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Colonial Marine Birds Influence Island Soil Chemistry Through Biotransport of Trace Elements

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Abstract Marine birds are important vectors of nutrient and contaminant transfer from sea to land. In eastern Nova Scotia, Canada, colonial marine birds nest on specific nearshore islands within archipelagoes, and we predicted that soils on islands with bird colonies would have higher concentrations of selected trace elements (notably K, Ca, As, Cd, Cu, Pb, Se, Hg, and Zn) than soils on islands without colonies. In this study, common eider (*Somateria mollissima*), Leach's storm petrel (*Oceanodroma leucorhoa*), black guillemot (*Cepphus grylle*), double-crested cormorant (*Phalacrocorax auritus*), great black-backed gull (*Larus marinus*), and herring gull (*Larus argentatus*) were considered to be the principal avian vectors for contaminant transfer. Results indicate that soils from islands with bird colonies had unique chemical compositions and commonly displayed elevated concentrations of K, Ca, Cu, Se, and Zn when compared to islands without colonies. Thus, marine birds feeding in the nearby marine zone move pollutants and nutrients from the ocean to nesting islands, potentially influencing habitat quality for coastal terrestrial species.

Keywords Biotransport · Trace elements · Colonial birds · Island · Soil

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1 Introduction

Mobile and migratory species move energy and nutrients from foraging areas to breeding areas and release these nutrients through processes of defecation, regurgitation, dropping food, or mortality, often fertilizing the breeding sites with critical nutrient subsidies (e.g., Cederholm et al. 1999; Helfield and Naiman 2001; Ellis 2005; Ellis et al. 2006; Mulder et al. 2011; Bauer and Hoye 2014). Through this same process of biotransport (Blais et al. 2007), contaminants derived from their diet are also moved to and concentrated around breeding sites (e.g., Walters et al. 2008). Because they feed relatively high in food chains, and thus tend to contain high concentrations of selected contaminants due to biomagnification through marine food webs (e.g., Mallory and Braune 2012), this process may be particularly pronounced for colonial marine birds. Notably, seabird guano is an effective vector of contaminants to soils (e.g., Liu et al. 2006; Evenset et al. 2007), and consequently, aquatic and terrestrial habitats around colonies can become markedly contaminated due to contributions of chemicals from birds (e.g., Blais et al. 2005; Brimble et al. 2009; Zhu et al. 2014). In turn, terrestrial biota living near a marine bird colony tend to ingest these chemicals of marine origin by feeding on biota grown in the contaminated habitats and thereby exhibit much higher contamination than conspecifics inhabiting similar habitats away from bird colonies (e.g., Evenset et al. 2007; Choy et al. 2010).

In the Arctic, Blais et al. (2005) demonstrated that biotransport from seabirds can account for greater input of contaminants to local freshwater ponds than atmospheric processes, and they also found that contaminant concentrations in local biota (primarily mercury and persistent organic pollutants) were directly related to proximity to the seabird colony. Michelutti et al. (2010) showed that there were detectable differences in the trace element chemistry of habitats that received seabird guano inputs depending on the species using small ponds. Arctic terns (*Sterna paradisaea*) fed at higher trophic levels and contributed more Hg, Cd, and As to receiving ponds, whereas common eider (*Somateria mollissima borealis*) fed at lower trophic levels, and receiving ponds were higher in Pb, Mn, and Al. Like the Arctic, biotransport of trace elements by colonial seabirds to their breeding habitats has also been found in temperate (Otero Perez 1998), tropical (Liu et al. 2006), and Antarctic habitats (Bargagli 2008; Huang et al. 2014).

