006), representing a significant fraction of the global species and an important nutrient source to the tundra. The Arctic climate is rapidly changing with increasing air and sea surface temperatures, declines in the extent and thickness of sea ice and reduction of snow cover (ACIA 2004). These changes will likely affect seabird populations; however, a paucity of long term data makes it difficult to predict the impact or direction of change (Gaston et al. 2006). Paleolimnological approaches aimed at reconstructing historical seabird population changes may provide valuable tools and fill important knowledge gaps. Seabird guano is characterized by unique chemical assemblages of trace elements and nutrients resulting from a marine based diet. Assuming that the seabird diet does not vary greatly over time, changes in the levels of chemical assemblages with depth in a guano affected sediment core are indicative of fluctuations in the amount of guano input over time and hence variations in population (Zale, 1994; Sun et al. 2004; Liu et al. 2006a).

Here, I present two studies examining the biotransport of nutrients and trace elements to a series of freshwater ponds beneath a northern fulmar (*Fulmarus glacialis*) colony at Cape Vera, on northern Devon Island, Nunavut. The first article, entitled "Bioenrichment of trace elements in a series of ponds near a northern fulmar colony at Cape Vera, Devon Island", used principal component analysis (PCA) axis 1 scores, summarizing several parameters (*i.e.* pH, chlorophyll-*a*, total nitrogen, total phosphorus, dissolved organic carbon, δ^{15}N) to define the ornithogenic gradient present at the site. This confirmed visual rankings defined *a priori* based on the presence of lush vegetation around the ponds. The relationship between the ornithogenic gradient and trace element levels in pond water was then used to assess bioenrichment. We showed that for As, Cd, Co, Cu, Li, Mn, Mo, Ni, Sb and Sr significantly followed the ornithogenic gradient and that the ponds located closest to the colony were the most contaminated.

The second article, "Impact of the northern fulmar (*Fulmarus glacialis*) on the sediment quality of a series of High Arctic freshwater ponds at Cape Vera, Devon Island, Canada" builds upon the findings of the first study. We demonstrate that not only is the northern fulmar a source of nutrients and trace elements to the terrestrial and limnic environments, but that it is capable of funneling marine-derived trace elements (As, Cd and

Zn) to levels exceeding Canadian Sediment Quality Guidelines for the Protection of Aquatic Life in ponds closest to the colony.

These studies add to a growing body of evidence on the importance of biotransport and are the first to examine the seabird biotransport of trace elements in the Canadian Arctic.

2.0 - Bioenrichment of trace elements in a series of ponds near a northern fulmar colony at Cape Vera, Devon Island

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2.1 - Abstract

Seabirds are an important link between their marine feeding areas and their terrestrial breeding environments, transporting both marine-derived nutrients and contaminants, and then depositing them on land in their guano. In this study, the impact of a large northern fulmar (*Fulmarus glacialis)* colony on the water chemistry of 26 nearby ponds spanning a gradient of seabird influence was investigated at Cape Vera, Devon Island, in the Canadian High Arctic. The presence of the fulmar colony has led to nutrient and trace element enrichment in the ponds, as evidenced by the close association between As, Cd, Co, Cu, Li, Mn, Mo, Ni, Sb and Sr and the ornithogenic gradient. The ponds most affected by the fulmar colony were characterized by increased primary production, high organic carbon concentrations and elevated pH; conditions favorable for the *in-situ* removal of metals from the water column. Despite this, the highest trace element concentrations were observed in the seabird-influenced ponds, suggesting that these elements were bioenriched.

Keywords

Biotransport, trace elements, Cape Vera

2.2 - Introduction

The Arctic tundra is sparsely covered with plant life due to its dry climate, low nutrients and extremely cold temperatures. Vegetation, mainly small cushion plants, mosses and lichens, is more common in wet areas proximate to nutrient sources (Billings 1973; Godzik 1991). The presence of seabird colonies creates hotspots of biological productivity at nest sites, due to the deposition of guano, which is rich in marine-derived nutrients (Bildstein et al. 1992; Ellis et al. 2006). Stimulated by the nutrient rich guano, the area surrounding a colony may become so biologically productive that the chlorophyll reflectance is even visible from space by Landsat satellite imagery (Blais et al. 2007).

Soil and sediments receiving guano display elevated $\delta^{15}N$ signatures compared to regions not affected by guano (Mizutani and Wada 1988; Garcia et al. 2002). This is attributable to (1) the high nitrogen isotope ratio of guano caused by an enrichment of ~3‰ per trophic level along the marine food chain (Garcia et al. 2002; Hobson and Clark 1992) and (2) post-depositional modification of isotope ratios. The light ^{14}N isotope may be preferentially lost by ammonia volatilization, nitrification and denitrification, increasing the ^{15}N in the residual nitrogen (Mizutani et al. 1986; Frank et al. 2004; Harding et al. 2004). Partial loss of nitrogen by ammonia volatilization has been shown to be the most important process in the alkaline soils of seabird rookeries (Lindeboom 1984; Yoneyama 1996); leading to isotope fractionation of 24.5 to 60‰ and enriching the $\delta^{15}N$ in the remaining nitrogen (Yoneyama 1996; Bedard-Haughn et al. 2003). Blais et al. (2005) used $\delta^{15}N$ in surface sediments as a proxy of seabird influence, demonstrating that the northern fulmar (*Fulmarus glacialis*) is an important vector of marine-derived nutrients and contaminants to an Arctic coastal pond ecosystem. Furthermore, Evenset et al. (2004, 2007), showed that high levels of persistent organic pollutants and metals in Lake Ellasjøen, Bjørnøya, were caused by inputs from little auk (*Alle alle),* black-legged kittiwakes (*Rissa tridactyla*) and glaucous gulls (*Larus hyperboreus).*

The composition of a seabird's guano reflects its dietary intake (Norheim 1987). In the eastern Canadian High Arctic, the marine food web is contaminated by a variety of metals whose levels in biota are comparable to those found in similar species in more temperate regions (Muir et al. 1999; Campbell et al. 2005). In the Northwater Polynya (Baffin Bay) food web, the northern fulmar has the highest hepatic concentrations of Cd, Mn, Rb and Zn of all avian biota (Campbell et al. 2005). Similar to the processes described for the biotransport of nutrients (above), metals taken up through feeding will likely be transported back to the terrestrial environment via guano deposition. Indeed, previous studies (see, e.g., Godzik 1991; Headley 1996; Dowdall et al. 2005) have found metals (e.g. Cd, Cu, Zn) and radionuclides (e.g. ^{137}Cs, ^{226}Ra, ^{238}U) to be significantly enriched in areas affected by seabird guano.

The seabird mediated enrichment of marine-derived metals into their nesting sites has led to the development of geochemical markers to reconstruct historical population variations of penguins in Antarctica (Zale 1994; Sun et al. 2004) and red-footed boobies (*Sula sula*) in the South China Sea (Liu et al. 2006). Our study provides a unique opportunity to examine the elemental composition of 26 ponds that span the full range of ornithogenic effects, and provides a test to determine which elements were enriched across a broad ornithogenic gradient. The applications for this information could include, among other things, paleoenvironmental reconstructions. As long-term population data for the northern fulmar in the Arctic do not exist, paleolimnological approaches aimed at reconstructing bird population histories may fill important knowledge gaps (Keatley et al. 2009).

2.3 - Methods

2.3.1 - Study Site

Cape Vera, located on northern Devon Island, Nunavut, Canada (76°15’ N, 89°15’W; Fig. 1), is home to the most northerly and isolated northern fulmar (*Fulmarus glacialis*) colony in the Canadian Arctic. The colony consists of at least 20,000 birds nesting on 6.4 km of cliffs (Gaston et al. 2006; Mallory 2006). A series of ponds receiving varying degrees of fulmar inputs (*i.e.,* guano, regurgitated stomach oils, feathers, and carcasses) are located beneath the cliffs, spanning a broad gradient of ornithogenic influence. The ponds in this study were small (<1 ha), shallow (<1.5 m deep), supersaturated in O_2 and supported basic aquatic life consisting of periphyton, phytoplankton, zooplankton and chironomids. At the time of sampling (July), many of the ponds in this study had no active inflows or outflows. However, the presence of dry, moss encrusted channels between many of the ponds and the proximity of the ponds (especially in the fulmar-affected area) make interconnections likely at times of high flow. Despite their coastal placement, the ponds receive minimal abiotic marine inputs as evidenced by the low specific conductivities (59 to 484 $\mu S \cdot cm^{-1}$), low concentrations of Na^+ and Cl^- and dominance of Ca^{2+} and dissolved inorganic carbon (DIC) (Keatley et al. 2009). Cape Vera provides a valuable opportunity to study the impact of the northern fulmar colony on the ponds as their proximity ensures that the ponds are underlain by similar bedrock and are subject to similar climatic conditions and atmospheric inputs.

Seabird-influenced ponds (CV3-9, 9a, 10, 13, 14, 15, 20, 30, 31, 43)

Fulmar guano reaches the affected ponds mainly via runoff, with areas of high impact easily distinguished by the presence of lush green mosses, cushion plants and flowers (mostly *Saxifraga oppositifolia* and *S. cespitosa).* As such, the hydrology of the site plays a large role in the extent of inputs from the colony. For example, two ponds, CV5 and 6, while located close to the cliffs, receive little runoff from the colony. Likewise, due to the drainage patterns of the site, two other ponds (CV7 and CV31) receive much higher inputs of glacial flour from a nearby melting glacier than the other ponds. In addition to visual cues, the impact of the birds on the ponds was established by measuring algal biomass, water chemistry variables and $\delta^{15}N$ in sediments.

Reference ponds (CV1, 2, 11, 12, 16, 17, 18, 22, 23, 24)

Reference (background) ponds were located outside the present range of the seabird colony (Figure 1). Unlike those in the vicinity of the colony, the catchments of the control ponds were rocky with little moss and few flowers. The presence of orange jewel lichen (*Xanthoria elegans*), which flourishes on guano-derived nutrients, on the cliffs at Cape Hawes (CV22, 23 and 24) and near CV16, 17 and 18 suggested that these were abandoned colony sites (Michelutti et al. 2009). Nevertheless, the water chemistry and nutrient concentrations of these ponds were comparable to other High Arctic ponds unaffected by seabirds (Michelutti et al. 2002; Antoniades et al. 2003; Lim and Douglas 2003).

2.3.2 - Sampling and Chemical Analysis

The water chemistry of a total of 26 ponds was sampled in July between 2004 and 2007. Due to logistic constraints, not all ponds were sampled each year. Water samples were collected 1 to 2m from the shore by submerging pre-washed bottles beneath the surface. Sampling procedures followed those of other high Arctic limnological studies (see Michelutti et al. 2002; Antoniades et al. 2003; Lim and Douglas 2003). Protocols for bottling, filtering and methods for chemical analysis are given in Environment Canada (1994a, b). Temperature (handheld thermometer), specific conductance (YSI model 33 conductivity meter) and pH (handheld Hanna pHEP meter), were measured in the field. Dissolved oxygen was measured in the field using a YSI in 2006 and 2007. Unfiltered water was used for the analysis of major ions (Ca, Cl, Mg, K, Na, SO_4), minor ions (Ba, Li, Sr), total trace elements (Ag, Al, As, Be, Bi, Cd, Co, Cr, Cu, Fe, Ga, La, Mn, Mo, Ni, Pb, Rb, Sb, Se, Sr, Tl, U, V, Zn), and total phosphorus - unfiltered (TPU). Water was filtered through a 0.45 μm Sartorius cellulose acetate filter for analysis of total phosphorus - filtered (TPF), total nitrogen (TN), nitrate-nitrite (NO_2-NO_3), ammonia (NH_3), dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC). Samples for particulate organic carbon [POC] and particulate organic nitrogen [PON] were filtered through pre-ignited 0.7 μm glass microfiber filters (Whatman GF/C). Samples for chl-*a* were obtained by filtering water through a separate glass fiber filter. The PON/POC and chl-*a* filters were placed in Petri dishes, wrapped in aluminum foil and kept on ice in a cooler along with water samples until shipping to the National Laboratory for Environmental Testing (NLET) at the National Water Research Institute in Burlington, Canada where analyses are performed with methods accredited by the Canadian Association for Environmental Analytical Laboratories. Trace metals were analyzed using ICP-MS with quality assurance/quality control (QA/QC) procedures carried out for every analytical run. Control and verification standards, blanks, duplicates, spiked samples and 3 reference water samples spiked with low, medium and high concentrations to cover the analytical range of each metal were used in every run in order to assure QC. Detection limits are listed in Table S1.

2.3.3 - Stable isotope analysis

The top ~1cm of sediment from the bottom of each pond was collected ~1m from shore by hand directly into Whirl-Pak® bags. Sediment samples were kept cool and in the dark while in the field and subsequently frozen upon return to the laboratory until analysis. Stable isotope analysis was completed by the G.G Hatch Stable Isotope Laboratory at the University of Ottawa. Freeze-dried sediment samples were flash combusted at 1800°C in an elemental analyzer (EA 1110, CE Instruments, Italy). The resulting gases were carried via helium through the EA to purify and separate into N_2 and CO_2. Gases were carried from the EA into an isotope ratio mass spectrometer (DeltaPlus Advantage IRMS, ThermoFinnigan, Germany) for isotope analysis via a Conflo interface (Conflo III). Data were normalized using internal standards calibrated with international standards IAEA-CH-6, IAEA-NBS22, IAEA-N1, IAEA-N2, USGS-40, USGS-41 with a precision of ± 0.2‰. Stable isotope concentrations were expressed in δ notation (‰) according to:

$$\delta^{15}N = [(^{15}N/\ ^{14}N_{sample})/(^{15}N/\ ^{14}N_{standard}) - 1] \times 1000$$

2.3.4 - Statistical and data analysis

Variables below the limit of detection (DL) in more than 50% of the ponds were removed from analysis. This resulted in the elimination of Ag (DL = 0.001 $\mu g \cdot L^{-1}$), Be (DL = 0.001 $\mu g \cdot L^{-1}$), Bi (DL = 0.001 $\mu g \cdot L^{-1}$) and Se (DL=0.05 $\mu g \cdot L^{-1}$) from analysis. A value of half the DL was used when single measurements were below DL. In the case of ponds sampled in multiple years, a weighted average for each variable was taken so that these ponds had the same contribution in statistical analyses as ponds sampled in only one year.

To evaluate whether the overall suite of metal concentrations differed between background and affected ponds, we first conducted a MANOVA on pond chemistries, using Wilk's lambda test criterion to indicate important effects. We followed the MANOVA with one-way ANOVAs on individual parameters, and used a sequential Bonferroni adjustment to our significance level to account for the number of statistical tests conducted (Rice 1989). Principal component analysis (PCA) was conducted using CANOCO 4.5 (ter Braak and Smilauer 2002). Environmental variables (Figure 2) were included in a PCA in order to summarize the main directions of environmental gradients. The scores of PCA axis 1 were subsequently used as a new independent variable in statistical analyses. A second PCA was run using the trace element concentrations in order to assess the similarity between sites in multivariate space. Pearson correlations were used to assess the strength of the relationship between the PCA axis 1 scores and trace element concentrations. CV7 and 31 were found to be outliers and were removed from the data set for correlation analysis. Systat® version 10.0 was used to perform the MANOVA, ANOVA and correlation analyses, with results considered statistically significant at $\alpha \leq 0.05$ (two-tailed). Finally, WATEQ4F (Ball and Nordstrom 1991) was used to compute the thermodynamic speciation of trace elements in the ponds as well as mineral solubility.

2.4 - Results and Discussion

The water chemistry of freshwater ponds can be significantly modified by the deposition of guano in their watersheds (Mallory et al. 2006). This was apparent at Cape Vera, where the water chemistry of the ponds spanned a broad gradient, apparently related to the level of ornithogenic impact (Table 1). The TPU and TPF ranged widely from 4 to 223 $\mu g \cdot L^{-1}$ (median 31 $\mu g \cdot L^{-1}$) and 2 to 52 $\mu g \cdot L^{-1}$ (median 9 $\mu g \cdot L^{-1}$), respectively. The TN concentrations for Cape Vera varied from 72 $\mu g \cdot L^{-1}$ to 1590 $\mu g \cdot L^{-1}$, with a median of 261 $\mu g \cdot L^{-1}$. While the majority of the Cape Vera ponds displayed TN concentrations comparable to other Canadian High Arctic ponds (*e.g.* Michelutti et al. 2002; Antoniades et al. 2003; Lim and Douglas 2003), the highly affected ponds greatly surpassed reported values (Table 2). In our study, TN concentrations in the heavily affected ponds (CV 3, 4, 8 and 43) were 1590, 995, 922 and 908 $\mu g \cdot L^{-1}$. These were similar to the TN concentrations found in Arctic ponds influenced by waterfowl on Southampton Island (Mallory et al. 2006).

The highly affected ponds were also the most productive. The chl-*a* concentrations varied greatly from pond to pond, ranging from 0.5 $\mu g \cdot L^{-1}$ in CV23 to 58.6 $\mu g \cdot L^{-1}$ in CV8. The chl-*a* concentrations in the highly affected ponds were up to 2 orders of magnitude higher than those of the less affected Cape Vera ponds (Table 1). This increase in biomass due to nutrient input from the colony, coupled with 24-hour sunlight in July, likely caused the high pH recorded in the seabird-influenced ponds. The pH of most Arctic ponds falls in the range of 7.1 to 8.4 (Lim and Douglas 2003); the pH of the seabird-influenced ponds exceeded this range, reaching 10.9.

Many Arctic water bodies are characterized by very low metal concentrations, with only Al, Mn, Fe, Cu and Zn typically above detection limits (Michelutti et al. 2002; Antoniades et al. 2003). Interestingly, at Cape Vera, of the 22 metals analyzed only Ag, Be, Bi and Se were below detection limits in more than 50% of the samples. In the high Arctic, only ponds located in an oasis on northern Ellesmere Island had metal concentrations as high as or higher than Cape Vera (Keatley et al. 2007). Metals are typically more soluble in acidic conditions; Cd, Cu and Zn precipitate as hydroxides or carbonates in alkaline waters and are removed from the water column (McNeely et al. 1979; Sigg 1987). The ponds most affected by the fulmar colony were characterized by increased productivity, high organic carbon concentration, high pH and increased sedimentation rates (Michelutti et al. 2008); favorable conditions for the *in-situ* removal of metals from the water column. WATEQ4F results demonstrate that metals (Cu, Cd, Ni, Pb and Zn) in the seabird-affected ponds are present largely as oversaturated hydroxides (Table 3; Appendix 1). It is important to note that, despite this, the highest concentrations of trace elements were found in the seabird-affected ponds, demonstrating that the northern fulmar is a source of trace elements to the ecosystem beneath the colony, maintaining the elevated levels.

Using MANOVA, the Wilk's lambda test criterion indicated that trace element concentrations in the ponds receiving ornithogenic inputs differed from the control ponds (Wilk's lambda = 0.14, $F_{14,41}$ = 13.06, p = 0.003). Using one-way ANOVAs, significant differences in the concentrations of As ($F_{1,24}$=12.1, p=0.002), Cd ($F_{1,24}$=11.5, p=0.002), Co ($F_{1,24}$=10.5, p=0.003), Cu ($F_{1,24}$=11.6, p=0.002), Li ($F_{1,24}$=10.9, p=0.003), Mn ($F_{1,24}$=11.1, p=0.003), Ni ($F_{1,24}$=12.3, p=0.002) and Sb ($F_{1,24}$=11.9, p=0.002) were found between affected and background ponds (Figure 3), supporting the ornithogenic enrichment of these elements. Surprisingly, significant differences were not found between groups for Zn and Rb, elements shown to biomagnify in the Northwater Polynya (Baffin Bay) foodweb (Campbell et al. 2005). We speculate that the ornithogenic signal was not distinguishable due to high inputs of these metals from the catchment.

