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Multi-Elements in Waters and Sediments of Shallow Lakes: Relationships with Water, Sediment, and Watershed Characteristics

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Abstract

We measured concentrations of multiple elements, including rare earth elements, in waters and sediments of 38 shallow lakes of varying turbidity and macrophyte cover in the Prairie Parkland (PP) and Laurentian Mixed Forest (LMF) provinces of Minnesota. PP shallow lakes had higher element concentrations in waters and sediments compared to LMF sites. Redundancy analysis indicated that a combination of site- and watershed-scale features explained a large proportion of among-lake variability in element concentrations in lake water and sediments. Percent woodland cover in watersheds, turbidity, open water area, and macrophyte cover collectively explained 65.2 % of variation in element concentrations in lake waters. Sediment fraction smaller than 63 μm, percent woodland in watersheds, open water area, and sediment organic matter collectively explained 64.2 % of variation in element concentrations in lake sediments. In contrast to earlier work on shallow lakes, our results showed the extent to which multiple elements in shallow lake waters and sediments were influenced by a combination of variables including sediment

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characteristics, lake morphology, and percent land cover in watersheds. These results are informative because they help illustrate the extent of functional connectivity between shallow lakes and adjacent lands within these lake watersheds.

Keywords

Redundancy analysis; Trace elements; Rare earth elements; Land cover; Shallow lake

Introduction

Local geology, climate, hydrology, and land use within watersheds play key roles in the sediment and water chemistry of surface waters (Moyle 1945; Newton et al. 1987; Nilsson and Håkanson 1992; Fraterrigo and Downing 2008). Several studies have indicated that water quality is related to surrounding land use, macrophyte abundance, and phytoplankton biomass (Crosbie and Chow-Fraser 1999; Lougheed et al. 2001; Akasaka et al. 2010; Sass et al. 2010; Carey and Fulweiler 2013), while few have considered relationships with physical and/or chemical aspects of bottom sediments (Crosbie and Chow-Fraser 1999; Rowan et al. 2012). In shallow lakes, water-sediment interactions are more common and have greater influence on chemistry compared to deeper lakes (Scheffer 2004). In shallow lakes without macrophytes, water-sediment mixing occurs frequently and sediment is more prone to resuspension and subsequent nutrient release (Faafeng and Mjelde 1998; Horppila and Nurminen 2003). When rooted macrophytes are present, in addition to stabilizing the sediments, they provide a crucial link between water and sediments and also play important roles in element cycling in these systems (St. Cyr et al. 1994; Barko and James 1998; Nurminen and Horppila 2009).

Dilute concentrations of alkali and alkaline earth compounds, in particular carbonates, bicarbonates, sulfates, and chlorides make up most of the ionic portion of freshwaters (Wetzel 2001). The concentrations of these compounds are influenced by geology, watershed transport, atmospheric deposition from natural and human activities, and exchanges between water and sediments (Wetzel 2001). Harder water, higher pH, and higher alkalinity are typical of lakes in western and southwestern Minnesota compared to lakes in the central and northern counties, and characteristics of the former reflect surface and underlying geology (Moyle 1945). The biogeochemical cycling of various elements is also influenced by changes in oxidation and reduction reactions, photosynthetic and microbial metabolism (Barnes 1980; Jackson et al. 1993; Wetzel 2001), and the organic matter and mineral content of the sediment (Mackereth 1965).

Macrophyte communities in shallow lakes are influenced by a combination of within-lake and watershed variables (Kissoon et al. 2013). Here, we examined concentrations of multiple elements in waters and sediments of shallow lakes of varying turbidities in the Prairie Parkland and Laurentian Mixed Forest provinces of Minnesota, to determine relationships with various environmental variables. These environmental variables included watershed features (lake watershed area and land cover in watersheds), within-lake aspects (basin area, open water area, macrophyte cover, and emergent vegetation area), water characteristics (pH, turbidity, and chlorophyll-a), and sediment characteristics (organic matter content and particle size). We hypothesized that land use within watersheds, along with water and sediment characteristics, influenced element concentrations in waters and sediments of shallow lakes. Earlier shallow lake studies focused on regime shifts, carbon, phosphorus and nitrogen cycling, phytoplankton biomass, and macrophyte abundance (Scheffer and Jeppesen 1998; Hansel-Welch et al. 2003; Schippers et al. 2006; Bayley et al. 2007, 2013; Zimmer et al. 2009; Brothers et al. 2013; Llames et al. 2013; Zhang et al. 2013; Robin et al. 2014). Most of these earlier works focused on influences of various environmental variables on water quality and chemistry, but few have considered physical or chemical aspects of shallow lake sediments (Barko and James 1998; Sahuquillo et al. 2012; Kissoon et al. 2013; Wu et al. 2014). Our study adds to findings from these earlier reports in several ways. First, we examined the concentrations of multiple elements including the rare earth elements of which little is known (Pais and Jones 1997). Second, we measured element concentrations in both the water and sediments of shallow lakes in contrast to earlier studies that measured element concentrations only in the water column (Hu et al. 2011; Medeiros et al. 2012; Bayley et al. 2013), while few measured elements in the sediment (Sahuquillo et al. 2012; Wu et al. 2014). Also we considered how sediment organic matter content and particle size might relate to element concentrations in lakes because of their role in element mobility (Cataldo and Wildung 1978).

Methods

Description of Study Sites

This study involved 38 shallow lakes in Minnesota sampled during August 9–19, 2010 and August 8–17, 2011. Twenty-six of these lakes were located in the Prairie Parkland province (PP) and 12 occurred in the Laurentian Mixed Forest province (LMF) (Fig. 1). Six of the PP lakes (west-central lakes) and all of the LMF lakes were sampled in 2010, while 20 PP lakes (south-western lakes) were sampled in 2011. The lakes occurred within watersheds ranging from 8–1384 ha, were from 1.8–59 ha in basin area, and averaged 1.4±0.6 m deep (Kissoon et al. 2013). Extensive areas of conifer forests, mixed hardwood, conifer bogs, and swamps exist throughout the LMF province (Minnesota Department of Natural Resources 1999). The LMF lakes occurred in areas dominated by large outwash plains and ground moraines with level to gently rolling topography and soils of various textures including very permeable sandy soils, calcareous loamy soils, and poorly drained organic soils overlying calcareous loamy glacial deposits. In contrast, the PP province has undergone extensive anthropogenic modification with areas that were once dominated by tallgrass and wet prairie now dominated by agricultural land (>79 % cover) (Minnesota Geospatial Information Office Staff 1999). The PP lakes were located in areas characterized mostly by loamy ground moraine with level to steeply rolling and hilly topography, well drained and poorly drained soils that formed in calcareous glacial or loamy till (Soil Survey Staff 2012).

Water Collection and Analysis

Water samples were collected at 10 locations within the perimeter of each lake, approximately equidistant from each other and at least 4 m from shore (Kissoon et al. 2013).Water samples were collected directly above vegetation, approximately 25 cm below the water's surface. A portion of each water sample was used on the same day as collection to measure turbidity using a HACH® portable turbidimeter (Model 2100P) and pH using a VWR Symphony SP90M5 Handheld Multi-meter. The remaining portion (approximately 50 ml) was filtered (0.45-μm pressure filter, Pall Corporation Supor® -450) and acidified with concentrated nitric acid (pH<2.0). Water samples were refrigerated at 4 °C for approximately 30 days and later analyzed for 32 elements with a Spectro Genesis Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). Recovery rates were calculated using the expected and measured values of a certified reference water standard (EnviroMAT Ground Water, High, ES-H-2). Elements that were at least one order of magnitude greater than the detection limit and had recovery rates within 10 % of expected values were used in the analysis (method detection limits listed in Table S.1). In 2010, 5–10 water samples from each lake were used for element analysis, while in 2011, 10 water samples from each lake were used for element analysis. Chlorophyll-a (Chl-a) and total phosphorus concentrations (TP) for each shallow lake were determined using methods described by Zimmer et al. (2009). Chl-a was determined using fluorometry following acetone extraction and TP was determined using methods of the American Public Health Association (1994).