Marine bird colonies are common around coastal Nova Scotia, Canada (e.g., Gaston et al. 2009), but the process of biotransport has not been investigated there. Our study took place in eastern Nova Scotia, where we investigated elemental concentrations at 10 sites (Fig. 1) that were separated into known colonial bird habitat and sites that did not accommodate bird colonies. In particular, we were interested in applying a different analytical technique than has been used in previous studies to determine whether trace elements are accumulating on islands with bird colonies. Traditional soil analysis methods call for wet digestion of the sample and can include heating the sample, processes that can lend themselves to error. In contrast, X-ray fluorescence (XRF) may be an optimal way to minimize sample preparation while obtaining a multi-element data output (e.g., Kaniu et al. 2012) with a high accuracy and precision. If the process of biotransport was occurring in eastern Nova Scotia in a similar fashion to other regions where marine birds breed, we predicted that soil from islands that supported marine bird colonies would have higher levels of trace elements or nutrients that are known to bioaccumulate or biomagnify in birds (e.g., Ligeza and Smal 2003; Mallory et al. 2004; Michelutti et al. 2010). Specifically, we predicted that islands with bird colonies would exhibit ornithogenic enrichment of nutrients (P, K, Ca) and potentially toxic trace elements ("contaminants"; As, Cd, Cu, Pb, Se, Hg, and Zn).

2 Methods

Field work was carried out at the Eastern Shore Islands Wildlife Management Area (ESIWMA), Nova Scotia, Canada (ESIWMA; 44° 54′ N, 62° 15′ W) from May to August 2013 (Fig. 1). The ESIWMA was created in 1976 with the purpose of preserving breeding habitat of various colonial marine birds, most notably the common eider (*S. mollissima*), as well as Leach's storm petrel (*Oceanodroma leucorhoa*), black guillemot (*Cepphus grylle*), double-crested cormorant (*Phalacrocorax auritus*), great black-backed gull (*Larus marinus*), and herring gull (*Larus argentatus*). The land mass within the ESIWMA constitutes 389 ha on 50 vegetated islands, most of which remain largely inaccessible to local anthropogenic impact because of their rocky shorelines and persistent ocean swell. Islands vary in vegetative cover from coniferous forest to grasses and shrubs. The climate is temperate with a significant marine influence, notably leading to extensive fog. Because of their close proximity to one another and their parallel distribution to the shoreline, we assumed that the islands experience similar climate, anthropogenic atmospheric pollution, and sea spray.

The study area lies in the Taylors Head geological formation (dominantly metasandstone and minor slate) of the Goldenville group of the Meguma terrane (Horne and Pelley 2007; White 2010), and till surveys showed that the dominant till of the Eastern Shore region is a loose, sandy, metasandstone till containing over 90 % local clasts (Stea and Fowler 1979). Local geology of an area can have a significant influence on trace metal concentrations in soil and sediments (Boruvka et al. 2005). Although sampling by Stea and Fowler (1979) did not extend from the mainland to the islands, our field observations suggest that till and background geological conditions were consistent across the islands. Site drainage was variable and ranged between rapid to moderate

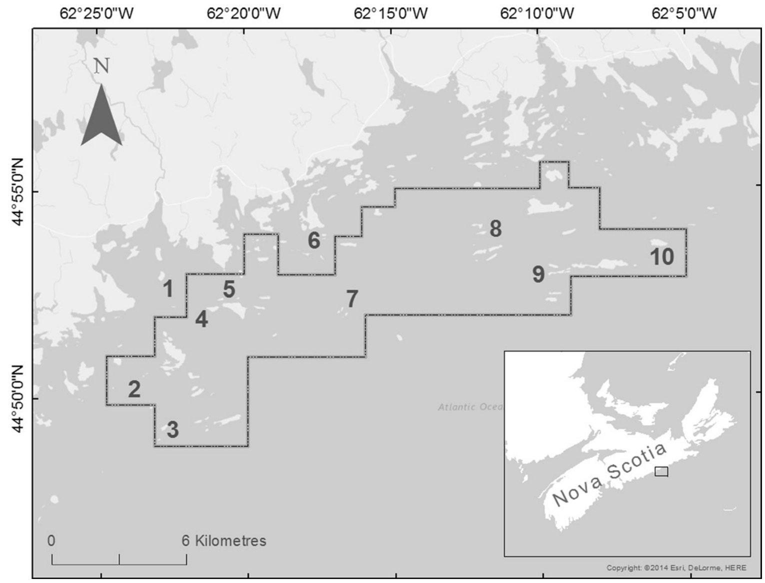

Fig. 1 Map of the study area along the eastern coast of Nova Scotia, Canada. The *line* notes the official border of the Eastern Shore Islands Wildlife Management Area (http://novascotia.ca/natr/wildlife/habitats/sanctuaries/pdfs/eastshore.pdf); two of our sites lay just outside of this border. The 10 islands sampled for soils are noted: Islands 1, 2, 3, 7, 9, and 10 had bird colonies, while islands 4, 5, 6, and 8 lacked colonies