Blais et al. (2005) and Keatley et al. (2009) used the sedimentary δ^{15}N signatures in the ponds as an indicator of ornithogenic influence at Cape Vera. However, it is also acknowledged that δ^{15}N values are subject to post-depositional modification through a variety of chemical processes. Ammonia volatilization, shown to be the most significant fractionation mechanism in seabird rookeries (Lindeboom 1984; Yoneyama 1996), is likely an important process in the seabird-affected ponds as it is pH-dependent and is particularly pronounced at $pH > 8.5$. In this study, we used PCA axis 1 scores, summarizing environmental variables, as a proxy for ornithogenic influence (hereafter referred to as the "ornithogenic gradient"). Axis 1 and 2 of the PCA accounted for 79% and 16% of the total variation, respectively. Variables loading highly (correlation >0.85) onto axis 1 were chl-*a*, TN, TPU, DIC, DOC, $\delta^{15}N$ and pH (Figure 2).

A PCA was conducted using the trace element concentrations to assess the similarity between sites in multivariate space (Figure 4). Ponds outside the influence of the fulmar colony clustered together to the left side of the diagram. The seabird-affected ponds were distributed along axis 1, with the heavily-influenced ponds located farthest to the right. CV7 and CV31 displayed distinct characteristics from the other ponds, plotting highly on PCA axis 2. The concentrations of Al, Cr, Fe, La, Mn, Ni, Pb, Rb and Zn in CV7 were up to an order of magnitude higher than in the other ponds. CV31, directly downstream of CV7, was a brilliant turquoise color, characteristic of suspended glacial flour in the water column (Chanudet and Filella 2007). Due to the hydrology of the site, the glacial flour would pass through CV7 before reaching CV31. Since the metals that were found in high concentrations are generally associated with local geological media (McNeely et al. 1979; Outridge et al. 2005), the input of glacial flour probably caused the high levels of these metals.

The strength of the relationship between the ornithogenic gradient and trace elements was used to assess bioenrichment. Significant positive relationships with the ornithogenic gradient were found for As, Cd, Co, Cu, Li, Mn, Mo, Ni, Sb and Sr (Figure 5). This indicates that trace elements were not only markedly bioenriched in ponds receiving guano compared to control ponds, but that the most contaminated ponds were those in closest proximity to the cliffs (presumably receiving the greatest concentration of guano). Given this consistent pattern in aquatic chemistry, we predict that aquatic biota in ponds closest to the fulmar colony will be the most contaminated. This may have significant implications for contaminant transfer in local food chains.

Northern fulmars nesting on the cliffs at Cape Vera not only provide nutrient supplements to the ponds, but this study confirms that trace elements are being transported by the northern fulmar from the ocean to the terrestrial environment, leading to contaminant bioenrichment in ponds receiving varying inputs of fulmar guano. Thus, our study from the high Arctic adds to the growing body of evidence suggesting that biotransport can be an important pathway of contaminant transfer between food webs (Blais et al. 2005; Evenset et al. 2004; Krümmel et al. 2003).

2.5 - Acknowledgements

This study was funded by the Natural Sciences and Engineering Research Council of Canada (NSERC), the Polar Continental Shelf Project, the Canadian Wildlife Service and the Northern Scientific Training Grants. The water chemistry analyses were greatly facilitated by X. Wang and D. Muir at the Canada Centre for Inland Waters, and the analyses were carried out at National Laboratory for Environmental Testing (NLET) at the National Water Research Institute in Burlington, Ontario. This is PCSP contribution # **vxxx.** We also thank all our colleagues who helped sample these ponds over the last four years.

Table 1 – Chemical parameters for Cape Vera ponds sampled July 2004-2007.

Pond	n	Latitude	Longitude	Surface Area (m^2)	pH	DO (mg·L^{-1})	DOC (mg·L^{-1})	TN (µg·L^{-1})	TPF (µg·L^{-1})	TPU (µg·L^{-1})	chl-*a* (µg·L^{-1}))	δ^{15}N (‰)
Seabird-affected ponds												
CV3	1	76°15’32.5"	89°12’04.5"	1300	9.63	n/a	3.9	1590	14	100	45.6	18.4
CV4	1	76°15’30.8"	89°12’04.6"	5650	9.95	n/a	7.1	1000	23	47	10.9	15.0
CV5	3	75°13'49.6"	89°12'55.6"	2400	7.83	11.50	0.7	120	7	13	2.9	9.0
CV6	3	77°13'48.8"	89°12'55.3"	1450	8.08	10.15	1.2	200	4	11	5.3	8.0
CV7	2	76°13'47.9"	89°13'31.7"	1250	8.23	n/a	1.0	160	9	35	6.4	11.9
CV8	3	76°13'46.8"	89°14'07.5"	2350	10.65	17.54	11.6	950	46	197	36.8	16.3
CV9	4	76°13'45.8"	89°14’25.6"	7100	9.32	13.10	2.0	350	24	35	6.8	13.7
CV9a	3	76°13'44"	89°14'33"	9100	10.11	13.87	6.6	620	52	131	35.7	10.9
CV10	2	76°13'45.8"	89°14'50.9"	1000	10.20	>20	7.2	570	26	32	15.4	13.3
CV13	3	76°14'0.4"	89°12'29.5"	4300	8.80	12.23	4.9	800	28	42	10.8	19.4
CV14	3	76°12'42'	89°13'13"	8900	8.83	12.83	5.0	460	14	31	1.0	8.2
CV15	3	76°13'44"	89°13'07”	900	8.22	14.21	2.6	290	5	9	1.9	16.3
CV20	3	76 °13'42"	89°13'31	3500	10.28	12.47	7.8	770	30	42	0.9	7.4
CV30	2	76°14'41.6"	89°15'1.5	7300	10.9	15.12	5.5	730	40	190	0.9	16.9
CV31	2	76°13'54.4"	89°12'30.9	2100	8.4	11.45	1.4	170	3	17	0.9	12.0
CV43	1	76°13’46.2	89°13’23.7	3000	n/a	17.80	9.6	910	30	115	45.2	n/a
Mean				3850	9.30	13.53	4.88	610	22	65	14.2	13.1
St. Dev.				2865	1.02	2.35	3.29	400	15	62	16.6	3.9
Max.				9100	10.90	>20	11.6	1590	52	197	45.6	19.4
Median				2700	9.32	12.97	4.95	600	39	39	6.6	13.3
Min.				900	7.83	10.15	0.7	120	3	9	0.9	7.4
Control ponds												

CV1	2	76°15’51.6"	89°14'17.7"	7000	8.42	12.46	1	203	5	6	5.5	6.62
CV2	1	76°15’48.8"	89°14’20.3"	7850	8.28	n/a	0.9	132	2	4	9.7	4.36
CV11	1	76°10’37.7"	89°31’22.2"	300	8.70	n/a	0.9	72	2	17	0.9	0.7
CV12	2	76°12'32"	89°13'42"	200	8.28	10.63	7.2	736	19	36	0.5	2.97
CV16	1	76°12'49"	89°18'15”	3000	7.65	n/a	n/a	119	5	11	2	5.99
CV17	1	76°12'49"	89°18'09"	n/a	7.35	n/a	1.4	153	6	14	0.9	n/a
CV18	1	76°12'53"	89°18'07”	n/a	7.85	n/a	n/a	141	9	10	1.5	6.46
CV22	1	76 °17'50"	89 °17'48"	n/a	7.55	n/a	1.8	261	3	36	0.9	2.78
CV23	1	76°17'50"	89°17'50”	n/a	7.20	n/a	1.5	210	3	8	0.6	1.61
CV24	1	76°17'39"	89°17'48”	n/a	8.00	n/a	1.5	162	11	10	0.5	1.62
Mean				3670	7.93	11.55	2.0	219	7	15	2.3	3.68
St. Dev.				3620	0.49	1.29	2.1	189	5	12	3.0	2.26
Max.				7850	8.70	12.46	7.2	736	19	36	9.7	6.62
Median				3000	7.93	11.55	1.5	158	5	11	0.9	2.97
Min.				200	7.20	10.63	0.9	72	2	4	0.5	0.70

Table 2: Mean selected water chemistry characteristics from recent limnological studies of Canadian High Arctic ponds and lakes.

Location	n	pH	TN ($mg \cdot L^{-1}$)	TPU ($mg \cdot L^{-1}$)	TPF ($mg \cdot L^{-1}$)	chl-*a* ($mg \cdot L^{-1}$)	Reference
Prince Patrick Island	35	7.9	616	16.5	8.5	0.8	1
Ellesmere Island	30	8.4	465	14.6	4.5	1.1	1
Ellef Rignes Island	24	6.8	295	41.9	6.1	1.4	2
Victoria Island	25	7.69	197	1.4	1.5	0.0003	3
Haughton Crater, Devon Island	25	8.3	148.4	3.7	4.1	0.76	4
Cape Vera, seabird-influenced ponds	16	9.3	610	65	22	14.2	5
Cape Vera, reference ponds	10	7.93	219	15	7	2.3	5

[1] Antoniades et al. 2003a; [2] Antoniades et al. 2003b; [3] Michelutti et al. 2002; [4] Lim and Douglas 2003; [5] This study.

Table 3: Speciation of Cd, Cu, Ni, Pb and Zn in selected Cape Vera ponds calculated using WATEQ4F. For example of a full WATEQ4F printout see Appendix 1.

	Species (ppm)										
Pond	Cd^{2+}	CdOH	$Cd(OH)_2$	Cu^{2+}	CuOH	$Cu(OH)_2$	$Cu(OH)_3$	Ni^{2+}	NiOH	$Ni(OH)_2$	$Ni(OH)_3$
Reference											
CV1	9.49	0.01	0.00	17.81	5.83	604.39	0.00	292.57	0.61	0.05	0.00
CV11	4.86	0.04	0.00	0.09	0.23	195.71	0.01	67.63	1.07	0.72	0.01
CV22	5.81	0.00	0.00	17.52	3.06	178.38	0.00	0.21	0.00	0.00	0.00
Seabird-influenced											
CV8	3.12	5.30	20.06	0.00	0.05	3632.32	17.30	3.92	12.94	686.52	546.13
CV9	28.21	1.39	0.25	0.03	0.48	1543.65	0.35	299.59	28.65	72.02	2.74
CV9a	13.39	6.61	4.90	0.00	0.22	4306.06	6.02	547.02	514.03	5436.00	1272.21
CV10	5.72	1.93	2.67	0.00	0.05	1193.01	2.08	42.02	27.54	531.56	154.70
CV30	2.49	2.62	31.06	0.00	0.04	4887.48	42.49	630.00	3.80	450.19	654.53

	Species (ppm)							
	Pb^{2+}	PbOH	$Pb(OH)_2$	$Pb(OH)_3$	Zn^{2+}	ZnOH	$Zn(OH)_2$	$Zn(OH)_3$
Reference								
CV1	64.94	35.36	0.61	0.00	520.90	7.88	10.55	0.00
CV11	24.8	104.31	14.86	0.13	65.77	7.60	85.20	0.23
CV22	0.01	6.39	73.17	60.55	290.98	2.290	1.77	0.00
Seabird-influenced								
CV8	0.01	6.39	73.17	60.55	0.07	1.76	1550.89	386.65
CV9	4.50	116.27	61.78	2.44	111.57	77.73	3250.40	38.65
CV9a	0.25	42.75	139.77	33.96	1.15	8.10	1383.48	101.27
CV10	0.03	5.02	20.48	6.19	0.47	2.24	719.19	65.50
CV30	0.01	4.71	95.84	144.71	0.03	0.58	1170.59	532.60

Figure captions

Figure 1: Map of study location. a) Cape Vera, Devon Island, Canada. b) Pond locations, adapted from Keatley et al. (2007).

Figure 2: PCA biplot summarizing 13 measured environmental variables at Cape Vera. Axis 1 scores were used as a proxy for ornithogenic influence.

Figure 3: Box plots comparing selected element concentrations between affected (A) and background (B) ponds. a)As; b) Cd; c) Co; d) Cu; e) Li; f) Mn; g) Ni; h) Zn; i) Rb. There were no significant differences between affected and control ponds for Zn or Rb. n=16 for (A) and n=10 for (B)

Figure 4: PCA biplot accessing the similarity between sites in multivariate space. Control ponds are represented by circles, affected ponds by squares. PCA axis 1 represents the degree of seabird influence. PCA axis 2 represents the influence of the geological media.

Figure 5: Bioenrichment of trace elements in Cape Vera ponds. Z-scores of elements are plotted against PCA axis 1 scores, representing the ornithogenic gradient. a) As; b) Cd; c) Co; d) Cu; e) Li; f) Mo; g) Ni; h) Sb; i) Sr. All correlations are significant ($p<0.05$). n=26.

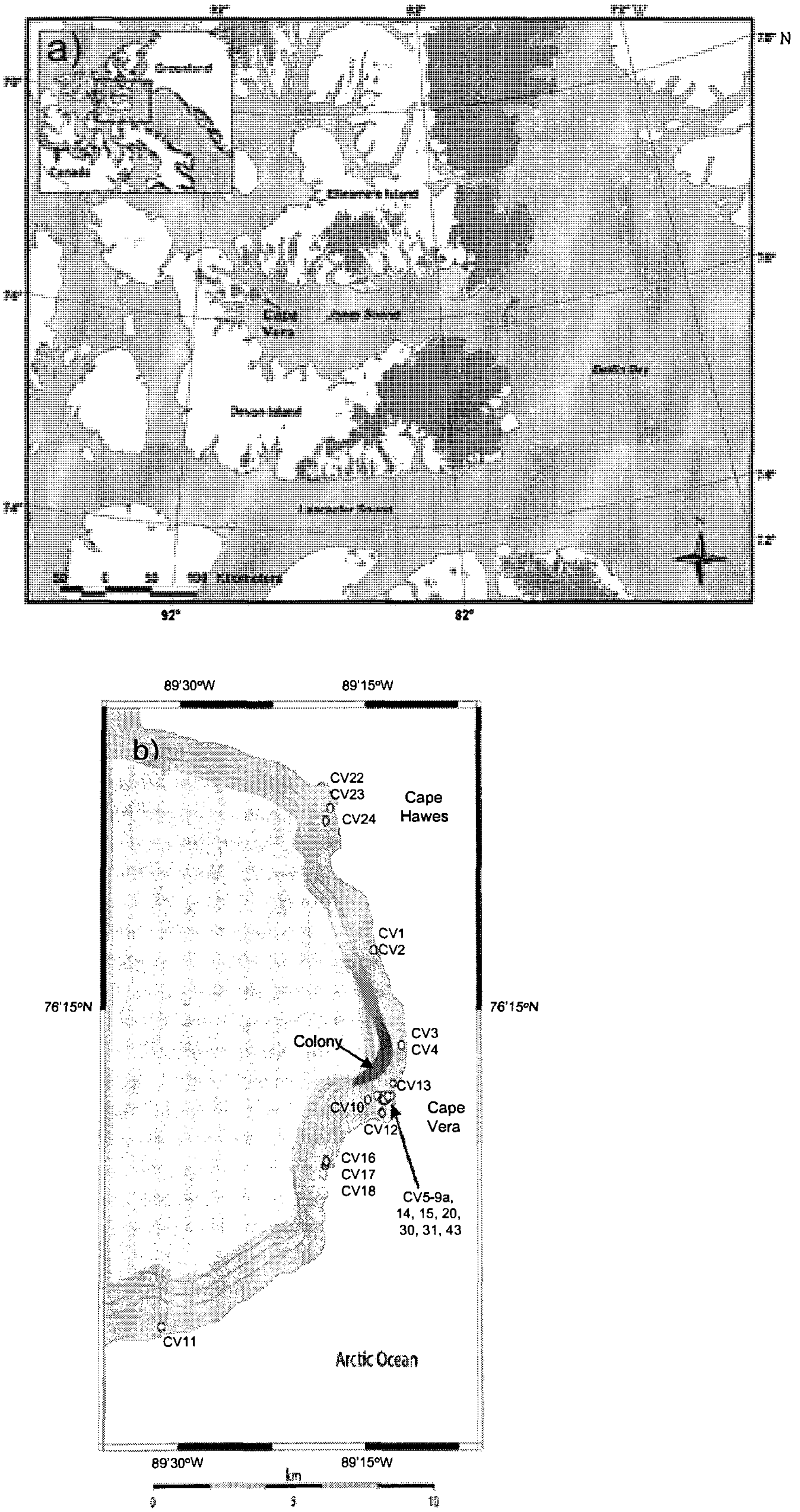

a)
Greenland
Canada
N
Ellesmere Island
Cape Vera
Jones Sound
Devon Island
Baffin Bay
Lancaster Sound
50 0 50 100 Kilometers
92°
82°
b)
89'30°W
89'15°W
76'15°N
CV22
CV23
CV24
Cape Hawes
CV1
CV2
CV3
CV4
Colony
CV13
CV10
CV12
Cape Vera
CV16
CV17
CV18
CV5-9a, 14, 15, 20, 30, 31, 43
CV11
Arctic Ocean
km
0
5
10

Figure 1

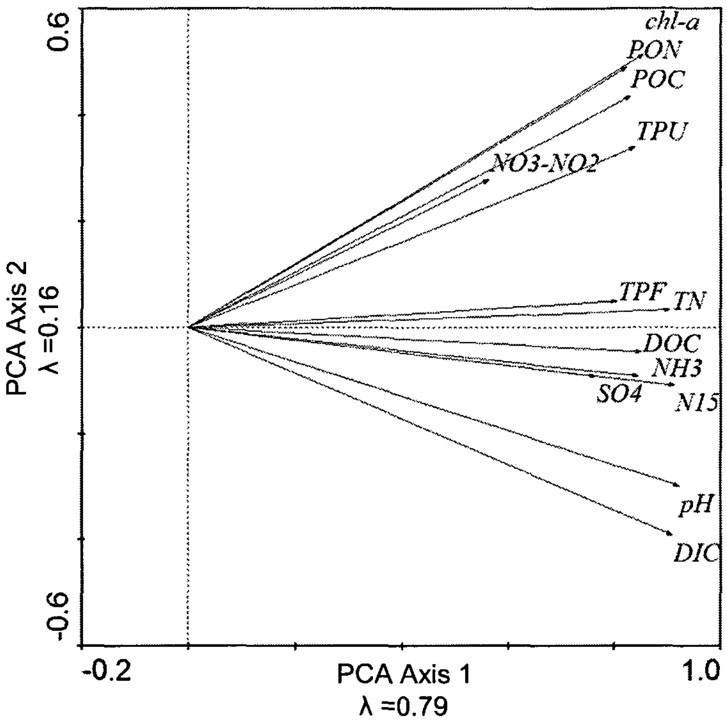

chl-a
PON
POC
TPU
NO3-NO2
TPF
TN
DOC
NH3
SO4
N15
pH
DIC
0.6
-0.6
PCA Axis 2
λ =0.16
-0.2
1.0
PCA Axis 1
λ =0.79