Sediment Collection and Analysis

Sediment samples were collected with a sediment corer from the top 1.5 m of the sediment bed at approximately the same 10 locations where macrophytes were surveyed and water samples were collected (Fig. 2, Kissoon et al. 2013). Samples were transported at 0–4 °C to the laboratory, placed in paper bags, oven-dried until constant weight at 60 °C, crushed with mortar and pestle, and homogenized. These dried samples were reserved for organic matter content (OM) by loss-on-ignition, particle size, and multi-element analysis. OM of sediment samples was determined by again drying the samples at 105 °C for two hours, weighing, and then ashing in a furnace at 360 °C for two hours. After ashing, the remaining sample material was cooled, weighed, and then passed through a 63-μm sieve under running water to estimate particle size. The sample that passed through the sieve was dried, weighed, and considered the fraction of sediment smaller than 63 μm (f<63), that is the proportion of clays and silts.

Another portion of the dried sediment samples was analyzed for 61 elements via Inductively Coupled Plasma Mass Spectrometry (ICP-MS) following Aqua Regia Digestion by a commercial laboratory (Activation Laboratories, Ltd, Accredited Laboratory, ISO/IEC 17025:2005). Method detection limits for these elements are listed in Table S.1. Recovery rates were calculated using the expected and measured values of a certified reference soil standard approved by the China National Analysis Center for Iron and Steel (NCS DC-73384). In 2010 and 2011, 5–10 sediment samples from each lake were used for element analysis.

Within Lake and Watershed Variables

We estimated total percent macrophyte cover using a transparent acrylic-bottomed cylinder at approximately the same locations where we collected water and sediment samples (Kissoon et al. 2013). Total percent macrophyte cover included *Bidens beckii, Brasenia* *schreberi, Ceratophyllum demersum, Elodea canadensis, Heteranthera dubia, Lemna minor, Lemna trisulca, Myriophyllum sibericum, Najas flexilis, Nitella* spp., *Nuphar* spp., *Nymphaea* spp., *Potamogeton amplifolious, Potamogeton gramineus, Potamogeton natans, Potamogeton praelongis, Potamogeton pusillus, Potamogeton richardsonii, Potamogeton zosterformis, Ruppia occidentalis, Sagittaria cristata, Sparganium americanum, Stuckenia pectinata*, and *Utricularia vulgaris,* as well as *Drepanocladus* spp., *Chara* spp., and filamentous algae. Lake watershed area (LWA), basin area (BSN), emergent vegetation area (EVA), open water area (OWT), and land cover proportions (woodland, grassland, shrubland, corn and soybeans, hay and grains, total agriculture) for the watershed of each lake were derived from digitized features determined using aerial photographs and GIS software (methods summarized by Hanson et al. 2012). Lake watershed area included the entire land area draining to the outlet of the study lake, and basin area included open water and emergent vegetation areas. Shrubland referred to the proportion of adjacent land with mixed grasses, shrubs, and trees and woodland referred to the proportion of adjacent land with >75 % mature trees. Total agriculture was the sum of the percent cover of adjacent land attributed to corn and soybeans, hayed areas, and small grain fields.

Statistical Analysis

Environmental variables and element concentrations were log or arcsine transformed as appropriate prior to statistical analysis to increase homogeneity of variance (McCune and Grace 2002). Environmental variables included water characteristics (pH, turbidity and Chl-a), sediment characteristics (OM and f <63), lake characteristics (open water area, submerged macrophyte cover, and emergent vegetation area), and watershed variables (the ratio lake watershed: basin area,% grassland,% shrubland, % woodland, % corn and soybeans, % hay and grains, % total agriculture). A General Linear Model with a nested design was used to assess differences between provinces and among lakes between provinces (p<0.01) using Minitab® statistical software (Minitab® 15 ©2006 Minitab Inc.). To test for relationships between element concentrations in water or sediment, Pearson correlations and their associated p-values were calculated in Minitab. Here we reported only correlations that explained 25 % or more of the variation ($r \geq 0.50$, p<0.01) (McClave and Sincich 2006).

We used direct gradient analysis to relate water and sediment element concentrations to environmental features of lakes and watersheds. Preliminary Detrended Correspondence Analysis (DCA) indicated that linear gradient analysis (RDA) was appropriate for analysis of the water and sediment data since the gradient lengths were <4.0 standard deviations (ter Braak and Šmilauer 2002). Prior to RDA we removed elements within an order of magnitude of the detection limits (including Ag, Al, As, B, Ba, Be, Cd, Ce, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, P, Pb, Sb, Se, Sn, Ti, Tl, V, and Zn in water and Ag, Au, Be, Bi, Er, Eu, Ge, Hf, Ho, In, Lu, Nb, Re, Sb, Se, Sn, Ta, Tb, Te, Ti, Tl, Tm, W, and Yb in sediment). Relationships between environmental variables (land cover proportions, lake watershed area: basin area ratio, open water area, turbidity, chlorophyll-*a*, LOI, f<63) and element concentrations of water and sediment were assessed using RDA in CANOCO (©2005 CANOCO Version 4.5). Forward selection procedures with Monte Carlo permutation tests (999 permutations) were used to determine the significant environmental variables to be included in final models ($p<0.05$). Further analysis was carried out to partition sources of variation attributed to spatial (Province) and environmental components independent of each other using partial redundancy analysis (pRDA) according to methods by Borcard et al. (1992). All environmental variables had low variance inflation factors (<20), which indicated that they did not correlate with each other, and therefore contributed uniquely to the analysis (ter Braak and Šmilauer 2002). An exception was Chl-a, which was removed from the analysis because it was highly correlated with turbidity ($r=0.889$). Because the rare earth elements (Ce, Dy, Gd, La, Nd, Pr, Sm) showed very similar chemical behavior and were highly correlated, Ce, which had the highest concentration, was chosen to represent these elements in the analysis.

Results

Differences Between Provinces and Among Lakes

Results of a nested ANOVA showed that total macrophyte cover, and sediment OM and $f<63$ varied significantly between provinces and among lakes within provinces, while turbidity, pH, Chl-a, and TP varied between provinces only (Table 1, $p<0.01$). Results of nested ANOVAs also showed that several elements varied significantly in waters and sediments between provinces and among lakes within provinces. PP lakes had significantly higher concentrations of elements in water and over 90 % of elements in sediment compared with LMF lakes. Ca, K, Mg, Na, S, Si, and Sr in water varied between provinces and also among lakes within provinces (Table 2). Concentrations of Al, As, B, Ba, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Fe, Ga, Gd, K, La, Li, Mg, Mn, Na, Nd, Ni, P, Pb, Pr, Rb, S, Sc, Sm, Sr, Th, U, V, Y, Zn, and Zr in sediment varied significantly between provinces and among lakes within provinces (Table 3). Mo varied among lakes within provinces only. Concentrations of Al, As, B, Cd, Ce, Co, Cr, Cs, Cu, Dy, Fe, Ga, Gd, K, La, Li, Mg, Mn, Na, Nd, Ni, P, Pb, Pr, Rb, S, Sc, Sm, Sr, Th, U, V, Y, Zn, and Zr were significantly greater in PP lake sediments while Ba and Ca were significantly greater in LMF lake sediments.