depending on slope position, slope percent, and subsoil permeability.

We selected islands to sample based on past research by government biologists at the site and categorized islands as having effectively no colonial marine bird colonies (n=4; "no colony islands") and islands with current or recently extant colonies of single or mixed species of marine birds (n=6; "colony islands"). Soil samples were collected from sites on islands to represent the range of cover types on each island (tall grass, shrubs, barren, and forested). This resulted in 80 samples being collected, from 42 discrete sampling locations.

We used a LaMotte sediment corer to collect at least 2 cm^3 of soil from a depth below the O-horizon of ~5 cm at each site. As well, triplicate samples were collected within a 15-cm-diameter circle of each other. Samples were stored in clear plastic vials with pop-off lids and transported in an opaque plastic bin until further preparation in laboratory. Soil sample transport time ranged from 1 to 7 days from the time of sampling.

We used XRF elemental analysis to determine trace element concentrations in soil samples, using an Innov-X X5000© portable benchtop XRF machine. This approach has been used extensively to look at lake sediments (e.g., Boyle 2000; Franz et al. 2006; Liu et al. 2013) and bedrock from various units in the Goldenville group (Nova Scotia Department of Natural Resources, unpublished data). The XRF unit measures 38 trace elements in samples, but we were principally interested in 12 essential and nonessential elements known to bioaccumulate and/or be released in measurable quantities from seabirds (detection limits in brackets; ppm): P (380), K (17), Ca (18), Cr (2), As (2), Ni (4), Cd (1), Cu (3), Pb (2), Se (1), Hg (3), and Zn (2) (see Mallory et al. 2004; Borgå et al. 2006; Ellis et al. 2006). In advance of XRF testing, samples were dried in their original containers in a Cole Palmer StableTemp© oven for 24 h at 60 °C. Dehydrated samples were stored in sealed glass or plastic containers which also included Drierite© anhydrous calcium sulfate (Stock #12005) as a desiccant. In preparation for XRF analyses, samples were ground with a mortar and pestle to maximize homogenization. Then, sample containers were covered in clear plastic wrap which was secured by elastic band with the lid removed. A subset of samples was tested in advance of full analysis to determine analytical methodology. Internal standard reference materials (CanARC 17, Can 277 cm) were analyzed once every 15 trials. For 10 trace elements (S, Cl, K, Ca, Ti, Co, Cu, Zn, Rb, Zr), precision of analyses on standardized samples was 19±2 % (n=40).

We used Fisher's exact tests to compare proportions of samples above detection limits between habitat types (using all 80 samples in calculations), and Mann–Whitney tests to compare the concentrations of trace elements between soils on islands with and without nesting birds (using one randomly selected sample from each discrete sampling location, hence 30 sites for bird islands and 12 sites for no colony islands). For trace elements where samples had >60 % detections, results below the assay detection limit were valued at 0.5 ppm below the detection limit, and the reported p values were not adjusted for multiple comparisons. Principle component analysis (Stat Soft 2013) was conducted on selected trace elements that were above detection limits in >60 % of samples and were of toxicological interest (Cu, Zn, Se, As, and Pb) to determine which elements in soils were suitable in grouping islands by explaining significant variability between bird islands and no colony islands.

3 Results

3.1 Soil Data

Soils at all sites were fresh, coarse-loamy dominated by a sandy loam texture. Soils on densely forested islands had thicker organic layers and generally contained more moisture, whereas in nonforested habitats, the organic layer was thinner (<5 cm). All soils sampled were "dark reddish brown" or "dark brown," 5–7.5 years 2.5–3/1.5–2.5, on a Munsell© soil color chart.