Figure 2

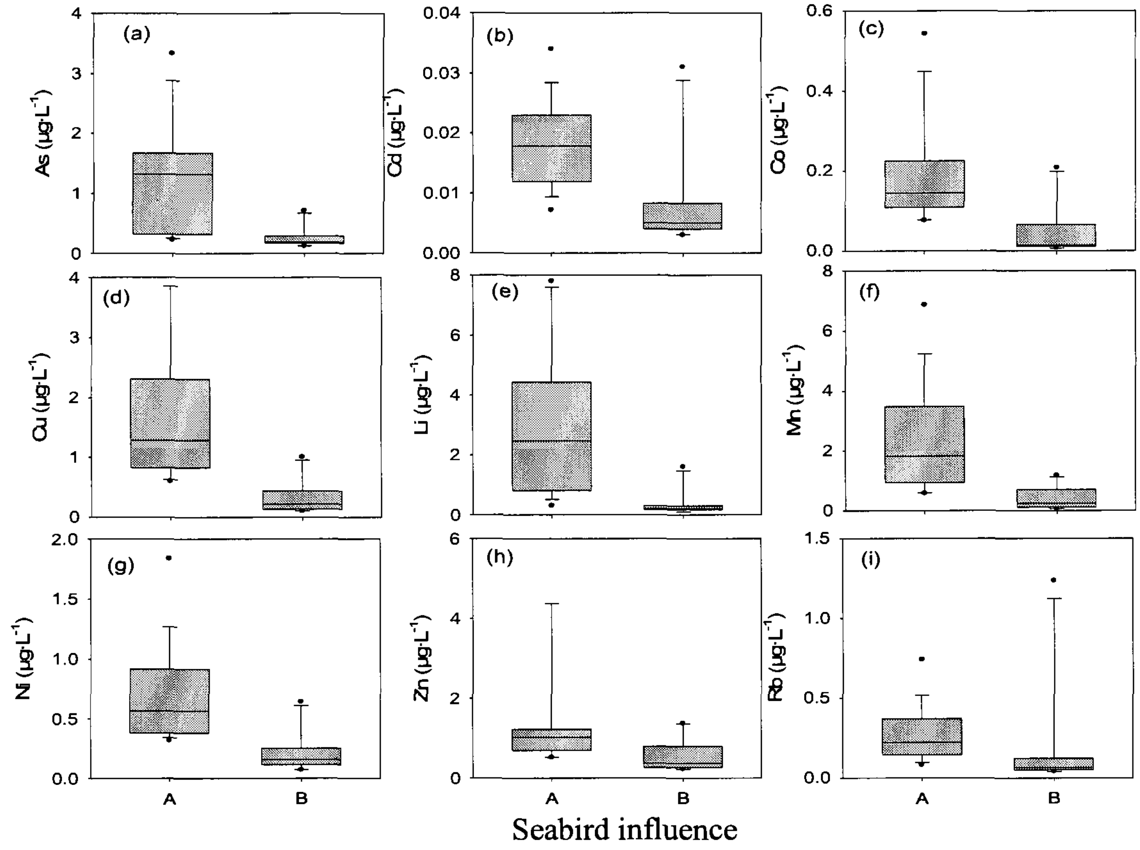

(a)
As (μg·L^{-1})
0
1
2
3
4
(b)
Cd (μg·L^{-1})
0.00
0.01
0.02
0.03
0.04
(c)
Co (μg·L^{-1})
0.0
0.2
0.4
0.6
(d)
Cu (μg·L^{-1})
0
1
2
3
4
(e)
Li (μg·L^{-1})
0
2
4
6
8
(f)
Mn (μg·L^{-1})
0
2
4
6
8
(g)
Ni (μg·L^{-1})
0.0
0.5
1.0
1.5
2.0
(h)
Zn (μg·L^{-1})
0
2
4
6
(i)
Rb (μg·L^{-1})
0.0
0.5
1.0
1.5
A
B
A
B
A
B
Seabird influence

Figure 3

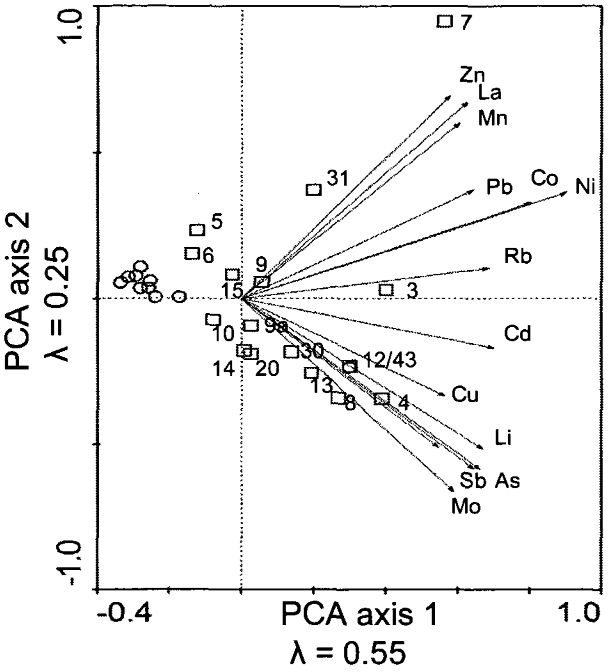
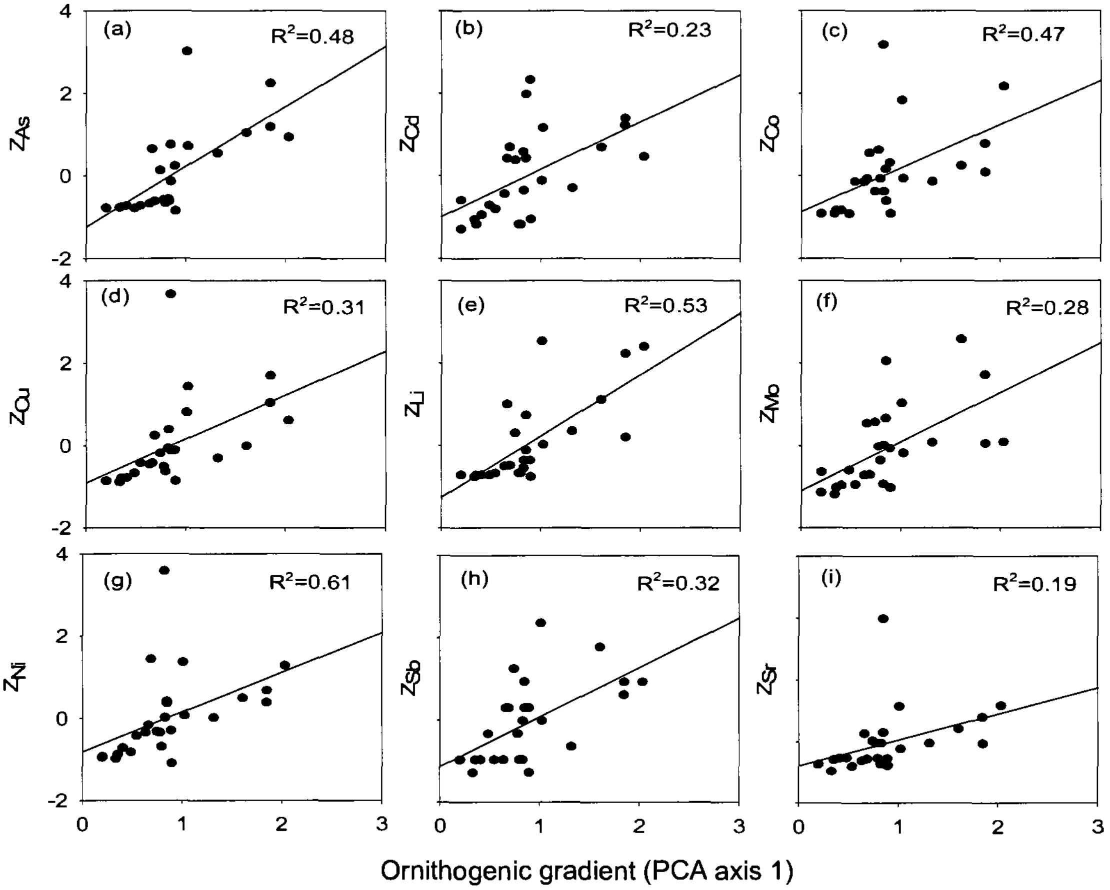

PCA axis 2
λ = 0.25
1.0
-1.0
PCA axis 1
λ = 0.55
-0.4
1.0
7
Zn
La
Mn
31
Pb
Co
Ni
5
6
9
15
Rb
3
Cd
10
9a
14
20
30
12/43
13
8
4
Cu
Li
Sb
As
Mo

Figure 4


(a)
R²=0.48
(b)
R²=0.23
(c)
R²=0.47
(d)
R²=0.31
(e)
R²=0.53
(f)
R²=0.28
(g)
R²=0.61
(h)
R²=0.32
(i)
R²=0.19
Z_As
Z_Cd
Z_Co
Z_Cu
Z_Li
Z_Mo
Z_Ni
Z_Sb
Z_Sr
4
2
0
-2
0
1
2
3
Ornithogenic gradient (PCA axis 1)

F

igure 5

Table S1: Trace element concentrations ($\mu g{\cdot}L^{-1}$) in pond water at Cape Vera, Devon Island

Analyte	**Al**	**As**	**Ba**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**La**	**Li**	**Mn**	**Mo**	**Ni**	**Pb**	**Rb**	**Sb**	**Sr**	**Zn**
Detection limits	0.2	0.01	0.05	0.001	0.002	0.005	0.02	0.5	0.001	0.2	0.05	0.005	0.02	0.005	0.01	0.001	0.05	0.05
Control																		
CV1	6.0	0.37	1.51	0.013	0.124	0.124	0.63	6.6	0.004	0.3	0.38	0.828	0.32	0.117	0.08	0.047	17.65	0.56
CV2	4.4	0.27	0.95	0.004	0.121	0.126	0.40	3.6	0.001	0.3	0.22	0.589	0.22	0.067	0.04	0.011	12.50	0.28
CV11	5.2	0.12	0.83	0.005	0.007	0.115	0.13	3.1	0.002	< 0.2	0.11	0.148	0.07	0.149	0.06	< 0.001	8.32	1.30
CV12	21.2	0.71	2.67	0.031	0.047	0.162	1.00	78.3	0.025	1.6	1.18	2.165	0.64	0.360	1.24	0.055	89.55	1.38
CV16	5.9	0.17	1.19	0.009	0.012	0.040	0.13	5.9	0.002	0.2	0.11	0.402	0.13	0.022	0.06	0.011	9.06	0.63
CV17	10.1	0.18	0.54	0.005	0.013	0.040	0.10	15.4	0.004	< 0.2	0.26	0.040	0.11	0.028	0.05	0.004	5.08	0.24
CV18	2.8	0.18	0.78	0.003	0.009	0.032	0.13	3.4	0.002	0.2	0.05	0.068	0.12	0.018	0.05	0.008	8.98	0.23
CV22	10.6	0.22	0.77	0.006	0.017	0.047	0.22	37.8	0.013	0.2	0.72	0.187	0.21	0.052	0.12	0.012	12.20	0.30
CV23	10.5	0.20	0.77	0.004	0.016	0.037	0.21	24.6	0.008	0.2	0.69	0.154	0.15	0.065	0.13	0.005	11.50	0.32
CV24	12.7	0.17	1.03	0.008	0.013	0.099	0.35	21.6	0.006	0.2	0.18	0.429	0.17	0.099	0.08	0.025	12.70	0.43
Max	21.2	0.71	2.67	0.031	0.124	0.162	1.00	78.3	0.025	1.6	1.18	2.165	0.64	0.360	1.24	0.055	89.55	1.38
Median	8.1	0.19	0.89	0.006	0.015	0.073	0.22	11.0	0.004	0.2	0.24	0.295	0.16	0.066	0.07	0.011	11.85	0.38
Min	2.8	0.12	0.54	0.003	0.007	0.032	0.10	3.1	0.001	< 0.2	0.05	0.040	0.07	0.018	0.04	0.004	5.08	0.23
CV-3	42.2	1.60	13.2	0.018	0.408	0.097	1.87	72.0	0.366	7.5	4.25	0.880	0.97	0.171	0.39	0.073	41.50	0.72
CV-4	21.8	3.33	8.52	0.013	0.366	0.080	2.11	64.9	0.102	7.8	2.54	1.500	1.00	0.076	0.31	0.115	41.20	0.53
CV5	70.4	0.22	2.79	0.0072	0.105	0.113	0.64	57.5	0.066	0.3	3.71	0.199	0.32	0.204	0.19	0.009	7.98	1.06
CV6	53.9	0.26	3.20	0.013	0.109	0.093	0.60	44.8	0.056	0.7	2.41	0.348	0.35	0.179	0.18	0.013	11.06	0.66
CV7	202.0	0.36	4.49	0.0190	0.542	0.240	1.07	180	0.493	0.6	6.87	0.212	1.84	0.963	0.74	0.012	9.39	6.87
CV8	7.5	2.69	5.47	0.0245	0.233	0.083	2.38	30.5	0.010	7.1	1.25	1.945	0.74	0.143	0.26	0.064	35.10	1.24
CV9	29.1	1.02	2.51	0.0340	0.166	0.065	1.01	81.3	0.030	1.0	2.78	0.779	0.37	0.169	0.14	0.053	12.34	2.34
CV9a	22.8	1.42	2.79	0.0240	0.123	0.071	2.84	64.0	0.014	1.9	1.20	0.696	0.51	0.193	0.12	0.042	17.60	0.99
CV10	11.6	1.28	2.47	0.0115	0.108	0.053	0.79	21.3	0.012	2.7	0.91	0.869	0.49	0.115	0.08	0.022	20.70	0.52
CV13	16.5	1.45	7.30	0.0177	0.153	0.085	5.49	39.2	0.018	3.6	0.63	1.256	0.62	0.350	0.20	0.070	26.67	1.00
CV14	5.7	0.93	3.93	0.0173	0.078	0.060	0.92	24.2	0.007	2.6	0.57	1.199	0.36	0.059	0.24	0.079	22.10	1.18

CV15	30.4	0.31	4.46	0.0110	0.076	0.102	1.61	52.8	0.011	1.0	4.54	0.830	0.49	0.146	0.16	0.041	20.77	1.09
CV20	4.9	1.36	3.22	0.0177	0.124	0.047	0.64	22.4	0.005	4.2	0.60	1.177	0.42	0.091	0.25	0.049	26.10	0.69
CV30	10.8	1.81	3.23	0.0260	0.137	0.061	3.16	58.4	0.015	2.4	1.03	0.858	0.63	0.253	0.11	0.070	20.50	1.06
CV31	112.9	0.31	4.39	0.0200	0.199	0.186	1.44	94.5	0.307	0.8	2.40	0.358	1.03	0.522	0.43	0.046	12.05	3.32
CV43	18.7	1.69	6.60	0.0200	0.160	0.054	1.14	42.3	0.007	4.5	1.08	2.510	0.67	1.030	0.39	0.097	28.60	0.99
Max	202.0	3.33	13.20	0.0340	0.542	0.240	5.49	180.0	0.493	7.8	6.87	2.510	1.84	1.030	0.74	0.115	41.50	6.87
Median	22.3	1.32	4.16	0.0178	0.145	0.081	1.29	55.2	0.016	2.5	1.82	0.863	0.57	0.175	0.22	0.051	20.73	1.03
Min	4.9	0.22	2.47	0.0072	0.076	0.047	0.60	21.3	0.005	0.3	0.57	0.199	0.32	0.059	0.08	0.009	7.98	0.52

3.0 - Impact of the northern fulmar (*Fulmarus glacialis*) on the sediment quality of a series of High Arctic freshwater ponds at Cape Vera, Devon Island, Canada.

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3.1 - Abstract

The northern fulmar (*Fulmarus glacialis)* is an important biovector for the transport of marine-derived nutrients and contaminants to a coastal freshwater ecosystem at Cape Vera, Devon Island, Canada. Here, we confirm the role of the fulmar in the transport of nutrients (N, K and P) and trace elements (As, Cd and Zn) to a series of 10 ponds located along a gradient of seabird influence below the fulmar colony. Concentrations in surface sediments and fluxes of these elements were highest in the pond closest to the colony and declined exponentially as distance increased. A number of the ponds exceeded Canadian Sediment Quality Guidelines for the Protection of Aquatic Life for As and Cd. The pond closest to the colony, and hence receiving the highest input of seabird subsidies, also exceeded the probable effects level for Zn. Cape Vera is located thousands of kilometers from the nearest industrial center and yet the northern fulmar has bioaccumulated As, Cd and Zn from the ocean and funneled these elements into the terrestrial environment at potentially toxic levels.

3.2 - Introduction

Seabirds are a keystone species in the Arctic, transporting marine-derived nutrients to their terrestrial nesting sites (Ellis et al. 2006; Stempniewicz et al. 2007; Keatley et al. 2009). Deposition of guano at densely populated colonies can significantly enrich nutrients on a local scale (Bildstein et al. 1992). As with nutrients, seabirds may also be a significant source of contaminants to the terrestrial environment because seabirds feed high on the marine food web and can accumulate high body burdens of certain pollutants (Buckman et al. 2005; Campbell et al. 2005). Blais *et al.* (2007) postulated that contaminant biovector transport is likely to be most significant for chemicals that biomagnify in food webs and are then funneled into receptor sites by an animal's social behavior. Indeed, many studies have found organic contaminants (*i.e.* PCBs, organochlorine pesticides) and Hg to be significantly enriched in sites receiving seabird subsidies (*e.g.* guano, regurgitated stomach oils, feathers, and carcasses) (Blais et al. 2005; Evenset et al. 2004; 2007). Although biomagnification processes do not apply to most metals (Evenset et al. 2007) the enrichment of metals at seabird nesting sites has been documented in both polar (Godzik 1991; Zale 1994; Headley 1996; Bargagli et al. 1998; Sun et al. 2004; Evenset et al. 2007; Brimble et al. submitted), and temperate/tropical regions (Hawke et al. 1999; Garcia et al. 2002; Liu et al. 2006a, b).

The biotransport of nutrients and contaminants has been well studied in a series of ponds located beneath a large northern fulmar (*Fulmarus glacialis)* colony at Cape Vera, Devon Island, Canada (Blais et al. 2005; Keatley et al. 2009; Michelutti et al. 2009; Brimble et al. submitted). The presence of the ponds across a broad gradient of seabird influence makes Cape Vera an ideal site to study biotransport as their proximity ensures that they are located on similar geology and receive comparable atmospheric inputs, climate and weather. This is particularly important when studying the biotransport of metals as local geology will influence the concentrations of metals found in soil, sediments and biota (Evenset 2007). Sedimentary Hg levels in three highly guano-affected ponds approached or exceeded the Canadian environmental quality guidelines for the protection of wildlife (Blais et al. 2005). Brimble et al. (submitted) found that As, Cd, Co, Cu, Li, Mn, Mo, Ni, Sb and Sr were bioenriched in Cape Vera pond water and that the ponds closest to the cliffs were the most contaminated. This is consistent with Godzik (1991), who observed that metal concentrations were highest in moss where nesting was densest but returned to background levels ~100 m outside of a little auk (*Alle alle*) colony. Here, we assess the role of the northern fulmar in enriching trace elements and determine the level of contamination in Cape Vera sediments due to this process.

3.3 - Methods

Study Site and Sampling

Cape Vera (76°15' N, 89°15'W; Fig. 1) is located on northern Devon Island in the Canadian Territory of Nunavut. From May through September, a colony of ~11 000 pairs of northern fulmars nest on the ~250 m high limestone and dolostone cliffs above a series of coastal freshwater ponds (Gaston 2006). The ponds span a gradient of ornithogenic influence, depending on both their distance from the cliffs and local hydrographic features. The ponds in this study were small (<1 ha), shallow (<1.5 m deep) and supported basic aquatic life consisting of periphyton, phytoplankton, zooplankton and chironomids. Each pond was assigned an unofficial designation, CV#.

Sampling occurred in July over the course of three field seasons: 2005, 2006 and 2007. Ten ponds containing adequate sediment for coring and spanning a gradient of ornithogenic influence were sampled. Temperature (handheld thermometer), specific conductance (YSI model 33 conductivity meter) and pH (handheld Hanna pHEP meter) were measured in the field. Sediment cores with undisturbed sediment-water interfaces were collected from each pond. Cores were taken by hand from the approximate center of the ponds by pushing a plexiglass core tube (inner diameter = 3.75 cm; Glew et al. 2001) into sediment until resistance was met, most likely due to permafrost/bedrock. Cores were extruded and sectioned in the field at 0.5 cm intervals using a Glew (1998) extruder.

In 2007, two fulmars were shot using shotguns with steel shot and dissected. The entire intestinal tract was removed and the contents of the small intestine were extruded into clean falcon tubes. For brevity, the contents of the small intestine shall be referred to as guano. All samples were stored on ice in coolers until they were returned to the lab and kept frozen until analysis.