Relationships Between Water Chemistry and Environmental Variables

We used a global RDA to identify environmental variables associated with element concentrations in lake waters. RDA showed that percent woodland cover in lake watersheds, turbidity, open water area, and macrophyte cover were significant sources of variance and together explained 65.2 % of the variation in element concentrations in water (Table 4, Fig. 3). Lakes with higher turbidity were associated with high concentrations of TP and Si, and such lakes usually occurred in the PP province. Lakes with greater open water area also occurred in the PP province and tended to have higher concentrations of Ca, Sr, Mg, Na, S, and K in the water. In contrast, lakes in the LMF province had lower concentrations of elements in water, greater macrophyte cover, and greater woodland cover in adjacent lands. We also used pRDA to estimate variation in element concentrations in water attributable to environmental variables after controlling for influence of province as a covariable. Results of the pRDA indicated that percent woodland, turbidity, and open water area explained 10.5 % of the variation in water element concentrations (Table 4). Province as a covariable accounted for 2.1 % and covariance (shared variance) accounted for 54.8 % of the variance, while the remaining 32.6 % of the variance was unexplained. Adding province as a spatial covariate to the model resulted in a decrease in the percent variance explained by percent woodland and a slight increase in the percent variance explained by turbidity, open water area, and macrophyte cover.

Pearson correlations supported results of RDA by indicating that various elements in the water were correlated to specific environmental variables. Turbidity correlated positively with Chl-a, TP, Si, and Sr, and negatively with sediment OM (Table 5). Water pH correlated positively with water TP, and Mg and negatively with sediment OM. Sediment OM correlated negatively with Chl-a, TP, Mg, S, and Sr in water, while sediment *f*<63 correlated positively with water Mg and Si. Chl-a correlated positively with TP, Mg, S, Si, and Sr in water, while TP correlated positively with K, Mg, S, and Sr in water.

Relationships Between Sediment Chemistry and Environmental Variables

We also used a global RDA to identify environmental variables associated with element concentrations in sediment. Results indicated that *f*<63, percent woodland in lake watersheds, open water area, and organic matter were significant sources of variance which collectively explained 64.2%of the variation in element concentrations in sediments (Fig. 4, Table 4). Ba concentrations were higher in lakes with high organic matter and high percent woodland in adjacent lands, and these lakes usually occurred in the LMF province. Open water area was positively associated with *f*<63 and both variables demonstrated positive relationships with several elements including Al, As, B, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, K, Li, Mg, Mn, Na, Ni, P, Pb, Rb, S, Sc, Sr, Th, U, V, Y, Zn, and Zr and rare earth elements (Ce, Dy, Gd, La, Nd, Pr, Sm). Lakes with higher element concentrations in sediment, greater open water area, and higher *f*<63 occurred in the PP province. Again, we also conducted a pRDA to estimate the variation in element concentrations in sediment attributable to environmental variables while controlling for province. Results of the pRDA indicated that *f*<63, percent woodland, open water area, and organic matter accounted for 31.1%of variation in element concentrations in the sediment. Province as a covariable accounted for 1.3 % and covariance (shared variance) accounted for 33.1 % of the variance, while the remaining 34.5 % of the variance was unexplained. When province was included as a covariable, the variance explained by *f*<63 and percent woodland decreased while influence of open water area and organic matter increased. Overall, the *f*<63 remained the most influential environmental variable explaining 26.1 % of the variation in sediment element concentrations.

Relationships Between Elements, Water and Sediment Characteristics

Results of Pearson correlations supported results of the RDA showing that various elements in sediment correlated with elements in water and with specific environmental variables. Chl-a, turbidity, pH, and *f*<63 showed positive correlations and OM showed negative correlations with several elements in sediment (Table 6). Total phosphorus, Ca, K, Mg, Na, S, Si, and Sr in water also correlated positively with several elements in sediment.

Discussion

Our study showed that concentrations of multiple elements in waters and sediments of shallow lakes were related to a combination of site- and watershed-scale variables including lake morphology, water and sediment physiochemical characteristics, and land use in adjacent lands. Overall, we observed a regional pattern of lower concentrations of elements in both water and sediment in LMF lakes than in PP lakes. Most earlier studies focused on the cycling of nutrients such as phosphorus, nitrogen, and dissolved organic carbon in lakes (Barko and Smart 1980; Downing and McCauley 1992; Medeiros et al. 2012; Wu et al. 2014), but a few have included other elements such as Cd, Cr, Cu, Fe, Mn, Ni, Pb, Si, and Zn (St. Cyr et al. 1994; Thorbergsdottir and Gislason 2004; Mi et al. 2008). Some research has explored how nutrients in lakes relate to nearby land use (Fraterrigo and Downing 2008; Wezel et al. 2013) and phytoplankton biomass (Grace et al. 2010; Borics et al. 2013). Related studies of shallow lakes have focused on identifying factors responsible for water-clarity regime shifts, variations in phytoplankton biomass, and macrophyte abundance (Schippers et al. 2006; Zimmer et al. 2009; Bayley et al. 2013; Brothers et al. 2013; Llames et al. 2013; Zhang et al. 2013; Robin et al. 2014). As mentioned previously, our study adds to these earlier works by examining concentrations of multiple elements, including the rare earth elements in the waters and sediments of shallow lakes. Also, we considered the role of sediment organic matter and particle size in the distribution of elements in shallow lakes waters and sediments. Finally, our work emphasized relationships between sediment element concentrations and features of adjacent watersheds, and related research indicates that these linkages have important implications for shallow lake ecology and management (Hobbs et al. 2012).

Elements in Water

We detected only Ca, K, Mg, Na, S, Si, and Sr in filtered water samples. Concentrations of most elements measured in the water were below our method detection limits probably because they were sequestered by macrophytes and plankton (Guilizzoni 1991; Horppila and Nurminen 2003; Mi et al. 2008) or bound to organic matter and suspended particles (Golterman 1969; APHA 1994). Physical and chemical characteristics of the sediments in our lakes may also have influenced the diffusion of elements from the sediment to water column and vice versa (Jaynes and Carpenter 1986). Macrophytes can also contribute to increasing element concentrations in the water by releasing elements upon senescence and decay (Landers 1979; Barko and Smart 1980, 1981) and, given the high prevalence of macrophytes in shallow lakes, this may have influenced element concentrations in our sites.

Concentrations of the dominant cations Ca, Mg, Na, and K play a role in salinity and are primarily influenced by weathering of soil and rock, precipitation, and climate (Wetzel 2001). The high concentrations of these elements are characteristic of hard waters and were probably derived from the weathering of calcareous deposits in the PP province. Sr is similar geochemically to Ca and Mg (Pais and Jones 1997) and its cycling in aquatic systems closely follows Ca (Wetzel 2001). Si is also associated with alkaline conditions (Pais and Jones 1997; Heegaard et al. 2001), is derived from the weathering of rocks (Håkanson and Jansson 1983; Mackie 2004), and is a major limiting nutrient for diatom growth (Martin-

Jezequel et al. 2000). Higher concentrations of these elements in the PP lakes might be due to the alkaline and hard water conditions typical of lakes in the PP province (Moyle 1945; Kissoon et al. 2013).