For all soil samples, concentrations of certain trace elements were detected in <30 % of the soil samples using XRF technology but still provided some insights into biotransport. For example, phosphorus was detected in 0 % of soil samples from no colony islands (n=33 samples) but was detected significantly more often (22 %) in samples from islands with colonies (n=47 samples; Fisher's exact test, p=0.002). Chromium was detected in 3 % of soil samples from no colony islands, significantly lower than in the 25 % of samples from islands with colonies (p=0.011), whereas Hg was found in 3 % of no colony soil samples but 30 % of islands with colonies soil samples (p=0.03). Cadmium was found in similar proportions of samples from no colony (21 %) and island with colonies' (23 %) soil samples (p=1.0) but overall was detected in only 24 % of all soil samples. Ni concentrations were below detection limits for all samples. Due to low detection frequencies, we did not use P, Cr, Hg, Cd, or Ni in further analyses.

Soil chemistries differed strongly between islands with marine bird colonies and those without colonies (Table 1). With the exception of Pb, soil samples on islands with colonies had higher mean levels of all tested trace elements compared to no colony islands, with significantly higher mean concentrations of K, Ca, Cu, Se, and Zn. However, variability in measured concentrations of trace elements in soils also differed among island types. The mean coefficient of variation for trace elements from soil samples on islands with colonies was 95.0±35.6 %, significantly higher than the mean value for soil samples on no colony islands (64.0±21.0 %; paired t test, t_7=2.96, p=0.02).

Using this set of seven trace elements, soils on islands with colonies could be distinguished from soils on no colony islands using principle component analysis (PCA; 70 % of total variance explained), but this was improved to 82 % by excluding K (which had weak loadings) and Ca (which mirrored the loadings of Zn) from the PCA (Fig. 2). The first component (PC1) explained 48.6 % of the variation in chemistry among samples and had high loadings of Cu and Se, while the second component (PC2) explained 33.3 % of the variation and had strong negative loadings of As and Pb and positive loadings of Zn. The average PC1 and PC2 scores for islands with colonies were −0.41±1.6 SD and 0.3±1.4 SD, respectively, which differed significantly from scores for no colony islands (PC1, 1.0±0.6 SD, n=12, t test t=4.1, p<0.001; PC2 −0.7±0.7 SD; t=3.0, p<0.005).

4 Discussion

The focusing of nutrients and contaminants by colonial seabirds at the breeding sites can have significant effects on local habitats, including alterations to productivity, alterations to species richness, habitat destruction, and enhancement of contamination (e.g., Ellis 2005; Wait et al. 2005; Ellis et al. 2006; Brimble et al. 2009; Choy et al. 2010). In terms of contamination, marine birds tend to accumulate high concentrations of many essential and nonessential trace elements from their diets, as bioaccumulation and biomagnification of these elements can be high in marine food webs (e.g., Rainbow and White 1989; Savinov et al. 2003; Campbell et al. 2005). The degree to which this process redistributes these elements at terrestrial sites varies by bird species (e.g., Michelutti et al. 2010), but the process occurs from pole to pole (Blais et al. 2007; Mulder et al. 2011).

Our study found that in islands along eastern Nova Scotia, Canada, colonial marine birds have elevated the concentrations of certain essential and nonessential trace elements in soils at their breeding colonies through the process of biotransport (Blais et al. 2007). Certain

Table 1 Statistical summary of XRF soil sample analysis, with mean (SE), median, range, and statistical comparison between soils from islands with (n=30) and without (n=12) bird colonies. All concentrations are in parts per million (ppm)