Sedimentation rate

Sediment cores were radiometrically analyzed using gamma spectrometry. Centrifuge tubes (8.4 cm high and 1.5 cm outer diameter) were filled up to a height 4 cm with sediment that had been freeze dried and ground to a fine powder. After being allowed to settle for 2-3 days, the tubes were sealed with epoxy and allowed to reach radioactive equilibrium for 3 weeks before counting using a digital high purity germanium well detector (DSPec, Ortec). Samples were counted for 23 h (82,800 seconds) to ensure a strong enough signal. The resulting spectrum files show ^{210}Pb activity with a peak at 46.5 keV, and ^{137}Cs at 662 keV. ^{226}Ra activity is determined by γ-ray emissions of its daughter isotope ^{214}Pb at 295 and 352 keV.

Following the methods used in Krümmel et al. (2005), sedimentation rates were calculated from total ^{210}Pb and cumulative dry mass by fitting an exponential curve through the data using the following equation:

$$C_{\mathrm{tot}}(t) = C_{\mathrm{uns}}e^{-\lambda t} + C_{\mathrm{sup}}(1 - e^{-\lambda t})$$

where C_{tot} is the total ^{210}Pb activity, λ is the radioactive decay constant for ^{210}Pb, C_{sup} is the ^{210}Pb activity supported by the parent radioisotope ^{226}Ra, and C_{uns} is the unsupported ^{210}Pb activity.

Elemental analysis

Nitrogen was determined at the G.G Hatch Stable Isotope Laboratory at the University of Ottawa using an elemental analyzer (EA 1110, CE Instruments, Italy). Freeze-dried sediment samples were combusted at 1800°C in the EA in order to purify and separate resulting gases into N_2 and CO_2. Data were normalized using internal standards calibrated with international standards IAEA-CH-6, IAEA-NBS22, IAEA-N1, IAEA-N2, USGS-40, USGS-41 with a precision of ± 0.2‰.

Metals analysis

Metal analysis was carried out on every other interval of the sediment cores (*i.e.* 0-0.5 cm, 1-1.5 cm, *etc.*). Sediment and guano subsamples were placed into acid washed vials and freeze-dried. Prior to analysis, sediment samples were pulverized in an agate bowl and then subjected to an aqua regia digestion in order to extract the environmentally relevant metals while preserving the silicate matrix. ICP-MS was used to analyze 28 metals (limit of detection in µg/g): Ag (0.01), Al (1), As (0.4), Ba (0.01), Be (0.02), Bi (0.09), Ca (1), Cd (0.02), Co (0.01), Cr (0.5), Cu (0.1), Fe (0.5), K (1), Li (2), Mg (1), Mn (0.1), Mo (0.1), Ni (0.1), P (5), Pb (0.05), Sb (0.1), Se (0.7), Sn (0.5), Ti (0.2), Tl (0.02), U (0.002), V (0.1), Zn (0.7). QA/QC was ensured by running certified reference material, internal standards, blanks and duplicated after every batch of 20 samples. Analyses were carried out by SGS Canada Inc., in both Toronto and Lakefield, Ontario, Canada.

Distance calculations

As the colony was spread out over a large distance along the cliffs, it was difficult to accurately determine the distance of the ponds from the colony. As such, a pond (CV8) located closest to the cliffs and defined *a priori* as being the most affected by ornithogenic inputs (Keatley 2007; Michelutti et al. *in press*; Brimble et al. submitted) was chosen as a waypoint for distance calculations. Using aerial photographs, CV8 was estimated to be 313 m from the cliffs. The distance of the ponds from CV8 was determined from GPS points.

Statistical analysis

Data were screened to remove variables below the detection limit in more than 30% of cases. This resulted in the removal of Bi, Sn and Ti from analyses. All statistical analyses were conducted using the mean concentration of each element in the first 5 cm of each core (hereafter referred to as surface sediment) to remain consistent with Canadian sediment quality guidelines. Fluxes were calculated by multiplying the mean element concentration in surface sediment by the sedimentation rate of the core to account for variable sedimentation rates between the ponds (Krümmel et al. 2005).

A biogenic enrichment factor was developed to predict elements expected to undergo biotransport in the Cape Vera ecosystem. The biogenic enrichment factor (B) was calculated as follows:

$$(B) = \frac{\text{Concentration of element in fulmar guano}}{\text{Concentration in surface sediment of control ponds}}$$

It was expected that elements with high concentrations in guano compared to background geological media, *i.e.* higher B values, would vary most dramatically along the seabird gradient.

Ponds were ranked based on distance from colony as follows: (1) those receiving high inputs of seabird subsidies located 0-500m from the colony, (2) those 500-1000m from colony, and (3) ponds >1000m from the colony with no significant seabird inputs in recent history. The Kolmogorov-Smirnov test was used to test normality of data. Parametric tests (ANOVA, *t*-test) with Bonferroni adjustments were used to assess differences in the levels of metals and nutrients between sites. Regression analysis was conducted to assess the relationship between element concentrations and distance from colony. The significance level for all tests was set at a type 1 error (α) of 0.05. All statistical analyses were completed using SYSTAT v. 10 (ANOVA, t-test) and SigmaPlot v. 10.0 (regressions).

3.4 - Results and Discussion

3.4.1 - Biogenic enrichment factor

We analyzed nutrient and trace element concentrations in guano and in surface sediments from reference ponds (Table 1). Phosphorus, Cd, K, Na, Zn, Sr and As had the highest B values, indicating that they were the most likely to undergo bioenrichment. These elements are typically enriched in ornithogenic soils (Zale 1994; Garcia et al. 2002; Sun et al. 2004; Liu 2006a, b; Xie and Sun 2008). Furthermore, with the exceptions of Na and Sr, concentrations of these elements decreased exponentially as distance from the colony increased (Fig. 2). Concentrations of Co, Cu, Ni and Pb are low in the northern fulmar (Mallory et al. 2004; Campbell et al. 2006; Borga et al 2006) and bioaccumulation of these elements in seabirds could not be related to diet (Borga et al. 2006), resulting in B values below 1. This paper will mainly focus on P, Cd, K, Zn, and As, hereafter referred to as "biovector elements" (Table 2).

3.4.2 -Bioenrichment of nutrients and trace elements

Biovector elements varied widely across the seabird gradient (Table 2). Consistent with our previous studies at Cape Vera (Keatley et al. 2007; Brimble et al. submitted for publication), nutrient concentrations in sediments were significantly higher in ponds receiving seabird subsidies. Surface sediments of guano-affected ponds had significantly higher levels of P ($t_{6.3}$= 2.42) and K (t_8= 2.95) than reference ponds (all $p<0.05$). We found a 7- to 59-fold variation in the concentration of K, N and P in pond sediments. This was expected since northern fulmars are generalist scavengers with a diet rich in zooplankton, squid and fish (Mallory 2006) and excrete high quantities of marine-derived K, N and P in their guano (Hutchinson 1950). Elevated levels of these elements have been reported in soils and vegetation influenced by seabird inputs (Ryan and Watkins 1989; Anderson and Polis 1999; Garcia et al. 2002; Tomassen et al. 2005), demonstrating that the products of biotransport may be incorporated into terrestrial food webs.

The concentration of As in surface sediments followed the pattern exhibited by nutrient concentrations. Ponds receiving greater seabird inputs of guano had significantly higher As concentrations than control ponds (One-way ANOVA; $F_{2,7} = 9.7$, $p < 0.05$; Fig. 3). However, contrary to expectations, Cd and Zn did not follow the same pattern. Concentrations of Zn ($F_{2,7} = 73.3$, $p < 0.001$) and Cd ($F_{2,7} = 12.3$, $p < 0.05$) were significantly higher in the pond closest to the colony (CV9, distance rank 1) than in the other ponds (Fig. 3), but no difference was found between ponds ranked (2) and (3) for distance. As mentioned above, concentrations of biovector elements decreased exponentially as distance from the colony increased. Fluxes of biovector elements were calculated in order to correct for the potential effects of differing sedimentation rates among ponds. With the exception of As, fluxes of biovector elements also significantly decreased with distance (Fig. 2).

Many elements are redox-sensitive and undergo redox-mediated migration in sediments; particularly at low sediment accumulation rates and organic carbon contents (Boyle 2001). Vertical sediment profiles from the Cape Vera ponds indicated that surface sediment concentrations of P, As and Cd were modified by post-depositional remobilization (Fig. 4). Under reducing conditions, As and P are released into solution, migrate upwards and are remineralized in surface sediments under oxidizing conditions, often associated with Fe oxide minerals (Whalen and Cornwell 1985; Farmer 1991; Rydin

2000). Arsenic was enriched in the surface sediments of ponds with a distance rank (2) and P concentrations increased in the surface sediments of all ponds. Cadmium concentrations increased with depth in the group (2) ponds, likely due to the downward diffusion of Cd (Gobeil et al. 1997). Sequestration of Cd at depth may explain the lower than expected surface concentrations in the group (2) cores. Concentrations of elements in the control ponds were low and probably represented mineralogical background. A noteworthy enrichment of Cd in the surface sediment of CV1 may imply an increase in the supply of Cd in recent times. However, a more likely explanation given the low concentrations at depth, is that the core has little capacity to sequester Cd (*i.e.* no sulphides present) so Cd may be released back to the water column.

Guano fertilization of the nutrient poor tundra creates 'oases' of biological productivity in the Arctic (Bildstein et al. 1992; Ellis et al. 2006). In nutrient poor regions like the terrestrial Arctic, plant diversity and the degree of vegetation cover may be directly related to seabird influence (Godzik 1991; Cocks et al. 1998). Godzik (1991) found that the concentrations of heavy metals in moss collected in a little auk (*Alle alle*) colony at Hornsund Fjord, Spitsbergen were highest where the nests were most densely arranged. The lack of correspondence between the ornithogenic gradient and heavy metals was surprising. While Zn and Cd concentrations and fluxes were clearly related to seabird influence in CV9, the concentrations in the other ponds receiving seabird subsidies were not significantly higher than in control sites. Ponds such as CV9a, CV10 and CV30 had higher nutrient concentrations and ranked higher than CV9 on the ornithogenic gradient developed in Brimble et al. (submitted) but the metal concentrations were not significantly different than background (Table 2). Nutrient inputs from the colony stimulated the growth of thick mats of moss around these ponds, further confirming the impact of the fulmars on pond chemistry. Mosses are able to concentrate heavy metals due to the high cation exchange capacities of their tissues, lack of cuticle and high surface-to-weight ratio (Tyler 1990). Thus, we speculate that absorption and storage by surrounding mosses may reduce the amount of these metals entering the ponds.

3.4.3 - Sediment quality at Cape Vera

To assess the level of trace element contamination in the Cape Vera freshwater ecosystem, we compared mean element concentrations in surface sediments to the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (Canadian Council of Ministers of the Environment 1999). The guidelines provide two assessment values: the interim sediment quality guideline (ISQG), below which adverse biological effects rarely occur, and the probable effects level (PEL). Above the PEL, adverse biological effects, including decreased benthic invertebrate abundance, increased mortality and behavioral changes in some biota are expected to occur frequently. Copper and Pb concentrations in all ponds were well below the ISQG (18.7 mg/kg and 30.2 mg/kg for Cu and Pb respectively), consistent with the low concentrations of these elements in fulmar guano and the resulting B-value below 1. A number of ponds influenced by seabird droppings exceeded the ISQGs for As and Cd (Fig. 2). CV9, located closest to the colony, exceeded the ISQG for As (5.9 mg/kg) and Cd (0.6 mg/kg) and was the only pond to exceed the PEL for Zn (315 mg/kg). The ISQG for Cd was also exceeded in CV1, a control pond with significant redox-remobilization of elements in the sediments. Nonetheless, whatever the source of Cd (and other contaminants) in surface sediments, exposure to elevated levels may cause adverse effects to aquatic life.

Near the colony, the enhanced productivity in the guano-affected ponds creates ideal conditions for high production of emergent insects, such as chironomids. Thus, ponds in which levels of As, Cd and Zn exceed concentrations for the protection of aquatic life could potentially adversely affect chironomid populations. Due to their close association with sediments, chironomids may accumulate high concentrations of heavy metals and transfer them to higher trophic levels (Desrosiers et al. 2008). Chironomids are an important food source for the snow bunting (*Plectrophenax nivalis*) population at Cape Vera (Falconer et al. 2008), presenting a possible pathway for contaminant transfer into the terrestrial food web.

3.5 - Conclusions

The northern fulmar is an important biovector for the transport of marine-derived nutrients (N, P and K) and trace elements (As, Cd, Zn) to the coastal ecosystem at Cape Vera, which is located thousands of kilometers from the nearest industrial centre. Nevertheless, biotransport by fulmars has created a situation where ponds below the colony are effectively waste lagoons, with potentially toxic concentrations of As, Cd and Zn, all bioaccumulated from the ocean. Coastal ecosystems are some of the most productive zones in the world (Talley, 2003) with seabirds often being the dominant form of wildlife. As such, the role of seabirds in the global cycling of contaminants should not be ignored.

3.6- Acknowledgements

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Table 1: Biogenic enrichment factors for select trace elements at Cape Vera. Background surface sediment values were calculated as the mean values from control ponds.

	Trace element concentration (µg/g d.w.)		Biogenic enrichment factor
	Fulmar guano (n=2)	Background surface sediment (n=3)	
P	9550 ± 2050	354.17 ± 292.11	26.96
Cd	8.4 ± 0.71	0.37 ± 0.24	22.50
K	18400 ± 14990.66	844.44 ± 394.87	21.79
Na	6350 ± 1626.35	377.78 ± 179.76	16.81
Zn	140 ± 28.28	32.00 ± 24.55	4.38
Sr	106.5 ± 118.09	53.89 ± 15.93	1.98
As	4.05 ± 6.36	2.07 ± 0.95	1.95
Cu	7.75 ± 1.20	13.45 ± 9.93	0.57
Mn	4.35 ± 2.33	53.72 ± 12.89	0.08
Fe	160 ± 42.42	2627.78 ± 900.21	0.06
Ni	0.55 ± 0.21	16.41 ± 13.11	0.03
Co	8.4 ± 0.01	2.46 ± 1.98	0.02
Pb	0.09 ± 0.01	6.28 ± 6.25	0.01

Table 2: Concentrations of biovector elements in surface sediment and fulmar guano from Cape Vera.

					Element (µg/g d.w.)							
	Distance from colony (m)	Distance ranking	Sedimentation rate (g/cm^2/yr)	pH	K	N	Na	P	As	Cd	Sr	Zn
Guano					18400.00	n/a	6350.00	9550.00	4.05	8.40	106.50	140.00
CV9	495	1	0.0469	9.25	2380.00	11383.33	540.00	1430.00	9.20	1.71	29.40	343.20
CV20	539	2	0.0419	10.28	3133.33	43950.00	558.33	6483.33	7.25	0.37	44.73	85.67
CV9a	552	2	0.0627	10.17	4100.00	51012.50	263.33	7383.33	7.57	0.76	30.60	47.67
CV10	660	2	0.0377	10.20	2066.67	21933.33	453.33	3208.33	6.02	0.85	14.67	94.83
CV30	767	2	0.0057	10.90	1381.67	10712.50	345.83	1210.83	4.90	0.44	10.57	57.00
CV6	810	2	0.0223	8.30	1316.67	8312.50	183.33	623.33	2.83	0.33	37.62	43.83
CV5	843	2	0.1110	8.30	1191.67	3183.33	241.67	587.50	6.58	0.26	38.53	43.92
CV12	2541	3	0.0099	8.9	633.33	2383.33	583.33	253.33	1.55	0.32	58.42	14.17
CV1	4238	3	0.0124	7.20	1300.00	12366.67	250.00	683.33	3.17	0.64	67.07	60.00
CV22	8092	3	0.0144	7.55	600.00	883.33	300.00	125.83	1.50	0.16	36.18	21.83

Figure captions

Figure 1: Map of study location. a) Cape Vera, Devon Island, Canada. b) Pond locations, adapted from Keatley et al., 2007a.

Figure 2: Surface sediment (0-5cm) loading of N and elements with a B>1. Column (A) element concentrations; (B) element fluxes. Both are plotted against distance from seabird colony using the formula $f = ae^{(-bx)}$. In the units, x represents mg for N, P and K and µg for As, Cd and Zn. N.s. = not statistically significant.

Figure 3: Mean concentrations of As, Cd and Zn at (1) ponds <500m from colony (n=1); (2) ponds 500-1000m away (n=6) and (3) control ponds >1000m from colony (=3). Error bars represent standard deviation. Upper dashed line (Zn) indicates the PEL and lower dashed lines indicated the CCME ISQG. Bars with the same letter did not significantly differ at a 5% significance level.

Figure 4: Vertical profiles of Cd, Zn, As, Fe, Mn and P for Cape Vera sediment cores. Cores are arranged by increasing distance from the fulmar colony.