Water Element Relationships with Turbidity and Open Water—Clay, silt, plankton, microscopic organisms, soluble organic compounds, finely divided organic and inorganic matter, and suspended precipitates are all potential sources of turbidity in shallow lakes (Swenson and Baldwin 1965; Hanson and Butler 1990). Turbidity was greater in PP lakes, and values were positively correlated with Chl-a, TP, Si, and Sr in water and negatively correlated with sediment OM. Bayley et al. (2007) found similar relationships between turbidity and elements in water and reported that turbid shallow lakes had higher concentrations of P and Si compared to clear sites. Si uptake is dominated by diatoms, sponges, and blue-green algae (Fraústo da Silva and Williams 2001; Quiroz-Vazquez et al. 2008) and its concentrations in water are primarily controlled by benthic macro-algae (Sigmon and Cahoon 1997). Si might be released or excreted from diatom grazers and decomposing diatom frustules which might explain increased Si concentrations in PP lakes (Parker et al. 1977; Ferrante and Parker 1978; Korstad 1983). Ahlgren (1970) and Egge and Aksnes (1992) reported that increases in diatom biomass were associated with increases in Si concentrations in water. Hobbs et al. (2012) showed that diatom assemblages in turbid-regime periods at Lake Christina, a shallow Minnesota lake, were dominated by colonial, planktonic taxa, while epiphytic species were predominant during historic clear-water periods. Like prevalence of planktonic diatoms, we suspect that high water-column Si levels may reflect turbid-water regime characteristics in shallow lakes.

Lakes in various landscapes can be connected to and are important parts of groundwater flow systems (Winter 1999; Ferone and Devito 2004; Smerdon et al. 2005). Lakes with larger open water areas occurred in the PP province, have lower relative elevation in the landscape than LMF lakes (Bischof 2013), and so may receive more discharge from regional and intermediate groundwater flow systems which may be a source of the higher element concentrations in the water column (Winter and Carr 1980). In our study, lakes with larger open water areas had higher element concentrations and possibly more groundwater discharge which could be a potential source of elements entering the water column (Kidmose et al. 2013). Shallow lakes with larger open water area have greater surface area that is open to sunlight and wind action which may contribute to greater sediment resuspension rates and subsequently higher internal nutrient loading and higher rates of primary productivity (Wetzel 2001). Lakes with larger open water areas also had larger watersheds which may magnify the effects of the dominant land cover (Carey and Fulweiler 2012, 2013). Fraterrigo and Downing (2008) indicated that the influence of land use on nutrient loading is dependent on the lake watershed size and capacity to transport nutrients.

Water Element Relationships with Land Cover—Our study found that element concentrations in waters of shallow lakes were related to land cover patterns in lake watersheds. Earlier studies also reported relationships between lake water chemistry and land cover in watersheds (Stewart and Kantrud 1972; Nilsson and Håkanson 1992; Lougheed et al. 2001; Whigham and Jordan 2003; Fraterrigo and Downing 2008; Del Pozo et al. 2011), but other reports did not identify such patterns (Bayley et al. 2013; Gorman et al. 2014). We observed a negative relationship between Si concentrations and percent woodland cover as did Carey and Fulweiler (2012) who attributed this to the uptake of Si by plants in adjacent lands, alterations in watershed hydrology due to changes in land cover, and the potential for urban areas to contribute Si to adjacent waters via runoff. Carey and Fulweiler (2012) also reported that variation in land cover and bedrock geology accounted for the variation in Si, but these authors did not consider possible influences of diatom prevalence during turbid conditions.

Woodland cover was the predominant cover type in watersheds within our LMF lakes and was negatively associated with turbidity in our models. Woodland cover in surrounding lands may decrease input of sediments and nutrients via runoff into surface waters due to the presence of constant vegetation cover (Lougheed et al. 2001). Woodland cover was also negatively associated with other elements including Ca, K, Mg, Na, S, Sr, and TP, and was the dominant land cover in surrounding lands of the LMF lakes. These relationships may be due to the soft water conditions characteristic of our LMF lakes (Moyle 1945; Wetzel 2001) and the low nutrient conditions and decreased runoff associated with woodland-dominated lands. Lands adjacent to the LMF lakes contain Northern Udalf soils which are less productive than their southern counterpart, support hardwood forests, and are somewhat acidic (Anderson et al. 2013). Additionally, tree roots of forested lands stabilize soils, reduce erosion and runoff, and decrease nutrient inputs into streams and lakes (Wood et al. 1984; Qualls et al. 1991; Lombi et al. 2001).

Overall, we observed elevated element concentrations in the PP lakes where well drained soils and vegetation patterns in adjacent lands probably facilitated transport of nutrients to our sites. Fraterrigo and Downing (2008) indicated that the influences of land use on lake water quality depend on watershed size and the potential for the transport of elements within the watershed. Our PP lakes, which were probably impacted by agricultural activities or runoff from nutrient-rich surrounding lands within the watershed, were nutrient-rich compared to the low nutrient LMF lakes in the northern portion of our study. Similarly,Atkinson et al. (2011) found the water chemistry of wetlands impacted by agriculture were very different from sites without agriculture; they reported that levels of suspended solids, pH, alkalinity, and soluble reactive phosphorus were significantly higher in waters adjacent to agriculture compared to non-agricultural wetlands. Wetlands within forested watersheds were found to have significantly different water and sediment chemistry as well as different macrophyte community composition compared to wetlands within agricultural watersheds (Lougheed et al. 2001). Nilsson and Håkanson (1992) reported relationships between agricultural land cover and water chemistry which may have been due to the soil characteristics (surrounding lands dominated by clayrich soils) and agricultural activities involving plowing and tillage practices leading to exposure, erosion, and runoff, along with addition of fertilizer, all of which contributes to nutrient loading (Ginting et al. 1998).

Elements in Sediments

Similar to element concentrations in water, sediment element concentrations were also higher in our PP lakes indicating that these lakes were generally more nutrient enriched than were our LMF lakes. Elements and nutrients can be exchanged or transported across the sediment-water interface (De Laune et al. 1981; Jaynes and Carpenter 1986; Weis and Weis 2004; Nurminen and Horppila 2009) and thus elements in water and sediments may be correlated with each other. In our study, Ca, Mg, Na, K, and Sr in water correlated with their concentrations in sediment and we suspect this reflects extent of element cycling and wind-related mixing in our shallow lakes. Rooted submerged macrophytes also transport elements between sediment and water column, thus plants play major roles in nutrient cycling (Carignan and Kalff 1980; Carpenter and Lodge 1986; Barko and James 1998; Fritioff and Greger 2006). Macrophytes also minimizes sediment suspension which subsequently decreases the exchange of nutrients between the sediments and overlying water and contributes to decreased water turbidity and internal loading of nutrients (Horppila and Nurminen 2003; Nurminen and Horppila 2009).