Element	Island soil without bird colonies (n=12)				Island soil with bird colonies (n=30)				Mann–Whitney test	
	Mean (SE)	CV	Median	Range	Mean (SE)	CV	Median	Range	*U*	*p*
As	23.5 (3.6)	52.3	25.7	2.3–43.3	28.0 (3.3)	64.4	28.3	5.0–82.7	155.5	0.5
Cu	2.2 (0.4)	69.4	1.5	1.0–5.7	13.8 (2.3)	89.9	11.0	1.5–60.7	34	<0.001
Pb	30.8 (3.5)	38.6	27.4	13.7–55.7	27.8 (3.1)	61.8	26.0	5.0–79.3	152.0	0.4
Se	1.8 (0.5)	78.7	1.0	0.5–5.7	8.8 (0.9)	55.3	8.5	0.5–20.0	26.5	<0.001
Zn	71.4 (13.4)	62.5	60.8	21.7–191.7	237.1 (44.0)	101.6	153.0	41.0–1,112.0	69.5	0.002
Ca	6,087 (1,767)	100.5	4,892	897–23,967	34,998 (10,393)	162.6	15,979	3,009–229,308	56.0	<0.001
K	703 (78)	38.2	722	275–1,158	2,606 (506)	106.4	1,643	459–11,423	58.0	<0.001

essential elements, K and Ca, are generally considered nutrients and were higher on islands with bird colonies, consistent with findings elsewhere (e.g., Mulder et al. 2011). Other trace elements (Cu, Se, and Zn) were also relatively elevated on bird colony islands, to the point where they may be affecting the suitability of soils for the protection of environmental health (Table 2). Increased concentrations of Cu, Se, and Zn are consistent with the presence of eider colonies on these islands, as eiders may acquire elevated levels of these trace elements through their diet of benthic marine organisms (e.g., Wang and Fisher 1996; Mallory et al. 2004, 2014). The surficial geology of this region tends to be naturally high in As (31.7 ppm in quartzite tills; Stea and Fowler 1979), and thus, high levels in soils likely do not reflect much influence of colonial birds. However, soils of islands with bird colonies also exhibited a higher proportion of samples which exceeded Canadian guidelines for soil quality for Se and Zn (both elements that may bioaccumulate in biota), and high levels of these elements in soils may be associated with toxicological risk to soil biota (CCME 2007; Beyer and Meador 2011).

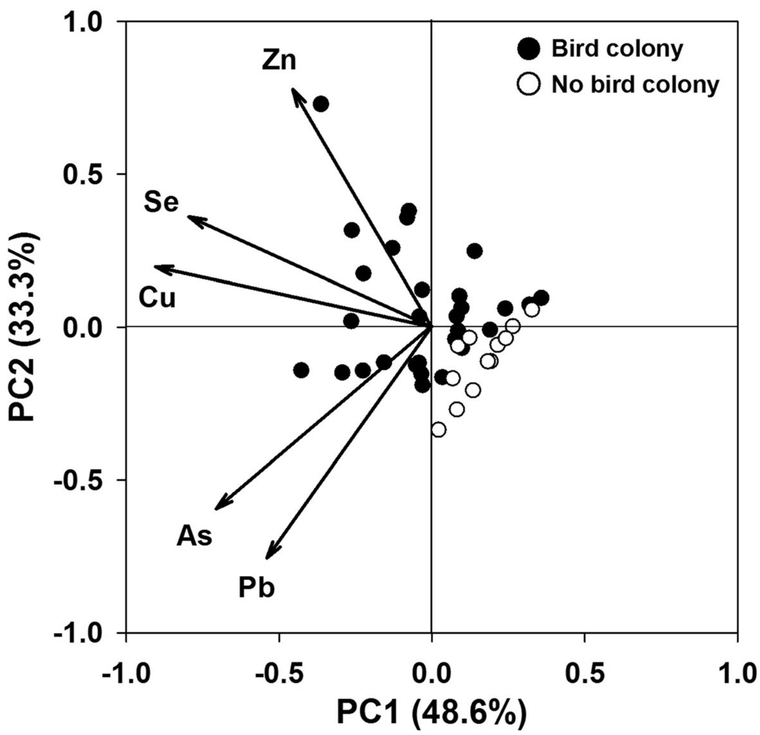

Fig. 2 Principal components biplot of the main patterns of variation between the five trace elements (*arrows*) and 42 soil sample sites from islands in the Eastern Shore Islands Wildlife Management Area, Nova Scotia. *Filled circles* represent soil samples from islands with colonial bird colonies, while *white circles* represent soil samples from islands lacking bird colonies