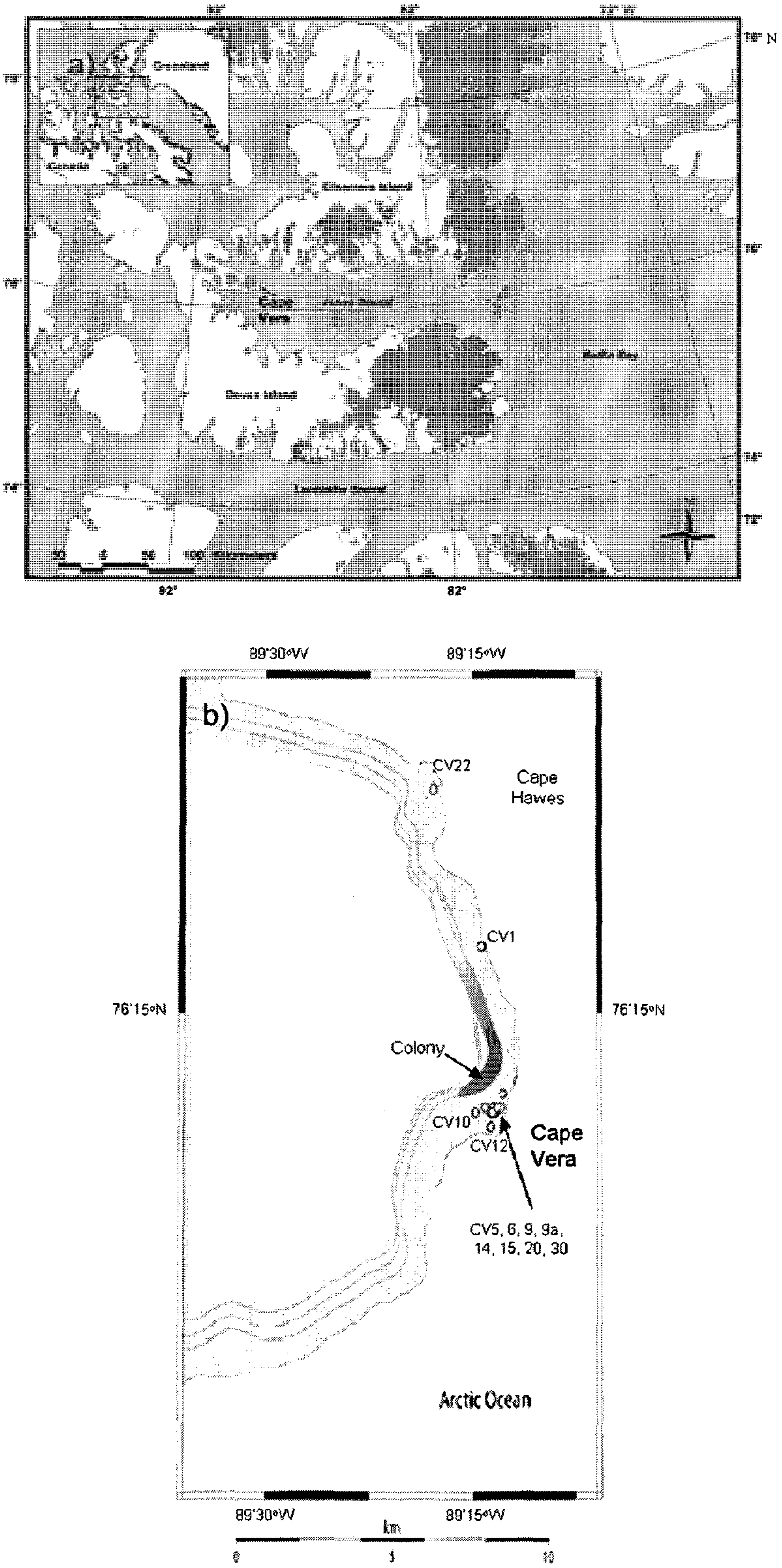
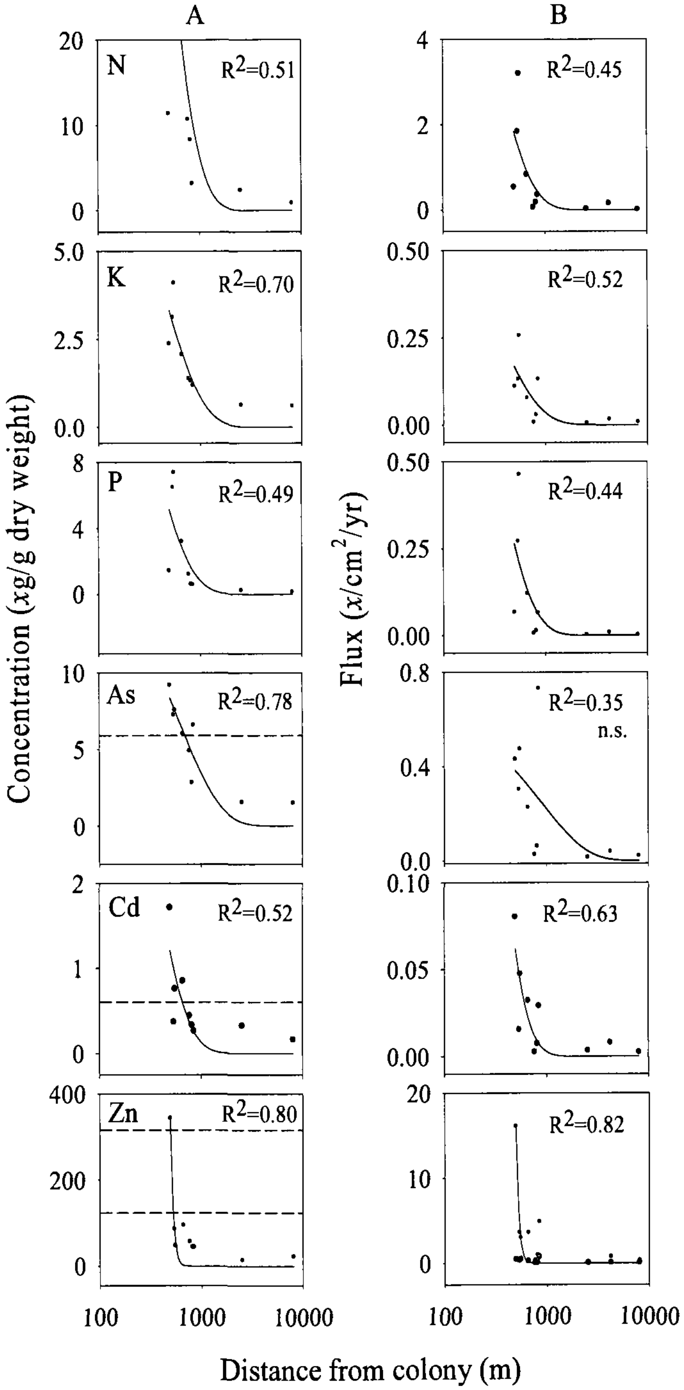
a)
Greenland
Canada
Ellesmere Island
Cape Vera
Jones Sound
Baffin Bay
Devon Island
Lancaster Sound
50 0 50 100 Kilometers
92°
82°
b)
89'30∘W
89'15∘W
CV22
Cape Hawes
CV1
76'15∘N
76'15∘N
Colony
CV10
CV12
Cape Vera
CV5, 6, 9, 9a, 14, 15, 20, 30
Arctic Ocean
89'30∘W
89'15∘W
km
0
5
10

Figure 1


A
B
N
R2=0.51
K
R2=0.70
P
R2=0.49
As
R2=0.78
Cd
R2=0.52
Zn
R2=0.80
R2=0.45
R2=0.52
R2=0.44
R2=0.35
n.s.
R2=0.63
R2=0.82
20
10
0
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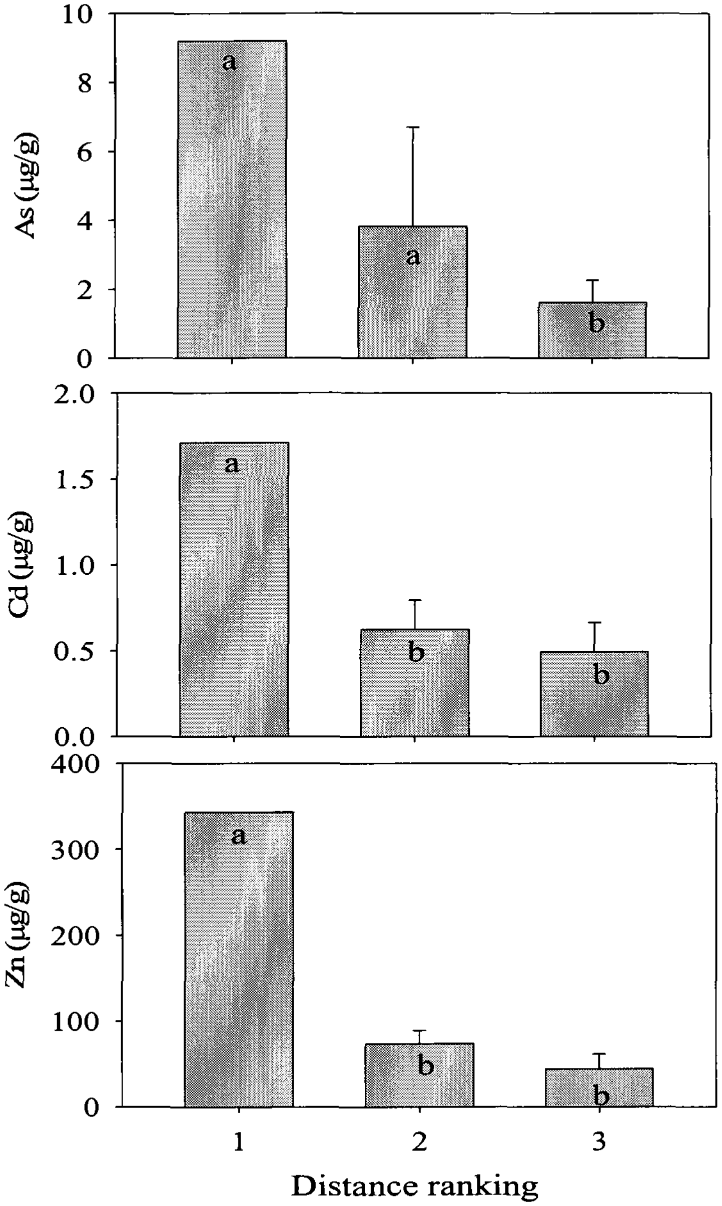
0.00
0.8
0.4
0.0
0.10
0.05
0.00
20
10
0
100
1000
10000
100
1000
10000
Concentration (xg/g dry weight)
Flux (x/cm2/yr)
Distance from colony (m)

Figure 2



10
8
6
4
2
0
As (μg/g)
a
a
b
2.0
1.5
1.0
0.5
0.0
Cd (μg/g)
a
b
b
400
300
200
100
0
Zn (μg/g)
a
b
b
1
2
3
Distance ranking

Figure 3

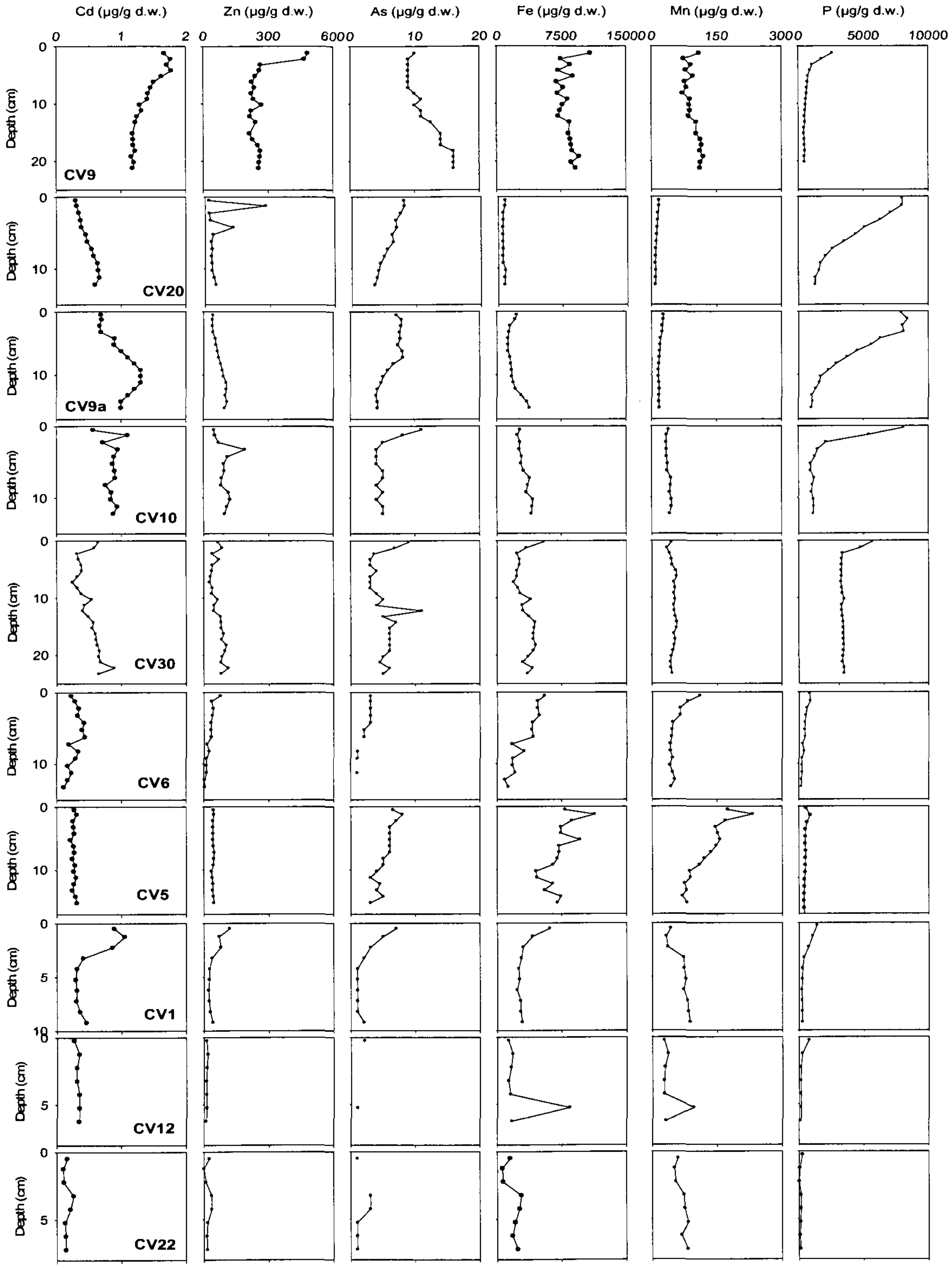

Cd (µg/g d.w.)
Zn (µg/g d.w.)
As (µg/g d.w.)
Fe (µg/g d.w.)
Mn (µg/g d.w.)
P (µg/g d.w.)
0
1
2
0
300
600
0
10
20
0
7500
15000
0
150
300
0
5000
10000
Depth (cm)
CV9
CV20
CV9a
CV10
CV30
CV6
CV5
CV1
CV12
CV22

Figure 4

4.0 - Discussion and conclusions

The seabird-influenced ponds at Cape Vera had markedly different limnological properties and sedimentary geochemical signatures when compared to non-affected ponds. The water chemistry and nutrient levels of the ponds outside of the range of the colony were comparable to other High Arctic ponds (Michelutti et al. 2002; Antoniades et al. 2003; Lim and Douglas 2003) but were significantly higher in ponds receiving seabird-subsidies. The concentrations of nutrients, organic carbon, chlorophyll-a, the pH and sedimentary $\delta^{15}N$ in the ponds were highly correlated to PCA axis 1, and were used to represent the ornithogenic gradient.

The close association between concentrations of As, Cd, Co, Cu, Li, Mn, Mo, Ni, Sb and Sr in the water of ponds and the ornithogenic gradient indicated that these elements were enriched in the ponds by the fulmar colony. Furthermore, the ponds located closest to the colony were the most contaminated, despite conditions favorable for the *in-situ* removal of these elements from the water column (Sigg 1987). Thus, the influx of guano to the ponds maintained the elevated levels of trace elements in spite of removal processes.

The fulmars may have also indirectly affecting trace element levels in the guano-affected ponds by affecting redox-cycling of elements in the sediments via the organic carbon cycle. Many trace elements are influenced by the carbon cycle of lakes as they readily complex with organic ligands (Rognerud et al. 1998). As such, organic carbon will scavenge trace elements from the water column into the sediments. Redox-associated diagenetic processes are known to mobilize naturally present metals from the sediment and release them into the overlying water column (Farmer 1991). The traditional model of metal remobilization due to an anoxic hypolimnion does not apply to the Cape Vera ponds as the water columns were shallow, well mixed and supersaturated with oxygen due to continuous photosynthesis (24-hour sunlight). However, metals may be released to the water column by the aerobic degradation of organic matter (Farmer 1991). Consequently, the sediments may be acting as a source of elements to the pond water at Cape Vera.

Biovector transport acts to focus contaminants into receptor sites, greatly enriching levels above background. Cape Vera is located in the Canadian High Arctic, thousands of kilometers from the nearest industrial center, and yet concentrations of As, Cd and Zn in many guano-affected ponds exceeded Canadian Sediment Quality Guidelines for the Protection of Aquatic Life. This study confirms that biotransport by seabird can amplify contaminants to potentially toxic concentrations and may expose ecologically sensitive coastal ecosystems to elevated contaminant levels. The lush green ecosystem resulting from guano-fertilization at Cape provides critical habitat for insects, lemmings, snow buntings, foxes, and a range of other animals, presenting a possible pathway for contaminant transfer into the terrestrial food web (E. Choy, unpublished data).

Although biotransport leads to the enrichment of contaminants into the terrestrial environment, the process can give rise to valuable paleolimnological tools. Seabird population dynamics have been reconstructed in Antarctica (Zale 1994; Sun et al. 2004) and in the South China Sea (Liu et al. 2006a) using fluctuations of trace element levels in guano-affected sediment cores. Cadmium, in particular, has been recognized as an indicator of seabird-influence as high levels of Cd have been found at breeding sites

(Hawke et al. 1999; Wagner 2001; Liu et al. 2006b). A biogenic enrichment factor of 22.5 was calculated for Cd at Cape Vera, the highest of all the metals. Indeed, the vertical profile of Cd in CV9 was used to reconstruct the northern fulmar population at Cape Vera along with several other proxies of seabird influence (*i.e.* inferred sedimentary chl-*a*, diatom head capsule abundance, $\delta^{15}N$ and PBC concentrations) (Michelutti et al. *in press*).

The northern fulmar is a source of both marine-derived nutrients and trace elements to the Cape Vera coastal ecosystem. These studies add to a growing body of evidence that suggest that biotransport can be an important pathway for contaminant transfer between food webs. Biotransport can amplify contaminant concentrations emitted thousands of kilometers away to potentially toxic levels, demonstrating the importance of this process in contaminant cycling.

References

ACIA. 2004. Impacts of a warming arctic: arctic climate impact assessment. Cambridge University Press, Cambridge, UK. 140 pp.

Anderson, W. and Polis, G. 1999. Nutrient fluxes from water to land: seabirds affect plant nutrient status on Gulf of California islands. Oecologia **18**(3): 324-332.

Antoniades, D., Douglas, M.S.V., Smol, J.P. 2003a. Comparative physical and chemical limnology of two Canadian High Arctic regions: Alert (Ellesmere Island, NU) and Mould Bay (Prince Patrick Island, NWT). Arch. Hydrobiol. **158**(4): 485–516.

Antoniades, D., Douglas, M.S.V., Smol, J.P. 2003b. The Physical and Chemical Limnology of 24 Ponds and One Lake from Isachsen, Ellef Ringnes Island, Canadian High Arctic. Internat. Rev. Hydrobiol. **88**(5): 519-538.

Ball, J.W., and Nordstrom, D.K., 1991, User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters: U.S. Geological Survey Open-File Report 91-183, 189 p. (Revised and reprinted August 1992.)

Bargagli, R., Sanchez-Hernandez, JC., Martella, L., Monaci, F. 1998. Mercury, cadmium and lead accumulation in Antarctic mosses growing along nutrient and moisture gradients. Polar Biol. **19**(5): 316-322.

Bedard-Haughn, A., van Groenigen, J.W., van Kessel, C. 2003. Tracing $\delta^{15}N$ through landscapes: potential uses and precautions. J. Hydrol. **272**: 175-190.

Bildstein, K., Blood, E., Frederick, P. 1992. The relative importance of biotic and abiotic vectors in nutrient transport. Estuaries **15**(2): 147-157.

Billings, W.D. 1973. Arctic and alpine vegetations: similarities, differences, and susceptibility to disturbance. Bioscience **23**(2): 697-704.

Blais, J.M., Kimpe, L.E., McMahon, D., Keatley, B.E., Mallory, M.L., Douglas, M.S.V., Smol J.P. 2005. Arctic seabirds transport marine-derived contaminants. Science **309**: 445.

Blais, J.M., Macdonald, R.W., Mackay, D., Webster, E., Harvey, C., Smol, J.P. 2007. Biologically mediated transport of contaminants to aquatic system. Environ. Sci. Technol. **41**(4): 1075-1084.

Borga, K., Campbell, L., Gabrielsen, G.W., Norstrom, R.J., Muir, D., Fisk, A.T., 2006. Regional and species specific bioaccumulation of major and trace elements in arctic seabirds. Environ. Toxicol. Chem. **25**(11): 2927–2936.

Boyle, J. 2001. Redox remobilization and the heavy metal record in lake sediments: a modelling approach. J. Paleolimnol. **26**(4): 423-431.

Brimble, S.K., Blais, J.M., Kimpe, L.E., Mallory, M., Keatley, B.E., Douglas, M.S.V., Smol, J.P Bioenrichment of trace elements in a series of ponds near a northern fulmar colony at Cape Vera, Devon Island. Can. J. Fish. Aquat. Sci. Submitted for publication.

Brooke, M.D. 2004. The food consumption of the world's seabirds. Proc. R. Soc. Lond., Ser. B: Biol. Sci. **271**: S246-S248.

Buckman, A.H., Norstrom, R.J., Hobson, K.A., Karnovsky, N.J., Duffe, J., Fisk, A.T. 2005. Organochlorine contaminants in seven species of Arctic seabirds from northern Baffin Bay. Environ. Pollut. **128**(3): 327-338.

Campbell, L., Norstrom R.J., Hobson K.A., Muir D., Backus S., Fisk, A.T. 2005. Mercury and other trace elements in a pelagic Arctic marine food web (Northwater Polynya, Baffin Bay*)*. Sci. Total. Environ. **351-352**: 247–263.

Canadian Council of Ministers of the Environment 1999. Canadian environmental quality guidelines. Canadian Council of the Ministers of the Environment, Winnipeg.