Our results support the concept that chemistry of lake sediments influence composition, chemistry, and quality of overlying water (Håkanson and Jansson 1983). Our study also identified several relationships indicating that sediment chemistry is influenced by local geology and land use within lake watersheds (Moyle 1945; Newton et al. 1987; Nilsson and Håkanson 1992; Fraterrigo and Downing 2008). Like elements in water, elements in the sediments may be related to alkalinity, pH, and water hardness. For example, Ba concentrations increase with decreasing pH, and availability decreases with increasing concentrations of Ca, Mg, and S (Pais and Jones 1997). Higher Ba concentrations were associated with the LMF lakes which had lower pH, alkalinity, and concentrations of Ca, Mg, and S than the PP lakes. Element concentrations in sediment are also influenced by redox reactions, organic matter content, particle size, clay mineral content, and the presence of sulfides and hydroxides (Lee 1975; Reimers et al. 1975; Jackson et al. 1993; Pais and Jones 1997; Fraústo da Silva and Williams 2001; Kabata-Pendias and Pendias 2001). Concentrations of rare earth elements in sediment are influenced by the geological origins and mineral composition of the sediments and these elements are reportedly more concentrated in alkaline compared to acidic environments which may explain their higher concentrations in the alkaline PP lakes (Kabata-Pendias and Pendias 2001).

Sediment Element Relationships with Open Water and Land Cover—Similar to elements in water, variation in sediment element concentrations was related to percent woodland cover in lake watersheds and extent of open water of our study lakes. Several factors may be responsible for these relationships including agriculture-dominated surrounding lands serving as a source of nutrients, with groundwater adding or diluting nutrients (Bischof 2013), and variable nutrient transport among watersheds (Fraterrigo and Downing 2008; Floyd et al. 2009; Evans et al. 2014). As mentioned previously, lakes with larger open water areas also had larger watersheds, which probably magnified the effects of the surrounding land cover and contributed to increased element inputs (Fraterrigo and Downing 2008). Runoff from surrounding land and groundwater inputs may be the source of the higher element concentrations in sediments (Winter and Carr 1980; Carey and Fulweiler

2012, 2013). Forested lands are less prone to sedimentation whereas lands with anthropogenic development are generally more prone to surface runoff and sedimentation (Lougheed et al. 2001). Forest cover types stabilize soils, reduce erosion, and decrease nutrient inputs into streams and lakes (Wood et al. 1984; Qualls et al. 1991; Lombi et al. 2001), which may help explain why shallow lakes in the LMF province have clearer lakes and lower element concentrations in their waters and sediments. Higher concentrations of some elements in PP lakes may reflect runoff from nutrient rich or fertilized adjacent lands (As, B, Cd, Cu, Cr, Fe, Mn, Mo, Ni, P, Pb, Zn, Zr) or deposition from air pollution (As, V) (Pais and Jones 1997; Gallego et al. 2013).

Sediment Element Relationships with Organic Matter and f<63—Sediment OM also plays a key role in the mobility and availability of elements in soils and sediments (Kirk 2004). Negative correlations were observed between sediment OM and elements in water and sediment, which may indicate that these elements are associated with the organic matter fraction of the sediment (Davies 1994; Jackson 1998) and hence are less mobile in the water and sediment of high OM lakes. The negative relationship between sediment OM and elements may also indicate that these elements are bound to the inorganic fraction or depleted or leached from the upper sediments due to low pH of the high OM lakes (Steinmann and Shotyk 1997; Yanes et al. 2006; Syrovetnik et al. 2007; Das et al. 2008). High OM associated with LMF lakes may reflect large inputs of organic material from surrounding woodland-dominated lands, high lake productivity, and redox conditions preventing decomposition (Mackereth 1965; Håkanson and Jansson 1983; Wetzel 2001). Runoff from agricultural land contributes to small or fine grained particles in lakes and thus agriculture-impacted wetlands tend to be dominated by finer grain particles such as silts and clays, which are more prone to disturbance and resuspension, and contribute to increased turbidity, and limited macrophyte growth (Hamilton and Mitchell 1997). On the other hand, lakes in woodland-dominated watersheds had larger particle size and higher organic matter content compared to lakes in sediments of agricultural watersheds (Lougheed et al. 2001). Particle size has also been shown to influence element mobility and availability in soils (Cataldo and Wildung 1978). Positive correlations were observed between f<63 and elements in water and sediment, which may indicate that this fraction of small particles are a source of most elements. Smaller particles (clays and silts) tend to bind elements since the active binding area of particles increases with decreased particle size (Håkanson and Jansson 1983). In contrast, sandy sediments have a low potential for the attenuation of elements due to the large pore spaces (Håkanson and Jansson 1983) and hence tend to have low nutrient availability (Barko and Smart 1986).

Our findings are consistent with the hypothesis that lake and watershed characteristics influenced element concentrations in water and sediments of shallow lakes in prairie and forested areas. Kissoon et al. (2013) also reported that lake and watershed characteristics were linked to macrophyte abundance and community composition in shallow Minnesota lakes. This research showed land cover in watersheds, open water area, turbidity, f<63, organic matter, emergent vegetation area were related to macrophyte abundance while turbidity, alkalinity, open water area, and land cover were related to macrophyte community composition. In the current study, relationships between element concentrations and sediment characteristics such as OM and *f*<63 indicated their key role in element mobility and reflect the soil and vegetation characteristics of surrounding lands, which are probably the main sources of OM and fine grain sediment particles (Mackereth 1965; Hamilton and Mitchell 1997; Wetzel 2001). Relationships between element concentrations in lake waters and sediments, extent of open water, and land cover in watersheds may also indicate influences of the morphology within these lakes and their corresponding watersheds.

Our global and partial RDA models identified a similar combination of environmental variables which explained the variation in water and sediment element concentrations. When province was added as a spatial covariable to these models, the extent of woodland cover in lake watersheds was no longer a significant source of variation, indicating that woodland cover was highly correlated with Province. Similar to Kissoon et al. (2013), lack of a land cover continuum or gradient in our study may have hidden the true contributions of land cover in explaining the variation in water and sediment element concentrations in our shallow lakes. However, extent of open water area, turbidity, sediment particle size and organic matter remained as significant variables in the models explaining the variation in water and/or sediment element concentrations. In addition to these variables, differences in geology and soil characteristics likely influenced element concentrations in the waters and sediments of our shallow lakes (Troelstrup and Perry 1989; Mann 1980; Wetzel 2001).

Conclusions

In contrast to earlier work on shallow lakes, we presented data for multiple elements in the waters as well as the sediments of shallow lakes. Our study adds to earlier shallow lakes work in several ways. First, we showed that trace elements, including rare earth elements are higher in shallow prairie lakes compared to shallow forested lakes. Also, we found that elements in lake waters and sediments related to sediment organic matter and particle size, and thus highlights the role of sediments in element distribution in shallow lakes. Finally, our work emphasized relationships between water and sediment element concentrations and features of adjacent watersheds, and related research indicates that these linkages have important implications for shallow lake ecology and management. Findings of our study indicated that a combination of site- and watershed-scale environmental variables explained the variation in element concentrations in water and sediments in shallow lakes. This indicates that management strategies need to pay attention to both lake and watershed characteristics in the rehabilitation and conservation of these systems. Water chemistry was related to extent of woodland cover in lake watersheds, turbidity, open water area, and macrophyte cover, while sediment chemistry was related to sediment particle size, extent of woodland cover, open water area, and organic matter. Open water area and land cover in watersheds were common variables related to element concentrations in both the waters and sediments of our shallow lakes. In addition to the roles of underlying factors such as geology, hydrology, and the influence of groundwater flow, our findings emphasize the importance of lake morphology and land-use patterns in lake watersheds in element distribution in shallow lakes, in particular the influence of soil and vegetation characteristics of surrounding lands.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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References

Ahlgren G. Limnological studies of Lake Norrviken, a eutrophicated Swedish lake. Swiss J Hydrol. 1970; 32:353–396.