Table 2 Proportions of soil samples from islands in the Eastern Shore Islands Wildlife Management Area that exceeded Canadian Soil Quality Guidelines for the Protection of Environmental Health (CCME 2007)

Trace element	Soil quality guideline (ppm)	Percentage of soil samples exceeding guideline (%)	
		Islands without birds (n=33)	Islands with birds (n=47)
As	12	58	74
Cd	10	3	3
Cu	63	0	6
Pb	140	0	0
Se[a]	1	42	81
Zn[a]	200	6	32

[a]Islands with birds had a significantly higher proportion of soil samples that exceeded guidelines than islands without birds (Fisher's exact tests, $p \leq 0.006$)

One unexpected result was that Pb in soil did not differ in concentrations between islands with and without bird colonies. Lead in eiders accumulates principally from the consumption of lead shot or from shot birds that survive, as eiders are a harvested game bird in eastern Canada (Krohn et al. 1992; Hicklin and Barrow 2004). Even though Canada banned lead shot in 1999 because of its effects on a variety of birds (e.g., Clark and Scheuhammer 2003), eiders in Nova Scotia contain embedded lead shot (Hicklin and Barrow 2004) from harvest elsewhere in their range and from consumption of residual shot left on the seafloor in areas where hunting has been a common pastime for decades. Consequently, we expected eiders in particular to have mobilized Pb through digestion and excretion and in some cases through mortality of adults and thus contributed to soils on islands with bird colonies. It may be that background Pb levels in local soils (98.7 ppm) are sufficiently high to not show much effect of subsidies from birds (Stea and Fowler 1979) or that sufficiently few birds carry Pb that their contributions are insignificant in local soils.

Similar to recent studies on contaminants in lake sediments (e.g., Franz et al. 2006; Liu et al. 2013), our research demonstrated that XRF analysis is effective for rapid, inexpensive, and precise multi-parameter analysis of soils, depending on the trace element in question. We found a higher occurrence of key trace elements above detection limits and higher levels of essential and nonessential trace elements at sites affected by colonial birds, and this worked at reduced analytical costs (effectively, the cost of purchasing the machine, compared to ~\$100/sample for inductively coupled plasma mass spectrometry [ICP-MS] analyses). Certain trace elements appear to occur at concentrations below the detection limits of this methodology (e.g., Hg, Cd). Hg in particular, due to the variety of species it can occur in, cannot be measured reliably using this technology and thus it may be impractical for some elements. Nonetheless, XRF analyses suggest that some sites have trace element levels above recommended guidelines for environmental protection in Canada (Table 2).

Aside from seabird input, organic soils in temperate regions are prone to accumulating metals from atmospheric deposition, as found by Steinnes and Friedland (2006). Their review of soil metal contamination literature indicates that Pb, Zn, As, Se, and Cd all undergo significant long-range transport via aerosol particles, as classified by their "enrichment factor" in aerosols when compared to composition in crustal material (Steinnes and Friedland 2006). These metals bind strongly to humic material in soil, a process which would have greater effect in control island soils of the ESIWMA, which have thick coniferous forest and more humic substance in top soil layers. However, biotransport by seabirds has been found to be a more efficient process than atmospheric deposition (Blais et al. 2005; Evenset et al. 2007), and that appears consistent with results for this study in the ESIWMA.

Our study was consistent with findings in many other locations around the world that through the process of biotransport (Blais et al. 2007), colonial birds elevate nutrients and nonessential trace elements in soils near their nesting colonies. In eastern Nova Scotia, certain levels are above Canadian guidelines for environmental health (CCME 2007). Given that certain trace elements that may bioaccumulate in birds are naturally high in soils in this region, we suspect that a similar study on persistent organic pollutants (POPs) would find more dramatic differences, as there are few natural sources of POPs.

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