Chanudet, V., and Filella, M. 2007. Submicron organic matter in a peri-alpine, ultra oligotrophic lake. Org. Geochem. **38**(7): 1146-1160.

Cocks, M.P., Belfour, D.A., Stock, W.D. 1998. On the uptake of ornithogenic products by plants on the inland mountains of Dronning Maud Land, Antarctica, using stable isotopes. Polar Biol. **20**(2): 107-111.

Desrosiers, M., Gagnon, C., Masson, S., Martel, L., Babut, M.P. 2008. Relationships among total recoverable and reactive metals and metalloid in St. Lawrence River sediment: Bioaccumulation by chironomids and implications for ecological risk assessment. Sci. Total. Environ. **389**(1): 101-114.

Dowdall, M., Gwynn, J.P, Gabrielson, G., Lind, B. 2005. Assessment of elevated radionuclide levels in soils associated with an avian colony in a High Arctic environment. Soil Sediment Contam. **14**: 1-11.

Ellis, J., Farina, J.M., Witman, J.D. 2006. Nutrient transfer from sea to land: the case of gulls and cormorants in the Gulf of Maine. J. Anim. Ecol. **75**: 565–574.

Environment Canada. 1994a. Manual of Analytical Methods. Major ions and nutrients, 1. National Laboratory for Environmental Testing, Canadian Centre for Inland Waters. Burlington, Ontario, Canada.

Environment Canada. 1994b. Manual of Analytical Methods. Trace metals, vol 1. National Laboratory for Environmental Testing, Canadian Centre for Inland Waters. Burlington, Ontario, Canada.

Evenset, A., Christensen, G.N., Skotvold, T., Fjeld, E., Schlabach, M., Wartena, E., Gregor, D. 2004. A comparison of organic contaminants in two high Arctic lake ecosystems, Bjørnøya, (Bear Island), Norway. Sci. Total. Environ. **318**: 125-141.

Evenset, A., Christensen, G.N., Carroll, J., Zaborska, A., Berger, U., Herzke, D., Gregor, D. 2007. Historical changes in persistent organic pollutants and metals recorded in sediment from Lake Ellasjøen, Bjørnøya, Norwegian Arctic. Environ. Pollut. **146**: 196-205.

Falconer, M.C., Nol, E., Mallory, M.L. 2008. Breeding biology and provisioning of nestling snow buntings (Plectrophenax nivalis) in the Canadian high Arctic. Polar Biol. **31**(4): 483-489.

Farmer, J.G. 1991. The pertubation of historical pollution records in aquatic sediments. Environ. Geochem. Health **13**(2): 76-83.

Frank, D.A., Evans, R.D., Tracy, B.F. 2004. The role of ammonia volatilization in controlling the natural ^{15}N abundance of a grazed grassland. Biogeochemistry **68**: 169-178.

Garcia, L.V., Maranon, T., Ojeda, F., Clemente, L., Redondo, R. 2002. Seagull influence on soil properties, chenopod shrub distribution, and leaf nutrient status in semi-arid Mediterranean islands. Oikos **98**: 75-86.

Gaston, A.J., Mallory, M.L., Gilchrist, H.G., O'Donovan, K. 2006. Status, trends and attendence patterns of the northern fulmar *Fulmarus glacialis,* in Nunavut, Canada Arctic. Ecography **59**(2): 165-178.

Glew, J. R., 1988. A portable extruding device for close interval sectioning of unconsolidated core samples. J. Paleolimnol. **2**(3): 241-243.

Glew, J. R., J. P. Smol, & W. M. Last, 2001. Sediment core collection and extrusion. In W. M. Last & J. P. Smol (eds), Basin Analysis, Coring, and Chronological Techniques. Kluwer Academic Publisher, Norwell: 73-106.

Gobeil, C., Macdonal, R.W., Sundby, B. 1997. Diagenetic separation of cadmium and manganese in suboxic continental margin sediments. Geochim. Cosmochim. Acta **61**(12): 4647-4654.

Godzik, B. 1991. Heavy metals and macroelements in the tundra of southern Spitsburgen: the effect of little auk *Alle alle* (L.) colonies. Polar Res. **9**(2): 121-131.

Harding, J.S., Hawke, D.J., Holdaway, R.N., Winterbourn, M.J. 2004. Incorporation of marine-derived nutrients from petrel breeding colonies into stream food webs. Freshw. Biol. **49**: 576-586.

Hawke, DJ., Holdaway, RN., Causer, JE., Ogden, S. 1999. Soil indicators of pre-European seabird breeding in New Zealand at sites identified by predator deposits. Australian Journal of Soil Research **37**(1): 103-113.

Headley, A. 1996. Heavy metal concentrations in peat profiles from the High Arctic. Sci. Total Environ. **177**: 105-111.

Hobson, K.A., Clark, R.G. 1992. Assessing avian diet using stable isotopes II: factors influencing diet-tissue fractionation. Condor **94**(1): 189-197.

Hutchinson, G.E. 1950. Survey of existing knowledge of biogeochemistry. 3. The biogeochemistry of vertebrate excretion. Bull. Am. Mus. Nat. His. **96**: 1-554.

Keatley, BE., Douglas, M.S.V., Blais, J.M., Mallory, M.L., Smol, J.P. 2009. Impacts of seabird-derived nutrients on water quality and diatom assemblages from Cape Vera, Devon Island, Canadian High Arctic. Hydrobiologia. **621**: 191-205.

Keatley, B.E., Douglas, M.S.V., Smol, J.P. 2007. Limnological characteristics of a High Arctic oasis and comparisons across Northern Ellesmere Island. Arctic **60**(3): 294-308.

Krümmel, E., Macdonald, R.W., Kimpe, L.E., Gregory-Eaves, I., Demers, M., Smol, J.P., Finney, B., Blais, J.M. 2003. Delivery of pollutants by spawning salmon. Nature **425**(6955): 255-256.

Lim, D.S.S. and Douglas, M.S.V. 2003. Limnological characteristics of 22 lakes and ponds in the Haughton Crater region of Devon Island, Nunavut, Canadian High Arctic. Arct. Antarct. Alp. Res. **35**(4): 509-519.

Lindeboom, H.J. 1984. Nitrogen pathway in a penguin rookery. Ecology **65**(1): 269-277.

Liu, X.D., Zhao, S.P., Sun, L.G., Luo, H.H., Yin, X.B., Xie, Z.Q., Wang, Y.H., Liu, K.X., Wu, X.H., Ding, X.F., Fu, D.P. 2006a. Geochemical evidence for the variation of historical seabird population on Dongdao Island of the South China Sea. J. Paleolimnol. **36**(3): 259-279.

Liu, X., Zhao, S., Sun, L., Yin, X., Xie, Z., Honghao, L., Wang, Y. 2006b. P and trace metal contents in biomaterials, soils, sediments and plants in colony of red-footed booby (*Sula sula*) in the Dongdao Island of South China Sea. Chemosphere **65**(4): 707-715.

Mallory, M.L., Wayland, M., Braune, B.M., Drouillard, K.G. 2004. Trace elements in marine birds, arctic hare and ringed seals breeding near Qikiqtarjuaq, Nunavut, Canada. Mar. Pollut. Bull. **49**(1-2**)**: 136–141.

Mallory, M.L. 2006. The Northern Fulmar (Fulmarus glacialis) in Arctic Canada: ecology, threats, and what it tells us about marine environmental conditions. Environ. Rev. **14**: 187-216.

Mallory, M.L., Fontaine, A.J., Smith, P.A., Wiebe Robertson, M.O., Gilchrist, H.G. 2006. Water chemistry of ponds on Southampton Island, Nunavut, Canada: effects of habitat and ornithogenic inputs. Arch. Hydrobiol. **166**(3): 411–432.

McNeely, R.N., Neimanis, V.P., Dwyer, L. 1979. Water Quality Sourcebook: A Guide to Water Quality Parameters. Minister of Supply and Services Canada, Ottawa, 88 pp.

Michelutti, N., Douglas, M.S.V., Lean, D.R.S., Smol, J.P. 2002. Physical and chemical limnology of 34 ultra-oligotrophic lakes and ponds near Wynniatt Bay, Victoria Island, Arctic Canada. Hydrobiologia **482** (1-3): 1-13.

Michelutti, N., Blais, J.M., Liu, H., Keatley, B.E., Douglas, M.S.V., Mallory, M.L., Smol, J.P. 2008. A test of the possible influence of seabird activity on the ^{210}Pb flux in high Arctic ponds at Cape Vera, Devon Island, Nunavut: implications for radiochronology. J. Paleolimnol. **40**(3): 783-791.

Michelutti, N., Keatley, B., Brimble, S.K, Blais, J., Liu, H., Douglas, M., Mallory, M., Macdonald, R. Smol, J.P. 2009. Seabird-driven shifts in Arctic pond ecosystem. Proc. R. Soc. London, Ser. B **276**(1656): 591-596.

Mizutani, H., Hasegawa, H., Wada, E. 1986. High nitrogen isotope ratio for soils of seabird rookeries. Biogeochemistry **2**(3): 221-247.

Mizutani, H., and Wada, E. 1988. Nitrogen and carbon isotope ratios in seabird rookeries and their ecological implications. Ecology **69**(2): 340-349.

Muir, D., Braune, B., DeMarch, B., Norstrom, R., Wagemann, R., Lockhart, L., Hargrave, B., Bright, D., Addison, R., Payne, J., Reimer, K. 1999. Spatial and temporal trends and effects of contaminants in the Canadian Arctic marine ecosystem: a review. Sci. Total Environ. **230** (1-3): 83-144.

Norheim, G. 1987. Levels and interactions of heavy metals in sea birds from Svalbard and the Antarctic. Environ. Pollut. **47**(2): 83-94.

Outridge, P.M., Stern, G.A., Hamilton, P.B., Percival, J.B., McNeely, R., Lockhart, W.L. 2005. Trace metal profiles in the varved sediment of an Arctic lake. Geochemim. Cosmochim. Acta **69**(20): 4881-4894.

Polis, G.A., Anderson, W.B., Holt, R.D. 1997. Toward an integration of landscape and food web ecology: the dynamics of spatially subsidized food webs. Annu. Rev. Ecol. Syst **28**: 289-316.

Rice, W. R. 1989. Analyzing tables of statistical tests. Evolution **43**(1):223-225.

Rognerud, S., Skotvold, T., Fjeld, E., Norton, S.A., Hobæk, A. 1998. Concentrations of trace elements in recent and preindustrial sediments from Norwegian and Russian Arctic lakes. Can. J. Fish. Aquat. Sci. **55**: 1512–1523.

Ryan, PG. and Watkins BP. 1989. The influence of physical factors and ornithogenic products on plant and arthropod abundance at an Inland Nunatak group in Antarctica. Polar Biol. **10**(2): 151-160.

Rydin, E. 2000. Potentially mobile phosphorus in Lake Erkin sediment. Water Res. **34**(7): 2037-2042.

Sigg, L. 1987. Surface chemical aspects of the distribution and fate of metal ions in lakes. *In* Aquatic Surface Chemistry: Chemical Processes at the Particle-Water Interface. *Edited by* W. Stumm. John Wiley & Sons, New York, pp. 319-345.

Stempniewicz, L., Blachowiak-Samolyk, K., Weslawski, J.M. 2007. Impact of climate change on zooplankton communities, seabird populations and arctic terrestrial ecosystem – A scenario. Deep Sea Res. Part II. **54**(23-26): 2934-2945.

Sun, L.G., Renbin, Z., Xuebin, Y., Xiaodong, L., Zhouqing, X., Yuhong, W. 2004. A geochemical method for the reconstruction of the occupation history of a penguin colony in the maritime Antarctic. Polar Biol. **27**(11): 670-678.

Talley, D., North, E., Juhl, A., Timothy, D., Condee, D., deBrouwer, J., Brown, G., Campbell, L., Garsteckii, T., Halla, C., Meysman, F., Nemerson, D., Souza Filho, P., Wood, R. 2003. Research challenges at the land-sea interface. Estuar. Coast. Shelf Sci. **58**(4): 699-702.

ter Braak, CJF, and Šmilauer, P. 2002. CANOCO reference manual and CANOdraw for Windows user guide: Software for Canonical Community Ordination (Version 4.5). Ithaca, U.S.A.

Tomassen, H., Smolders, A., Lamers, L., and Roelofs, J. 2005. How bird droppings can affect the vegetation composition of ombrotrophic bogs. Can. J. Bot **83**(8): 1046-1056.

Tyler, G. 1990. Bryophytes and heavy metals: a literature review. Bot. J. Linn. Soc. **104**(1-3): 231-253.

Whalen, S.C. and Cornwell, J.C. 1985. Nitrogen, phosphorus, and organic carbon cycling in an Arctic lake. Can. J. Fish. Aquat. Sci. **42**(4): 797-808.

Xie, Z. and Sun, L. 2008. A 1,800-year record of arsenic concentration in the penguin dropping sediment, Antarctic. Environ. Geol. **55**(5): 1055-1059.

Yoneyama, T. 1996. Characterization of natural ^{15}N abundance of soils. *In* Mass Spectrometry of Soils. *Edited by* T.W.B.S. Yamasaki. Marcel Dekker, New York, pp 205-233.

Zale, R. 1994. Changes in size of the Hope Bay Adelie penguin rookery as inferred from Lake Boeckella sediment. Ecography **17**(4): 297-304.

Appendix 1: WATEQ4F printout for CV8 – Metal and ion speciation and mineral saturation indices

T	pH	TDS ppm	Effective Ionic Str
14.3	10.65	96907.7	1.86659

Species	Charge	Anal ppm	Calc ppm	Anal Molal	Calc Molal	Activity	Act Coeff	-Log Act
Ca	2	27.47	27.441	7.59E-04	7.58E-04	2.19E-04	0.2893	3.659
CaOH	1		0.049		9.53E-07	9.35E-07	0.9801	6.029
CaSO4 aq	0		0.007237		5.89E-08	9.05E-08	1.5369	7.044
CaHSO4	1		0		9.70E-18	9.50E-18	0.9801	17.022
Mg	2	10.45	10.348	4.76E-04	4.71E-04	1.80E-04	0.3814	3.745
MgOH	1		0.177		4.74E-06	4.64E-06	0.9801	5.333
MgSO4 aq	0		0.004598		4.23E-08	6.50E-08	1.5369	7.187
Na	1	20.27	20.275	9.76E-04	9.76E-04	7.66E-04	0.7842	3.116
NaSO4	-1		0.000871		8.10E-09	7.94E-09	0.9801	8.1
K	1	1.98	1.981	5.61E-05	5.61E-05	3.23E-05	0.5768	4.49
KSO4	-1		0.000052		4.24E-10	4.16E-10	0.9801	9.381
H	1		0		3.06E-11	2.24E-11	0.7306	10.65
OH	-1		2.866		1.87E-04	1.83E-04	0.9801	3.738
HCO3	-1	14.6		2.65E-04				
SO4	-2	5.45	1.607	6.28E-05	1.85E-05	2.22E-06	0.1199	5.654
HSO4	-1		0		3.68E-15	3.61E-15	0.9801	14.443
Cl	-1	38.87	36.774	1.21E-03	1.15E-03	6.62E-04	0.5768	3.179
SiO2 tot	0	1.08		1.99E-05				
H4SiO4aq	0		0.3		3.46E-06	5.32E-06	1.5369	5.274
H3SiO4	-1		1.378		1.60E-05	1.57E-05	0.9801	4.804
H2SiO4	-2		0.034		4.04E-07	3.73E-07	0.9229	6.428
B tot	0	2450		2.51E-01				
H3BO3 aq	0		419.162		7.50E-03	1.15E-02	1.5369	1.938
H2BO3	-1		13375.65		2.43E-01	2.39E-01	0.9801	0.622
NO2	-1	4	4.001	9.63E-05	9.63E-05	9.44E-05	0.9801	4.025
NO3	-1	0.01	0.01	1.79E-07	1.79E-07	1.75E-07	0.9801	6.757

37 NH3 aq	0		0.042		2.70E-06	4.16E-06	1.5369	5.381
38 NH4	1	0.05	0.005947	3.07E-06	3.65E-07	3.58E-07	0.9801	6.446
91 NH4SO4	-1		0.000001		1.04E-11	1.02E-11	0.9801	10.99
50 Al	3	7500	0	3.08E-01	1.69E-19	1.41E-19	0.8348	18.85
51 AlOH	2		0		3.18E-14	2.94E-14	0.9229	13.532
52 Al(OH)2	1		0.001161		2.11E-08	2.07E-08	0.9801	7.685
181 Al(OH)3	0		51.19		7.27E-04	1.12E-03	1.5369	2.952
53 Al(OH)4	-1		26354.84		3.07E-01	3.01E-01	0.9801	0.521
58 AlSO4	1		0		2.93E-22	2.87E-22	0.9801	21.543
59 Al(SO4)2	-1		0		4.94E-26	4.84E-26	0.9801	25.315
203 AlHSO4	2		0		1.59E-33	1.47E-33	0.9229	32.834
16 Fe total	2	30450		6.04E-01				
109 Mn	2	1250	877.81	2.52E-02	1.77E-02	1.63E-02	0.9229	1.787
111 MnCl	1		3.644		4.46E-05	4.37E-05	0.9801	4.359
112 MnCl2 aq	0		0.000582		5.12E-09	7.87E-09	1.5369	8.104
113 MnCl3	-1		0		2.40E-12	2.35E-12	0.9801	11.629
114 MnOH	1		483.352		7.44E-03	7.29E-03	0.9801	2.137
115 Mn(OH)3	-1		1.999		2.09E-05	2.05E-05	0.9801	4.689
118 Mn(NO3)2	0		0		1.33E-15	2.04E-15	1.5369	14.69
117 MnSO4 aq	0		0.511		3.75E-06	5.76E-06	1.5369	5.24
130 Cu	2	2375	0.000102	4.14E-02	1.78E-09	1.65E-09	0.9229	8.784
133 CuCl	1		0		1.74E-12	1.70E-12	0.9801	11.769
134 CuCl2 aq	0		0		3.50E-16	5.37E-16	1.5369	15.27
135 CuCl3	-1		0		1.06E-21	1.04E-21	0.9801	20.984
136 CuCl4	-2		0		2.89E-27	2.66E-27	0.9229	26.575
138 CuOH	1		0.052		7.21E-07	7.06E-07	0.9801	6.151
139 Cu(OH)2	0		3632.324		4.12E-02	6.34E-02	1.5369	1.198
140 Cu(OH)3	-1		17.303		1.67E-04	1.64E-04	0.9801	3.786
141 Cu(OH)4	-2		0.181		1.52E-06	1.40E-06	0.9229	5.853
142 Cu2(OH)2	2		0.011		7.86E-08	7.26E-08	0.9229	7.139
143 CuSO4 aq	0		0		4.50E-13	6.91E-13	1.5369	12.161
145 Zn	2	1240	0.073	2.10E-02	1.24E-06	1.14E-06	0.9229	5.941
146 ZnCl	1		0.000116		1.28E-09	1.25E-09	0.9801	8.903
147 ZnCl2 aq	0		0		5.40E-13	8.30E-13	1.5369	12.081