Akasaka M, Takamura N, Mitsuhashi H, Kadono Y. Effects of land use on aquatic macrophyte diversity and water quality of ponds. Freshw Biol. 2010; 55:909–922.

American Public Health Association (APHA). Standards methods for the examination of water and wastewater. Washington D.C.: American Public Health Association; 1994.

Anderson, JL.; Bell, JC.; Cooper, TH.; Grigal, DF. Soils and landscapes of Minnesota. St. Paul, MN: University of Minnesota; 2013. http://www.extension.umn.edu/agriculture/tillage/soils-and-landscapes-ofminnesota/ [Accessed 25 Feb 2014]

Atkinson CL, Golladay SW, First MR. Water quality and planktonic microbial assemblages of isolated wetlands in an agricultural landscape. Wetlands. 2011; 31:885–894.

Barko, JW.; James, WF. Effects of submerged aquatic macrophytes on nutrient dynamics, sedimentation, and resuspension. In: Jeppeson, E.; Sondergaard, M.; Christoffersen, K., editors. The structuring role of submerged macrophytes in lakes. Ecological Studies. Vol. 131. New York: Springer; 1998. p. 197-214.

Barko JW, Smart RM. Mobilization of sediment phosphorus by submersed fresh-water macrophytes. Freshw Biol. 1980; 10:229–238.

Barko JW, Smart RM. Sediment-based nutrition of submersed macrophytes. Aquat Bot. 1981; 10:339–352.

Barko JW, Smart RM. Sediment-related mechanisms of growth limitation in submersed macrophytes. Ecology. 1986; 67:1328–1340.

Barnes, RSK. The unity and diversity of aquatic systems. In: Barnes, RSK.; Mann, KH., editors. Fundamentals of aquatic ecosystems. London: Blackwell Scientific Publications; 1980. p. 5-23.

Bayley SE, Creed IF, Sass GZ, Wong AS. Frequent regime shifts in trophic states in shallow lakes on the Boreal Plain: alternative Bunstable^ states? Limnol Oceanogr. 2007; 52:2002–2012.

Bayley SE, Wong AS, Thompson JE. Effects of agricultural encroachment and drought on wetlands and shallow lakes in the boreal transition zone of Canada. Wetlands. 2013; 33:17–28.

Bischof, SM. Master's Thesis. Bemidji, MN: School of Graduate Studies, Bemidji State University; 2013. Groundwater exchange in shallow lakes of Itasca State Park and West-Central Minnesota.

Borcard D, Legendre P, Drapeau P. Partialling out the spatial component of ecological variation. Ecology. 1992; 73:1045–1055.

Borics G, Nagy L, Miron S, Grigorszky I, Laszlo-Nagy Z, Lukacs B, G-Toth L, Varbiro G. Which factors affect phytoplankton biomass in shallow eutrophic lakes? Hydrobiologia. 2013; 714:93–104.

Brothers SM, Hilt S, Attermeyer K, Grossart HP, Kosten S, Lischke B, Mehner T, Meyer N, Scharnweber K, Kohler J. A regime shift from macrophyte to phytoplankton dominance enhances carbon burial in a shallow, eutrophic lake. Ecosphere. 2013; 4 art 137.

Carey JC, Fulweiler RW. Human activities directly alter watershed dissolved silica fluxes. Biogeochemistry. 2012; 111:125–138.

Carey JC, Fulweiler RW. Watershed land use alters riverine silica cycling. Biogeochemistry. 2013; 113:525–544.

Carignan R, Kalff J. Phosphorus sources for aquatic weeds: water or sediments? Science. 1980; 207:987–989. [PubMed: 17830461]

Carpenter SR, Lodge DM. Effects of submersed macrophytes on ecosystem processes. Aquat Bot. 1986; 26:341–370.

Cataldo DA, Wildung RE. Soil and plant factors influencing the accumulation of heavy-metals by plants. Environ Health Perspect. 1978; 27:149–159. [PubMed: 367766]

Crosbie B, Chow-Fraser P. Percentage land use in the watershed determines the water and sediment quality of 22 marshes in the Great Lakes basin. Can J Fish Aquat Sci. 1999; 56:1781–1791.

Das BK, Gaye B, Kaur P. Geochemistry of Renuka Lake and wetland sediments, lesser Himalya (India): implications for source-area weathering, provenance, and tectonic setting. Environ Geol. 2008; 54:147–163.

Davies, BE. Soil chemistry and bioavailability with special reference to trace elements. Plants and the chemical elements: biochemistry, uptake. In: Farago, M., editor. Tolerance and Toxicity. Weinheim: VCH Verlagsgesellschaft; 1994. p. 2-30.

De Laune RD, Reddy CN, Patrick WH. Effect of pH and redox potential on concentration of dissolved nutrients in an estuarine sediment. J Environ Qual. 1981; 10:276–279.

Del Pozo R, Fernandez-Alaez C, Fernadez-Alaez M. The relative importance of natural and anthropogenic effects on community composition of aquatic macrophytes in Mediterranean ponds. Mar Freshw Res. 2011; 62:101–109.

Downing JA, McCauley E. The nitrogen - phosphorus relationship in lakes. Limnol Oceanogr. 1992; 37:936–945.

Egge JK, Aksnes DL. Silicate as regulating nutrient in phytoplankton competition. Mar Ecol Prog Ser. 1992; 83:281–289.

Evans DM, Schoenholtz SH, Wigington PJ, Griffith SM, Floyd WC. Spatial and temporal patterns of dissolved nitrogen and phosphorus in surface waters of a multi-land use basin. Environ Monit Assess. 2014; 186:873–887. [PubMed: 24046242]

Faafeng BA, Mjelde M. Clear and turbid water in shallow Norwegian lakes related to submerged vegetation. Structuring Role of Submerged Macrophytes in Lakes. 1998; 131:361–368.

Ferone JM, Devito KJ. Shallow groundwater-surface water interactions in pond-peatland complexes along a Boreal Plains topographic gradient. J Hydrol. 2004; 292:75–95.

Ferrante JG, Parker JI. The influence of planktonic and benthic crustaceans on silicon cycling in Lake Michigan, USA. Verhandlungen des Internationalen Verein Limnologie. 1978; 20:324–328.

Floyd WC, Schoenholtz SH, Griffith SM, Wigington PJ, Steiner JJ. Nitrate-nitrogen, land use/land cover, and soil drainage associations at multiple spatial scales. J Environ Qual. 2009; 38:1473–1482. [PubMed: 19465723]

Fraterrigo JM, Downing JA. The influence of land use on lake nutrients varies with watershed transport capacity. Ecosystems. 2008; 11:1021–1034.

Fraústo da Silva, JJR.; Williams, RJP. The biological chemistry of the elements. 2nd edn. New York: Oxford University Press; 2001.

Fritioff A, Greger M. Uptake and distribution of Zn, Cu, Cd and Pb in an aquatic plant Potamogeton natans. Chemosphere. 2006; 63:220–227. [PubMed: 16213560]

Gallego JLR, Ortiz JE, Sierra C, Torres T, Llamas JF. Multivariate study of trace element distribution in the geological record of Ronanzas Peat Bog (Asturias, N. Spain). Paleoenvironmental evolution and human activities over the last 8000 cal yr BP. Sci Total Environ. 2013; 454:16–29. [PubMed: 23542478]

Ginting D, Moncrief JF, Gupta SC, Evans SD. Interaction between manure and tillage system on phosphorus uptake and runoff losses. J Environ Qual. 1998; 27:1403–1410.