148 ZnCl3	-1		0		5.88E-16	5.77E-16	0.9801	15.239
149 ZnCl4	-2		0		1.90E-19	1.75E-19	0.9229	18.756
151 ZnOH	1		1.762		2.37E-05	2.32E-05	0.9801	4.634
152 Zn(OH)2	0		1550.891		1.73E-02	2.66E-02	1.5369	1.576
153 Zn(OH)3	-1		386.654		3.68E-03	3.60E-03	0.9801	2.443
154 Zn(OH)4	-2		3.202		2.66E-05	2.45E-05	0.9229	4.61
155 ZnOHClaq	0		0.075		7.01E-07	1.08E-06	1.5369	5.968
158 ZnSO4 aq	0		0.000052		3.56E-10	5.47E-10	1.5369	9.262
159 Zn(SO4)2	-2		0		1.17E-14	1.08E-14	0.9229	13.969
160 Cd	2	25	3.115	2.46E-04	3.07E-05	2.83E-05	0.9229	4.548
161 CdCl	1		0.235		1.76E-06	1.73E-06	0.9801	5.763
162 CdCl2 aq	0		0.000493		2.98E-09	4.57E-09	1.5369	8.34
163 CdCl3	-1		0		1.65E-12	1.62E-12	0.9801	11.791
167 CdOH	1		5.295		4.53E-05	4.44E-05	0.9801	4.353
168 Cd(OH)2	0		20.058		1.52E-04	2.33E-04	1.5369	3.632
169 Cd(OH)3	-1		0.169		1.15E-06	1.12E-06	0.9801	5.95
170 Cd(OH)4	-2		0.000076		4.66E-10	4.30E-10	0.9229	9.367
171 Cd2OH	3		0.001849		8.47E-09	7.07E-09	0.8348	8.151
172 CdOHClaq	0		2.341		1.57E-05	2.42E-05	1.5369	4.617
173 CdNO3	1		0.000003		1.76E-11	1.73E-11	0.9801	10.763
174 CdSO4 aq	0		0.002076		1.10E-08	1.69E-08	1.5369	7.771
277 Cd(SO4)2	-2		0		4.78E-13	4.42E-13	0.9229	12.355
182 Pb	2	143	0.007487	7.64E-04	4.00E-08	3.69E-08	0.9229	7.433
183 PbCl	1		0.000165		7.54E-10	7.39E-10	0.9801	9.131
184 PbCl2 aq	0		0		6.21E-13	9.55E-13	1.5369	12.02
185 PbCl3	-1		0		4.79E-16	4.69E-16	0.9801	15.329
186 PbCl4	-2		0		1.48E-19	1.37E-19	0.9229	18.865
192 PbOH	1		6.386		3.15E-05	3.09E-05	0.9801	4.51
193 Pb(OH)2	0		73.173		3.36E-04	5.16E-04	1.5369	3.287
194 Pb(OH)3	-1		60.545		2.60E-04	2.54E-04	0.9801	3.594
242 Pb(OH)4	-2		6.74		2.71E-05	2.50E-05	0.9229	4.602
195 Pb2OH	3		0.000011		2.73E-11	2.28E-11	0.8348	10.643
200 Pb3(OH)4	2		22.877		3.67E-05	3.39E-05	0.9229	4.47
196 PbNO3	1		0		9.75E-14	9.56E-14	0.9801	13.02

197 PbSO4 aq	0		0.000008		3.00E-11	4.61E-11	1.5369	10.336
243 Pb(SO4)2	-2		0		5.82E-16	5.37E-16	0.9229	15.27
204 Ni	2	740	3.922	1.40E-02	7.40E-05	6.83E-05	0.9229	4.166
206 NiCl	1		0.009855		1.16E-07	1.14E-07	0.9801	6.945
279 NiCl2	0		0.000021		1.78E-10	2.73E-10	1.5369	9.564
208 NiOH	1		12.935		1.89E-04	1.85E-04	0.9801	3.732
209 Ni(OH)2	0		685.518		8.18E-03	1.26E-02	1.5369	1.9
210 Ni(OH)3	-1		546.129		5.51E-03	5.40E-03	0.9801	2.268
211 NiSO4 aq	0		0.002443		1.75E-08	2.69E-08	1.5369	7.571
283 Ni(SO4)2	-2		0		3.82E-15	3.52E-15	0.9229	14.453
212 Ag	1	0.5	0.242	5.13E-06	2.49E-06	2.44E-06	0.9801	5.613
215 AgCl aq	0		0.3		2.31E-06	3.56E-06	1.5369	5.449
216 AgCl2	-1		0.042		2.60E-07	2.55E-07	0.9801	6.594
217 AgCl3	-2		0.000029		1.50E-10	1.38E-10	0.9229	9.86
218 AgCl4	-3		0		1.82E-13	1.52E-13	0.8348	12.819
224 AgOH aq	0		0.007677		6.81E-08	1.05E-07	1.5369	6.98
225 Ag(OH)2	-1		0.000587		4.58E-09	4.49E-09	0.9801	8.348
226 AgSO4	-1		0.000018		9.80E-11	9.61E-11	0.9801	10.017
227 AgNO3 aq	0		0		1.42E-13	2.19E-13	1.5369	12.66
228 Ag(NO2)2	-1		0.000001		3.67E-12	3.60E-12	0.9801	11.444
249 As total	0	2685		3.97E-02				
80 Li	1	7100	7101.854	1.13E+00	1.13E+00	1.11E+00	0.9801	-0.046
82 LiSO4	-1		1.022		1.10E-05	1.08E-05	0.9801	4.968
87 Sr	2	35100	35093.057	4.44E-01	4.43E-01	1.14E-01	0.2562	0.945
88 SrOH	1		19.641		2.08E-04	1.28E-04	0.6143	3.894
89 Ba	2	5470	5464.069	4.41E-02	4.40E-02	4.07E-02	0.9229	1.391
90 BaOH	1		4.227		3.03E-05	2.97E-05	0.9801	4.527
201 BaSO4 aq	0		6.206		2.94E-05	4.52E-05	1.5369	4.345
94 Rb	1	255	255.069	3.30E-03	3.30E-03	3.24E-03	0.9801	2.49

COMPUTED RESULTS: SATURATION INDICES (Log AP/KT)	Log AP/KT	Sigma(A)	Sigma(T)	Log AP/MinKT	Log AP/MaxKT	Log AP	Log KT	Log MinKT	Log MaxKT

39 Adularia	0.717				-20.697	-21.414		
40 Albite	-0.614				-19.323	-18.709		
140 AlOH3 (a)	1.901		2.59		-30.064	-31.965	-32.654	
471 AlOHSO4	-10.641		-10.481	-10.801	-13.871	-3.23	-3.39	-3.07
472 Al4(OH)10SO4	2.572				25.272	22.7		
157 Allophane(a)	4.541				16.733	12.192		
158 Allophane(F)	5.945				16.733	10.788		
338 Alum k	-29.488				-34.855	-5.367		
50 Alunite	-8.629				-94.776	-86.148		
42 Analcime	-0.902				-14.1	-13.198		
17 Anhydrite	-4.778				-9.312	-4.534		
41 Anorthite	4.917				-15.113	-20.03		
144 Barite	3.103			2.9	-7.045	-10.147		-9.944
48 Beidellite	4.644				-42.275	-46.919		
52 Boehmite	3.694		4.207		-30.047	-33.741	-34.254	
19 Brucite	0.006				-11.221	-11.227		
143 Celestite	-0.146			-0.262	-6.598	-6.452		-6.336
97 Chalcedony	-1.591				-5.24	-3.649		
49 Chlorite 14A	25.532	6	30.807	16.808	98.045	72.513	67.238	81.237
125 Chlorite 7A	22.057	6			98.045	75.988		
20 Chrysotile	8.426				-44.127	-52.553		
29 Clinoenstite	0.396		0.762	0.102	-16.444	-16.84	-17.206	-16.546
56 Clinoptilolte	-				-28.296			
99 Cristobalite	1.503				-5.24	-3.737		
154 Diaspore	5.494				-30.047	-35.541		
28 Diopside	3.88				-32.802	-36.682		
340 Epsomite	-7.303				-9.52	-2.217		
55 Erionite					-21.995			
27 Forsterite	0.179				-27.648	-27.827		
51 Gibbsite ©	3.656	0.2	3.939	2.986	13.048	9.392	9.109	10.062
18 Gypsum	-4.74				-9.347	-4.607		

64 Halite	-7.852					-6.295	1.557		
47 Halloysite	1.278					-32.771	-34.049		
45 Illite	5.882					-35.877	-41.759		
46 Kaolinite	5.491			6.37	4.39	-32.771	-38.262	-39.141	-37.161
43 Kmica	15.312		1.3	16.71	13.633	29.635	14.323	12.925	16.002
128 Laumontite	6.379					-25.662	-32.041		
147 Leonhardite	20.907					-51.306	-72.213		
98 Magadiite	-16.306					-30.606	-14.3		
63 Montmoril Ca	4.343					-42.276	-46.62		
57 Mordenite						-25.668			
66 Mirabilite	-10.426					-12.058	-1.632		
54 Phillipsite	-0.153					-20.027	-19.874		
44 Phlogopite	-12.556		3			31.898	44.454		
141 Prehnite	9.232					-2.746	-11.978		
53 Pyrophyllite	5.08			8.376	3.246	-43.234	-48.314	-51.61	-46.48
101 Quartz	-1.064					-5.24	-4.176		
36 Sepiolite©	3.198					19.295	16.096		
153 Sepiolite(a)	0.635					19.295	18.66		
100 SiO2 (a,L)	-2.101					-5.24	-3.139		
395 SiO2 (a,M)	-2.423					-5.24	-2.817		
37 Talc	8.971		2	11.139	7.223	31.635	22.664	20.496	24.412
65 Thenardite	-11.722					-11.885	-0.163		
31 Tremolite	21.694					-120.193	-141.887		
155 Wairkite	1.794					-25.627	-27.421		
187 Hausmannite	15.9					79.626	63.727		
188 Pyrocroite	3.774				3.481	19.478	15.704		15.997
191 MnCl2, 4H2O	-10.45					-8.214	2.236		
182 MnSO4	-10.532					-7.441	3.091		
230 Melanothalli	-19.208				-19.928	-15.142	4.066		4.786

234 Cu(OH)2	3.426			2.866	12.482	9.056		9.616
237 Atacamite	3.302		3.402	3.152	11.152	7.85	7.75	8
238 Cu2(OH)3NO3	-2.14			-2.21	7.574	9.713		9.783
239 Antlerite	2.236			1.626	10.526	8.29		8.9
240 Brochantite	7.668	0.16	7.858	7.508	23.008	15.34	15.15	15.5
241 Langite	5.12			4.51	22.991	17.871		18.481
242 Tenorite	4.463		4.733	4.193	12.499	8.036	7.766	8.306
243 CuOCuSO4	-35.739				-23.238	12.501		
247 CuSO4	-17.942		-17.582	-18.352	-14.437	3.505	3.145	3.915
248 Chalcanthite	-11.844		-11.524	-12.349	-14.524	-2.679	-2.999	-2.174
420 Dioptase	0.497				7.242	6.744		
265 Zn metal	-32.559			-32.592	-5.798	26.76		26.793
266 Zn(BO2)2	3.227				11.517	8.29		
267 ZnCl2	-19.806			-19.836	-12.299	7.507		7.537
271 Zn(OH)2 (a)	2.874		3.064	2.844	15.324	12.45	12.26	12.48
272 Zn(OH)2 (c)	3.124				15.324	12.2		
273 Zn(OH)2 (b)	3.574	0.02	4.004	3.434	15.324	11.75	11.32	11.89
274 Zn(OH)2 (g)	3.614		4.134	3.484	15.324	11.71	11.19	11.84
275 Zn(OH)2 (e)	3.824	0.03	4.374	3.704	15.324	11.5	10.95	11.62
276 Zn2(OH)3Cl	1.636				16.836	15.2		
277 Zn5(OH)8Cl	10.497				48.997	38.5		
278 Zn2(OH)2SO4	-3.771				3.729	7.5		
279 Zn4(OH)6SO4	5.977				34.377	28.4		
280 ZnNO3)2,6H2O	-22.848				-19.559	3.29		

281 ZnO(active)	4.031		3.771	3.481	15.341	11.31	11.57	11.86
282 Zincite	3.605		3.755	3.205	15.341	11.736	11.586	12.136
283 Zn3O(SO4)2	-28.56				-7.849	20.712		
288 ZnSiO3	6.673				10.101	3.428		
289 Willemite	9.202		11.182		25.443	16.24	14.26	
290 Zincosite	-15.129			-16.049	-11.595	3.534		4.454
291 ZnSO4, 1H2O	-11.333			-11.403	-11.612	-0.28		-0.21
292 Bianchite	-9.938			-10.683	-11.698	-1.761		-1.016
293 Goslarite	-9.666			-9.756	-11.716	-2.05		-1.96
312 Cd metal	-18.386			-18.536	-4.405	13.981		14.131
313 Gamma Cd	-18.49				-4.405	14.085		
314 Cd(BO2)2	3.07				12.91	9.84		
316 CdCl2	-10.348			-10.558	-10.906	-0.558		-0.348
317 CdCl2, 1H2O	-9.263				-10.923	-1.66		
318 CdCl2,2.5H2O	-8.962				-10.949	-1.987		
320 Cd(OH)2 (a)	2.421		2.541	1.851	16.718	14.297	14.177	14.867
321 Cd(OH)2 (c)	3.068	0.04			16.718	13.65		
322 CdOHCl	-0.816		-0.596		2.906	3.722	3.502	
323 Cd3(OH)4SO4	0.674				23.234	22.56		
324 Cd3OH2(SO4)2	-10.396				-3.686	6.71		
325 Cd4(OH)6SO4	11.551				39.951	28.4		
326 Monteponite	0.939			0.319	16.735	15.796		16.416
328 CdSiO3	1.981		3.081		11.495	9.514	8.414	
329 CdSO4	-10.504		-10.474	-10.554	-10.202	0.302	0.272	0.352
330 CdSO4, 1H2O	-8.767		-8.744	-8.794	-10.219	-1.452	-1.475	-1.425

331 CdSO4,2.7H2O	-8.492		-8.475	-8.505	-10.247	-1.756	-1.773	-1.743
360 Pb metal	-11.549		-11.349	-11.589	-7.289	4.259	4.059	4.299
361 Pb(BO2)2	2.257				10.026	7.768		
362 Cotunnite	-8.868		-8.662	-8.968	-13.791	-4.923	-5.129	-4.823
367 Massicot	0.482		0.602		13.85	13.368	13.248	
368 Litharge	0.683		0.763	0.333	13.85	13.167	13.087	13.517
369 PbO, .3H2O	0.864				13.844	12.98		
371 Larnakite	0.868		6.888		0.764	-0.104	-6.124	
372 Pb3O2SO4	3.648				14.614	10.966		
373 Pb4O3SO4	5.407				28.464	23.057		
382 PbSiO3	1.037		2.237	0.717	8.61	7.573	6.373	7.893
383 Pb2SiO4	1.991		2.531	1.251	22.46	20.469	19.929	21.209
384 Anglesite	-5.238	0.02	-5.158		-13.086	-7.849	-7.929	
386 Plattnerite	-16.24		-15.94		34.989	51.23	50.93	
387 Pb2O3	-12.201				48.839	61.04		
388 Minium	-13.804		-10.914		62.689	76.494	73.604	
389 Pb(OH)2 (c)	5.301			-0.179	13.833	8.532		14.012
390 Laurionite	-0.602		-0.154		0.021	0.623	0.175	
391 Pb2(OH)3Cl	5.061				13.854	8.793		
393 Pb2O(OH)2	1.483			0.583	27.683	26.2		27.1
394 Pb4(OH)6SO4	7.312				28.412	21.1		
411 Ni(OH)2	7.13	0.1	7.34	4.63	17.1	9.969	9.759	12.469
412 Ni4(OH)6SO4	9.479				41.479	32		
413 Bunsenite	4.014			4.074	17.117	13.103		13.043
416 Retgersite	-7.853				-9.923	-2.07		
417 Morenosite	-7.5				-9.94	-2.44		
418 Ni2SiO4	13.544				28.994	15.45		
437 Ag metal	8.657				-5.542	-14.198		
439 Cerargyrite	1.385				-8.792	-10.177		

443 Ag2O	-2.808	0.1	10.056	12.865
446 Ag2SO4	-11.844		-16.88	-5.036

Appendix 2: Trace element concentrations in Cape Vera sediment cores. D.L = detection limit

		Al	Ba	Cr	Cu	Fe	K	Mg	Mn	Na	P	Sr	Zn	As	Cd	Co	Mo	Ni	Pb	Sb
D.L	Depth	0.01	5	1	0.5	0.01	0.01	0.01	5	0.01	50	0.5	1	1	0.01	0.1	0.05	0.5	0.2	0.05
Units		%	µg/g	µg/g	µg/g	%	%	%	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
CV8	1.25	0.31	30	7	47.4	1.09	0.26	5.03	110	300	2610	30.7	483	10	1.67	7.3	1.55	26.1	19	0.56
	2.25	0.3	24	6	35.7	0.75	0.19	5.73	74	200	1800	29.1	467	9	1.77	6.9	2.02	27	18.3	0.55
	3.25	0.55	23	240	21.2	0.86	0.26	4.5	91	900	1070	29.6	265	9	1.71	6.8	6.85	33.1	19.9	0.56
	4.25	0.5	20	90	22	0.72	0.23	4.51	79	700	910	28.3	260	9	1.78	7.2	2.83	24.7	20.6	0.58
	5.25	0.55	25	329	20.3	0.89	0.25	5.11	96	600	760	29.3	241	9	1.63	7.5	8.57	38.1	19.3	0.56
	6.25	0.48	21	84	20.4	0.7	0.21	5.19	77	400	730	27.7	225	9	1.51	7.1	2.6	25	21.4	0.5
	7.25	0.54	23	195	18.7	0.78	0.24	5.25	81	400	660	27.8	237	9	1.46	7.2	5.96	32.6	20.9	0.5
	8.25	0.51	22	84	19.6	0.71	0.22	5.3	72	400	650	27.1	223	10	1.42	7.4	2.61	25.3	21.7	0.52
	9.25	0.54	23	222	20.7	0.83	0.23	5.56	89	300	590	28.6	233	11	1.41	8.6	13.7	31.7	22.5	0.64
	10.25	0.55	25	101	25.8	0.77	0.24	6.28	87	300	570	32.3	269	10	1.29	8.4	2.86	31.8	22.7	0.65
	11.25	0.5	22	116	21	0.74	0.22	5.63	89	300	530	28.4	222	11	1.32	9.5	6.82	30.3	23.2	0.7
	12.25	0.48	20	86	22.5	0.72	0.22	5.64	86	200	480	28.5	216	11	1.25	9.2	3.05	28.1	21.7	0.66
	13.25	0.52	24	93	25.05	0.85	0.23	5.79	104	250	530	30.3	243	12.5	1.23	10.1	5.965	32.4	21.8	0.73
	15.25	0.52	22	63	21.4	0.84	0.22	5.64	103	200	440	29.5	215	14	1.18	10.7	8.73	28.7	22.3	0.7
	16.25	0.55	23	68	22.3	0.86	0.23	5.6	113	200	440	29.3	228	14	1.19	10.9	9.14	30.1	22.8	0.82
	17.25	0.68	28	83	24.1	0.87	0.28	5.27	116	200	460	28.1	252	14	1.19	12.1	7.23	33.5	25.1	0.91
	18.25	0.68	27	69	26.5	0.88	0.28	5	112	200	480	26.8	264	16	1.22	13.1	5.21	37.8	26	0.95
	19.25	0.7	30	126	25.4	0.96	0.29	5.1	120	300	510	27.5	262	16	1.16	13	9.8	37.5	25.2	0.95
	20.25	0.65	26	67	26.3	0.87	0.26	5.26	113	200	460	27.3	258	16	1.2	12.3	5.1	33.2	24.9	0.94
	21.25	0.7	28	84	24.8	0.92	0.29	5.25	112	200	480	27.9	257	16	1.18	13.1	8.85	35.4	24.9	0.92
CV30	0.25	0.14	12	3	13	0.54	0.37	16	45	300	3700	31	67	9	0.64	2.8	2	17	15	0.3
	1.25	0.14	8	2.7	13	0.34	0.2	16	34	310	2400	35	86	6.8	0.58	2.3	2.6	16	13	0.2
	2.25	0.11	5.3	2.35	7.25	0.23	0.06	17	41	365	375	48.7	40	3.6	0.32	1.85	2.84	12.65	8.65	0.22
	3.25	0.14	<5	4	11.7	0.26	0.08	11.2	45	400	280	51.6	71	3	0.34	2.1	2.95	16.2	8.5	0.27
	4.25	0.12	<5	3	7.2	0.26	0.07	10.6	46	400	270	49.8	40	3	0.38	2.5	2.95	16.5	8.9	0.26
	5.25	0.12	<5	3	8.1	0.23	0.05	10.6	55	300	240	52.3	38	4	0.39	2.3	2.99	15.5	8.1	0.29
	6.25	0.11	<5	4	7.3	0.23	0.05	10.7	57	300	260	51.9	31	3	0.32	2.2	2.89	17.4	7.4	0.26
	7.25	0.08	<5	3	4.9	0.19	0.04	9.86	50	300	200	47.3	28	3	0.24	1.7	2.9	14.1	5.8	0.21
	8.25	0.11	<5	3	6.4	0.24	0.05	9.91	53	300	300	48.5	40	3	0.32	2.4	2.83	17.7	7.6	0.25
	9.25	0.10	<5	2	10.55	0.27	0.05	9.78	50.5	300	355	48.7	38	4	0.38	2.5	2.565	19.3	9.3	0.28

	10.25	0.18	<5	3	13.7	0.39	0.09	9.3	53	300	560	46.7	65	5	0.54	3.3	2.36	23.3	12.3	0.34
	11.25	0.14	<5	3	14.8	0.29	0.07	10	50	300	290	49.7	48	4	0.43	2.6	3.04	19.7	10.2	0.31
	12.25	0.15	<5	15	13.8	0.3	0.08	9.74	51	300	290	48.1	47	11	0.4	2.7	2.99	21.7	11.1	0.57
	13.25	0.18	<5	4	14.7	0.37	0.09	9.31	53	300	350	46.5	78	5	0.49	3.8	2.64	24.9	14.1	0.44
	14.25	0.25	5	4	19.4	0.44	0.11	8.71	57	300	440	44.5	80	7	0.57	4.9	2.58	30.3	16.1	0.45
	15.25	0.22	6	4	20.4	0.43	0.1	9.16	56	300	450	47.3	81	6	0.55	4.4	2.43	27.5	15.4	0.42
	16.25	0.21	<5	4	31.9	0.42	0.1	8.36	50	200	450	42.8	92	6	0.6	4.2	2.36	27.9	16.9	0.47
	17.25	0.23	<5	4	20.4	0.42	0.1	8.39	53	200	460	42.6	83	6	0.61	4.6	2.46	29.4	16.9	0.44
	18.25	0.24	5	5	24.6	0.45	0.1	8.28	51	200	520	42.7	104	6	0.63	4.6	2.38	32.7	17.1	0.46
	19.25	0.23	<5	4	31.3	0.42	0.1	8.34	48	200	480	42	98	6	0.66	4.2	2.52	29.8	17.8	0.47
	20.25	0.22	5	9	19.4	0.36	0.1	7.78	44	200	410	38.7	85	5	0.65	3.7	2.52	29.9	16.8	0.44
	21.25	0.17	<5	3	16.2	0.30	0.08	8.19	42.5	200	365	43.9	79.5	4.5	0.68	3.35	2.495	27.65	14.95	0.34
	22.25	0.28	7	5	22.9	0.41	0.12	7.03	43	200	560	35.3	113	6	0.89	4.2	2.37	33	18.6	0.45
	23.25	0.21	<5	4	15.4	0.35	0.1	8.14	46	200	530	39.5	79	5	0.65	3.6	2.81	28.7	14.5	0.4
CV10	0.5	0	12	2.2	8.5	0.27	0	2	39	710	8100	20	49	11	0.57	1.6	1.4	9.8	6.8	<0.05
	1.25	0	11	2.7	9.5	0.24	0	11	34	470	5400	26	53	8.1	1.1	1.9	30	13	9.8	22
	2.25	0	11	2.6	12	0.27	0	15	33	440	2100	34	70	5.0	0.72	2.3	2.3	15	13	0.3
	3.25	0.2	6	4	75.4	0.26	0.12	6.64	34	400	1470	33	192	4	0.95	2.4	2.45	18.6	14.7	0.14
	4.25	0.2	7	4	32.1	0.29	0.12	7.42	34	400	1260	35.2	111	4	0.89	2.5	2.39	19.3	13	0.14
	5.25	0.2	5	4	15.7	0.28	0.11	7.57	36	300	920	35.4	94	4	0.87	2.5	2.37	19.4	13	0.14
	6.25	0.2	6	4	17.5	0.31	0.1	6.66	35	300	930	31	96	5	0.9	2.9	2.27	22.7	14.9	0.2
	7.25	0.2	7	3	12.5	0.38	0.1	7.16	44	300	1190	34	84	5	0.91	3.2	2.27	23.7	15.7	0.25
	8.25	0.21	7	3	11.2	0.36	0.1	8	43	200	1060	38	81	4	0.76	2.7	1.96	20.7	13.1	0.21
	9.25	0.19	8	3	11.8	0.34	0.1	7.4	41	300	990	36.1	115	5	0.85	2.9	1.88	21.3	15	0.22
	10.25	0.22	8	4	36.9	0.42	0.11	7.98	45	300	1150	39.3	122	4	0.84	3.2	1.81	21.6	16.1	0.22
	11.25	0.22	8	14	16.1	0.41	0.11	7.74	45	300	1160	38.2	108	5	0.94	3.9	1.99	27.2	16.4	0.24
	12.25	0.22	8	4	15.8	0.4	0.11	7.36	41	300	1130	35	98	5	0.88	3.1	1.97	21.8	15.4	0.23
CV20	0.25	0	5.8	1.8	7.6	0.08	0.46	0.63	17	600	8000	16	19	8.0	0.30	1.1	1.9	5.9	1.2	0.3
	1.25	0	5.7	1.9	9.9	0.08	0.39	0.63	17	560	8000	15	280	8.1	0.32	1.2	2.2	6.1	1.3	0.2
	2.25	0	4.6	1.7	8.3	0.05	0.34	0.54	15	520	7100	13	20	7.5	0.35	1.1	2.9	6.1	1.1	0.2
	3.25	0	4.7	1.8	11	0.06	0.29	0.52	14	550	6300	13	26	6.8	0.38	1.2	3.2	6.9	1.4	0.2
	4.25	0	4.9	1.9	12	0.05	0.22	0.54	13	550	5100	16	130	6.9	0.39	1.4	3.8	7.9	1.6	0.2
	5.25	0	4.1	1.8	16	0.05	0.18	0.55	12	570	4400	15	39	6.2	0.46	1.4	4.0	8.1	1.7	0.2
	6.25	0	4.2	1.8	11	0.05	0.12	0.53	11	550	3500	15	30	6.4	0.48	1.6	5.0	8.6	1.6	0.2
	7.25	0	4.6	2.2	11	0.06	0.08	0.53	9.6	500	2600	15	34	5.5	0.55	1.5	4.8	8.9	1.8	0.2

	8.25	0	4.4	2.1	11	0.05	0.05	0.49	9.0	450	2100	15	31	5.0	0.58	1.4	5.3	9.1	1.7	0.2
	9.25	0	5.3	2.5	12	0.06	0.04	0.51	8.7	410	1700	16	33	4.4	0.64	1.4	5.6	9.4	1.7	0.2
	10.25	0	6.0	3.0	12	0.08	0.03	0.58	10	380	1600	18	33	4.1	0.65	1.3	5.8	11	1.8	0.2
	11.25	0	7.5	2.7	14	0.08	0.03	0.74	9.3	330	1300	21	43	3.9	0.67	1.3	6.7	10	2.3	0.2
	12.25	0	7.6	2.5	13	0.08	0.04	0.71	8.4	330	1300	23	51	3.5	0.60	1.2	5.6	9.7	2.1	0.2
CV9a	0.25	0	8.6	2.6	11	0.23	0.52	0.75	27	320	7900	12	44	7.1	0.69	1.5	0.9	11	4.5	0.1
	1.25	0	9.5	2.8	11	0.21	0.49	0.72	26	270	8400	13	43	7.9	0.70	1.6	1.0	11	4.6	< 0.1
	2.25	0	5.4	2.8	12	0.15	0.42	0.72	24	250	8000	9.7	42	7.8	0.67	1.6	1.4	11	4.7	< 0.1
	3.25	0	5.3	3.1	12	0.14	0.41	0.70	24	240	8100	9.1	44	7.6	0.69	1.6	1.5	12	4.6	< 0.1
	4.25	0	5.9	4.3	14	0.13	0.33	0.76	20	250	6300	9.9	55	7.7	0.90	2.1	1.9	14	5.9	< 0.1
	5.25	0	6.2	3.6	15	0.13	0.29	0.77	19	250	5600	9.7	58	7.3	0.89	2.1	1.7	14	6.2	< 0.1
	6.25	0	6.3	4.0	16	0.13	0.21	0.81	18	260	4500	9.5	65	8.0	1.0	2.4	1.8	16	7.4	< 0.1
	7.25	0	6.4	4.1	16	0.15	0.16	0.89	17	270	3700	9.2	70	8.1	1.1	2.9	1.8	22	8.1	0.1
	8.25	0	7.2	4.3	17	0.16	0.12	0.99	16	240	2900	9.4	79	6.6	1.2	2.8	2.0	19	8.9	0.1
	9.25	0	7.5	4.4	17	0.17	0.10	1.10	15	220	2300	9.4	87	5.7	1.3	2.7	2.3	19	9.6	0.1
	10.25	0	8.3	4.4	16	0.17	0.08	1.10	15	220	1700	10.0	92	5.0	1.3	2.6	2.1	19	11	0.1
	11.25	0	9.7	4.9	16	0.19	0.09	1.30	16	220	1600	11	104	4.7	1.3	2.9	2.0	21	13	0.1
	12.25	0	10	5.2	17	0.21	0.09	1.40	17	210	1300	12	105	4.1	1.2	3.3	2.3	21	12	0.2
	13.25	0	11	5.5	18	0.28	0.10	1.50	16	190	1000	13	99	3.9	1.1	3.7	3.1	23	12	0.2
	14.25	0	12	6.2	27	0.35	0.12	1.50	17	170	1100	14	110	4.2	1.0	3.9	3.8	23	13	0.2
	15.25	0	12	5.6	20	0.38	0.10	1.50	18	150	1000	14	98	4.2	1.0	4.1	4.1	23	13	0.3
CV5	0.25	0.29	20	5.5	18.75	0.79	0.12	8.65	175	250	535	38.3	45.5	6.5	0.27	7.7	1.85	18.4	14.1	0.39
	1.25	0.26	29	5	16.2	1.13	0.12	6.42	232	200	870	32.6	47	8	0.31	10	1.58	20.1	11.2	0.38
	2.25	0.31	23	5	17.2	0.87	0.13	8.38	169	200	620	37.2	43	7	0.25	7.3	1.79	19.5	13.1	0.41
	3.25	0.32	16	5	16	0.74	0.12	8.93	146	200	500	39.2	43	6	0.26	7.3	1.98	18.7	12.5	0.41
	4.25	0.3	18	6	16.5	0.74	0.11	8.92	151	300	510	38.8	43	6	0.27	7.2	2.07	18.9	12.2	0.43
	5.25	0.32	16	8	21.7	0.96	0.12	9.11	156	300	490	39.6	42	6	0.21	7.8	2.18	20.2	12.4	0.43
	6.25	0.36	19	6	16.5	0.72	0.13	8.85	148	300	520	38.3	44	6	0.26	6.7	1.72	19.2	11.8	0.33
	7.25	0.37	19	6	17.2	0.72	0.13	8.64	135	300	510	37.6	48	6	0.27	7.5	2.01	20.5	12.7	0.32
	8.25	0.38	20	7	16.9	0.7	0.14	8.22	120	200	510	35.7	46	5	0.24	7.1	2.04	19.9	12.4	0.35
	9.25	0.33	17	6	15.8	0.65	0.11	7.96	109	200	480	35	45	5	0.28	6.8	2.21	19.1	12.2	0.35
	10.25	0.29	18	5	12.9	0.45	0.10	6.95	86	200	420	35.6	36	4	0.26	5.5	2.27	16.7	10.1	0.25
	11.25	0.3	16	5	13.8	0.46	0.10	7.10	88	200	420	35.5	40	3	0.3	5.5	2.38	17.6	11.4	0.3
	12.25	0.33	12.5	5.5	14.3	0.65	0.12	8.59	74	250	395	35	43	4.5	0.265	6.4	3.815	18.9	12.05	0.27
	13.25	0.32	13	5	13.6	0.55	0.12	8.92	79	300	380	35.3	41	4	0.24	6.4	3.16	17.8	11.4	0.26

	14.25	0.34	12	6	15	0.74	0.12	8.25	69	200	410	34.6	45	5	0.29	6.4	4.47	20	12.7	0.28
	15.25	0.37	13	6	15.3	0.7	0.13	8.29	80	200	420	35.9	47	3	0.31	6	4.61	20.1	12.6	0.26
CV6	0.25	0.27	31	5	11.6	0.55	0.17	2.78	110	200	830	40.8	77	3	0.22	4.7	0.7	14.2	7.4	0.25
	1.25	0.33	28	6	13.5	0.47	0.16	3.43	82	200	880	38.8	36	3	0.28	5.7	1.59	15.9	8.8	0.25
	2.25	0.36	27	6	16	0.47	0.14	3.75	64	200	600	34.9	44	3	0.34	5.9	2.75	19.3	10.4	0.29
	3.25	0.34	27	6	16.2	0.49	0.13	3.03	64	200	530	39.4	40	3	0.32	6.2	4.65	18.3	8.7	0.27
	4.25	0.25	27	5	14.7	0.41	0.10	1.87	47	100	460	39.3	33	3	0.42	5.1	6.61	15.8	6.1	0.29
	5.25	0.25	27	5	15	0.4	0.09	1.76	45	200	440	38	33	2	0.39	4.4	5.72	15.5	5.9	0.25
	6.25	0.27	28	5	15.4	0.42	0.10	1.74	44	150	470	38.2	35.5	2	0.435	4.25	5.47	16.15	6	0.24
	7.25	0.11	9	3	5.6	0.17	0.05	9.28	41	200	260	56.5	14	0.5	0.18	2.4	2.34	6.5	2.6	0.12
	8.25	0.18	19	3	9.7	0.31	0.07	5.43	41	200	380	44.7	25	1	0.33	3.3	4.08	11	3.9	0.19
	9.25	0.09	6	3	4.6	0.18	0.04	9.85	46	300	230	55.5	13	1	0.29	2	4.09	5.6	2	0.11
	10.25	0.09	7	2	5	0.18	0.04	9.98	41	300	240	61.2	13	0.5	0.17	1.8	2.73	5.6	2.1	0.1
	11.25	0.11	7	3	4.8	0.21	0.05	9.43	47	300	250	60.7	14	1	0.23	2.2	4.06	5.9	2.5	0.1
	12.25	0.04	<5	2	1.7	0.09	0.03	12.50	52	300	180	63	5	0.5	0.17	1.5	2.55	2.2	0.9	0.06
	13.25	0.03	<5	3	1.7	0.13	0.02	12.50	43	300	180	59.4	6	0.5	0.11	1.4	2.33	2.3	1.4	0.07
CV1	0.25	0.44	31	11	41.6	0.61	0.22	1.39	42	200	1390	25.7	119	7	0.89	5.4	1.21	33.8	14.6	0.57
	1.25	0.48	13	12	37.1	0.41	0.17	1.13	32	100	1050	17.9	71	5	1.05	6.4	1.21	44.3	20.1	0.37
	2.25	0.37	13	10	33.1	0.3	0.15	1.30	35	200	750	24.8	79	3	0.86	6.3	0.78	39.2	21.5	0.26
	3.25	0.2	15	5	15.3	0.28	0.09	1.22	72	400	380	51.4	38	2	0.41	4	0.39	26.9	9.6	0.11
	4.25	0.16	12	4	9.5	0.25	0.07	0.97	73	300	270	47.5	27	1	0.31	3.2	0.28	23.3	7.8	0.08
	5.25	0.16	12	3	10	0.26	0.08	0.98	77	300	260	49.8	26	1	0.29	3.2	0.29	21	6.9	0.09
	6.25	0.13	10	3	7.8	0.23	0.07	0.82	72	300	210	47.2	22	1	0.31	2.9	0.25	20.2	7.1	0.08
	7.25	0.14	13	3	7.6	0.27	0.09	0.89	81	400	230	52.6	24	1	0.3	2.9	0.29	19.2	6.3	0.08
	8.25	0.17	15	4	9.7	0.27	0.10	0.95	83	400	240	47.1	30	1	0.36	3.2	0.39	20.8	7.9	0.08
	9.25	0.2	17	4	13.1	0.29	0.11	1.05	87	400	260	49.5	42	2	0.46	3.8	0.7	23.3	8.7	0.11
CV12	0.25	0	12	1.8	1.5	0	0.16	9.20	27	1200	760	156	13	2.1	0.27	0.52	1.4	6.6	2.1	< 0.1
	1.25	0.09	6	74	7.6	0.18	0.06	9.12	36	600	250	64.1	19	<1	0.35	1.1	6.76	5.9	1.9	<0.05
	2.25	0.08	<5	81	2.5	0.16	0.04	8.61	29	400	140	49.5	15	<1	0.31	1	10.8	6.4	1.9	<0.05
	3.25	0.08	<5	49	3.9	0.13	0.04	8.83	27	400	130	45.4	12	<1	0.31	1	7.21	4.3	1	<0.05
	4.25	0.09	<5	56	2.1	0.15	0.04	8.95	27	400	120	44.1	13	<1	0.35	1	10.8	4.6	1.9	<0.05
	5.25	0.08	<5	719	13.1	0.84	0.04	8.75	95	500	120	43.3	13	1	0.35	2.8	7.7	15.3	1.5	0.08
	6.25	0.08	<5	82	2.2	0.17	0.04	8.90	31	500	120	44.2	11	<1	0.35	0.9	6.82	4.9	1.6	<0.05
CV22	0.25	0.05	<5	1	22.2	0.15	0.04	7.17	59	300	270	55.6	26	1	0.16	0.8	2.17	12.5	2.8	0.09
	1.25	0.03	<5	<1	8.8	0.06	0.02	6.63	51	200	60	48.3	1	<1	0.1	0.6	1.92	10.1	1.7	<0.05

2.25	0.03	<5	27	13.1	0.07	0.02	6.94	54	300	<50	51.3	11	<1	0.11	0.7	2.62	18.6	1.9	<0.05
3.25	0.22	10	82	8.1	0.28	0.11	8.49	73	300	140	61.3	37	3	0.26	2.6	2.74	8.5	6.1	0.07
4.25	0.2	11	94	4.6	0.26	0.11	8.67	75	300	140	60.6	37	3	0.21	2.4	6.67	8.8	5.9	0.08
5.25	0.1	6	79	8	0.21	0.06	9.70	83	400	120	73.4	19	1	0.13	1.4	2.31	5.3	4	<0.05
6.25	0.09	<5	84	3.4	0.18	0.05	8.80	68	300	90	64	15	1	0.14	1.3	5.46	6.3	4.7	<0.05
7.25	0.11	7.5	92.5	8.7	0.24	0.06	9.99	82	400	120	71.6	17	1	0.145	1.5	2.78	5.7	3.8	<0.05

Statement of contributions of collaborators

Included in this M.Sc. thesis are two co-authored articles presenting data from multiple years of field work. Samples from the 2004-2006 field seasons were collected by other members of the Cape Vera project from the Blais lab (Huijin Liu, Karen Foster, Linda Kimpe) and from the Paleoecological Environmental Assessment and Research Lab *(*PEARL*)* at Queen's University (Bronwyn Keatley, Neal Michelutti). Guano samples were collected and analyzed by K. Foster.

The redaction of both articles and data analysis are my own work. Comments and suggestions to improve the manuscripts were provided by co-authors. Furthermore, the first article "Bioenrichment of trace elements in a series of ponds near a northern fulmar colony at Cape Vera, Devon Island" has been submitted for publication and has undergone a series of reviews after which improvements were made to the manuscript.