Golterman, HL. Methods for chemical analysis of fresh waters. Oxford: Blackwell Scientific; 1969. p. 16-19.

Gorman MW, Zimmer KD, Herwig BR, Hanson MA, Wright RG, Vaughn SR, Younk JA. Relative importance of phosphorus, fish biomass, and watershed land use as drivers of phytoplankton abundance in shallow lakes. Sci Total Environ. 2014; 466:849–855. [PubMed: 23978583]

Grace MR, Scicluna TR, Vithana CL, Symes P, Lansdown KP. Biogeochemistry and cyanobacterial blooms: investigating the relationship in a shallow, polymictic, temperate lake. Environ Chem. 2010; 7:443–456.

Guilizzoni P. The role of heavy metals and toxic materials in the physiological ecology of submersed macrophytes. Aquat Bot. 1991; 41:87–109.

Håkanson, L.; Jansson, M. Principles of Lake Sedimentology. Berlin: Springer; 1983.

Hamilton DP, Mitchell SF. Wave-induced shear stresses, plant nutrients and chlorophyll in seven shallow lakes. Freshw Biol. 1997; 38:159–168.

Hansel-Welch N, Butler MG, Carlson TJ, Hanson MA. Changes in macrophyte community structure in Lake Christina (Minnesota), a large shallow lake, following biomanipulation. Aquat Bot. 2003; 75:323–337.

Hanson MA, Butler MG. Early responses of plankton and turbidity to biomanipulation in a shallow prairie lake. Hydrobiologia. 1990; 200:317–327.

Hanson MA, Herwig BR, Zimmer KD, Fieberg J, Vaughn SR, Wright RG, Younk JA. Comparing effects of lake-and watershed-scale influences on communities of aquatic invertebrates in shallow lakes. PLoS ONE. 2012; 7:e44644. [PubMed: 22970275]

Heegaard E, Birks HH, Gibson CE, Smith SJ, Wolfe-Murphy S. Species-environmental relationships of aquatic macrophytes in Northern Ireland. Aquat Bot. 2001; 70:175–223.

Hobbs WO, Ramstach Hobbs JM, LAFrancois T, Zimmer KD, Theissen K, Edlund M, Michelutti N, Butler MG, Hanson MA, Carlson TJ. A 200-year perspective on alternative stable state theory and lake management from a biomanipulated shallow lake. Ecol Appl. 2012; 22:1483–1496. [PubMed: 22908708]

Horppila J, Nurminen L. Effects of submerged macrophytes on sediment resuspension and internal phosphorus loading in Lake Hiidenvesi (southern Finland). Water Res. 2003; 37:4468–4474. [PubMed: 14511717]

Hu SH, Zhou QH, Gao YN, He F, Liang W, Xiao ER, Wu ZB. Annual variation of nitrogen, phosphorus and silica levels, and their effects on phytoplankton distribution (diatoms and cyanobacteria) and eutrophication of small shallow lakes. Fresenius Environ Bull. 2011; 20:2824–2833.

Jackson LJ, Kalff J, Rasmussen JB. Sediment pH and redox potential affect the bioavailability of Al, Cu, Fe, Mn, and Zn to rooted aquatic macrophytes. Can J Fish Aquat Sci. 1993; 50:143–148.

Jackson LJ. Paradigms of metal accumulation in rooted aquatic vascular plants. Sci Total Environ. 1998; 219:223–231.

Jaynes ML, Carpenter SR. Effects of vascular and non-vascular macrophytes on sediment redox and solute dynamics. Ecology. 1986; 67:875–882.

Kabata-Pendias, A.; Pendias, H. Trace elements in soils and plants. Boca Raton: CRC press LLC; 2001.

Kidmose J, Nilsson B, Engesgaard P, Frandsen M, Karan S, Landkildehus F, Sondergaard M, Jeppesen E. Focused groundwater discharge of phosphorus to a eutrophic seepage lake (Lake V'ng, Denmark): implications for lake ecological state and restoration. Hydrogeol J. 2013; 21:1787–1802.

Kirk, G. The biogeochemistry of submerged soils. West Sussex: John Wiley and Sons, Ltd; 2004.

Kissoon LTT, Jacob DL, Hanson MA, Herwig BR, Bowe SE, Otte ML. Macrophytes in shallow lakes: relationships with water, sediment and watershed characteristics. Aquat Bot. 2013; 109:39–48. [PubMed: 23997402]

Korstad J. nutrient regeneration by zooplankton in southern Lake Huron. J Great Lakes Res. 1983; 9:374–388.

Landers, DH. Nutrient release from senescing milfoil and phytoplankton response. In: Breck, JE.; Prentki, RT.; Loucks, OL., editors. Aquatic Plants, Lake Management, and Ecosystem Consequences of lake Harvesting; Proceedings of Conference at Madison; Wisconsin. 1979. p. 127-143.

Llames ME, del Giorgio PA, Zagarese H, Ferraro M, Izaguirre I. Alternative states drive the patterns in the bacterioplankton composition in shallow Pampean lakes (Argentina). Environ Microbiol Rep. 2013; 5:310–321. [PubMed: 23584972]

Lee, GF. Role of hydrous metal oxides in the transport of heavy metals in the environment. In: Krnekel, PA., editor. Heavy metals in the aquatic environment, an international conference. Oxford: Pergamon; 1975. p. 137-147.

Lombi, E.; Wenzel, WW.; Gobran, GR.; Adriano, DC. Dependency of phytoavailability of metals on indigenous and induced rhizosphere processes: a review. In: Gobran, GR.; Wenzel, WW.; Lombi, E., editors. Trace elements in the rhizopshere. Boca Raton: CRC; 2001. p. 3-24.

Lougheed VL, Crosbie B, Chow-Fraser P. Primary determinants of macrophyte community structure in 62 marshes across the Great Lakes basin: latitude, land use, and water quality effects. Can J Fish Aquat Sci. 2001; 58:1603–1612.

Mackereth FJH. Chemical investigations of lake sediments and their interpretation. Proc R Soc Lond Ser B. 1965; 161:295–309.

Mackie, G. Applied aquatic ecosystem concepts. 2nd edn. Dubuque: Kendall-Hunt Publishing Company; 2004.

Madsen JD, Wersal RM, Woolf TE. A new core sampler for estimating biomass of submersed aquatic macrophytes. J Aquat Plant Manag. 2007; 45:31–34.

Mann, KH. Organisms and ecosystems. In: Barnes, RSK.; Mann, KH., editors. Fundamentals of aquatic ecosystems. London: Blackwell Scientific Publications; 1980. p. 21-24.

Martin-Jezequel V, Hildebrand M, Brzezinski MA. Silicon metabolism in diatoms: implications for growth. J Phycol. 2000; 36:821–840.

McClave, JT.; Sincich, T. Statistics. 10th edn. Upper saddle River: Pearson Education, Inc; 2006.

McCune, B.; Grace, JB. Analysis of ecological communities. Gleneden Beach: MjM Software Design; 2002.

Medeiros AS, Biastoch RG, Luszczek CE, Wang XA, Muir DCG, Quinlan R. Patterns in the limnology of lakes and ponds across multiple local and regional environmental gradients in the eastern Canadian Arctic. Inland Waters. 2012; 2:59–76.

Mi WJ, Zhu DW, Zhou YY, Zhou HD, Yang TW, Hamilton DP. Influence of *Potamogeton crispus* growth on nutrients in the sediment and water of Lake Tangxunhu. Hydrobiologia. 2008; 603:139–146.

Minnesota Department of Natural Resources. Ecological classification system. Grand Rapids, MN: Minnesota Department of Natural Resources, Division of Forestry Resource Assessment Program; 1999. http://www.dnr.state.mn.us/ecs/index.html [Accessed 27 Feb 2014]

Minnesota Geospatial Information Office Staff. Minnesota Land Use and Cover: 1990s Census of the Land. St. Paul, MN: Minnesota Geospatial Information Office; 1999. http://www.mngeo.state.mn.us/landuse/ [Accessed 27 Feb 2014]

Moyle JB. Some chemical factors influencing the distribution of aquatic plants in Minnesota. Am Midl Nat. 1945; 34:402–420.

Newton RM, Weintraub J, April R. The relationship between surface water chemistry and geology in the North Branch of the Moose River. Biogeochemistry. 1987; 3:21–35.

Nilsson A, Håkanson A. Relationships between drainage area characteristics and lake water quality. Environ Geol Water Sci. 1992; 19:75–81.

Nurminen L, Horppila J. Life form dependent impacts of macrophyte vegetation on the ratio of resuspended nutrients. Water Res. 2009; 43:3217–3226. [PubMed: 19505709]

Pais, I.; Jones, JB, Jr. The handbook of trace elements. Boca Raton: St. Lucie; 1997.

Parker JI, Conway HL, Yaguchi EM. Dissolution of diatom frustules and recycling of amorphous silicon in Lake-Michigan. J Fish Res Board Can. 1977; 34:545–551.

Qualls RG, Haines BL, Swank WT. Fluxes of dissolved organic nutrients and humic substances in a deciduous forest. Ecology. 1991; 72:254–266.

Quiroz-Vazquez P, White KN, Sigee DC. Aluminium, silicon and transition metal dynamics in a non-polluted lake: aquatic concentrations and phytoplankton uptake. Hydrobiologia. 2008; 607:131–142.

Reimers, RS.; Krenkel, PA.; Eagle, M.; Tragitt, G. Sorption phenomenon in the organics of bottom sediments. In: Krnekel, PA., editor. Heavy metals in the aquatic environment, an international conference. Oxford: Pergamon; 1975. p. 117-129.

Robin J, Wezel A, Bornette G, Arthaud F, Angelibert S, Rosset V, Oertli B. Biodiversity in eutrophicated shallow lakes: determination of tipping points and tools for monitoring. Hydrobiologia. 2014; 723:63–75.

Rowan JS, Black S, Franks SW. Sediment fingerprinting as an environmental forensics tool explaining cyanobacteria blooms in lakes. Appl Geogr. 2012; 32:832–843.

Sahuquillo M, Miracle MR, Morata SM, Vicente E. Nutrient dynamics in water and sediment of Mediterranean ponds across a wide hydroperiod gradient. Limnologica. 2012; 42:282–290.

Sass LL, Bozek MA, Hauxwell JA, Wagner K, Knight S. Response of aquatic macrophytes to human land use perturbations in the watersheds of Wisconsin lakes, USA. Aquat Bot. 2010; 93:1–8.

Scheffer, M. Ecology of Shallow Lakes. In: Usher, MB.; DeAngelis, DL.; Manly, BFJ., editors. Population and community Biology Series 202. Dordrecht: Kluwer Academic Publishers; 2004.

Scheffer, M.; Jeppesen, E. Alternative stable states. In: Jeppesen, E.; Sondergaard, M.; Sondergaard, M.; Christofferson, K., editors. The structuring role of submerged macrophytes in lakes, ecological studies. Vol. 131. New York: Springer, Verlag; 1998. p. 397-406.

Schippers P, van de Weerd H, de Klein J, de Jong B, Scheffer M. Impacts of agricultural phosphorus use in catchments on shallow lake water quality: about buffers, time delays and equilibria. Sci Total Environ. 2006; 369:280–294. [PubMed: 16781763]

Sigmon DE, Cahoon LB. Comparative effects of benthic microalgae and phytoplankton on dissolved silica fluxes. Aquat Microb Ecol. 1997; 13:275–284.

Smerdon BD, Devito KJ, Mendoza CA. Interaction of groundwater and shallow lakes on outwash sediments in the sub-humid Boreal Plains of Canada. J Hydrol. 2005; 314:246–262.

Soil Survey Staff. [Accessed 16 Feb 2012] Official Soil Series Descriptions. Natural Resources Conservation Service, United States Department of Agriculture. 2012. http://soils.usda.gov/technical/classification/osd/index.html

St. Cyr L, Campbell PGC, Guertin K. Evaluation of the role of submerged plant beds in the metal budget of a fluvial lake. Hydrobiologia. 1994; 291:141–156.

Steinmann P, Shotyk W. Geochemistry, mineralogy, and geochemical mass balance on major elements in two peat bog profiles (Jura Mountains: Switzerland). Chem Geol. 1997; 138:25–53.

Stewart, RE.; Kantrud, HA. U.S. Department of the Interior, Geological Survey Professional Paper 585-D. Washington, D.C.: U.S. Government Printing Office; 1972. Vegetation of prairie potholes, North Dakota, in relation to quality of water and other environmental factors.

Swenson, HA.; Baldwin, HL. A primer on water quality. Washington, D.C.: U.S. Geological Survey; 1965.

Syrovetnik K, Malmstrom ME, Neretnieks I. Accumulation of heavy metals in the Oostriku peat bog, Estonia: determination of binding processes by means of sequential leaching. Environ Pollut. 2007; 147:291–300. [PubMed: 17267085]

ter Braak, CJF.; Šmilauer, P. Cancoco Reference Manual and CanoDraw for Windows User's Guide. Wageningen, The Netherlands: Biometris, Wageningen University and Research Center; 2002.

Thorbergsdottir IM, Gislason SR. Internal loading of nutrients and certain metals in the shallow eutrophic Lake Myvatn, Iceland. Aquat Ecol. 2004; 38:191–207.

Troelstrup NH Jr, Perry J. Water quality in southeastern Minnesota streams: observations along a gradient of land use and geology. J Minnesota Acad Sci. 1989; 55:6–16.

Weis JS, Weis P. Metal uptake, transport and release by wetland plants: implications for phytoremediation and restoration. Environ Int. 2004; 30:685–700. [PubMed: 15051245]

Wetzel, RG. Limnology: lake and river ecosystems. 3rd edn. San Diego: Academic; 2001.

Wezel A, Arthaud F, Dufloux C, Renoud F, Vallod D, Robin J, Sarrazin B. Varied impact of land use on water and sediment parameters in fish ponds of the Dombes agro-ecosystem, France. Hydrol Sci Jjournal Des Sciences Hydrologiques. 2013; 58:854–871.

Whigham DF, Jordan TE. Isolated wetland and water quality. Wetlands. 2003; 23:541–549.

Winter TC. Relation of streams, lakes, and wetlands to groundwater flow systems. Hydrogeol J. 1999; 7:28–45.

Winter, TC.; Carr, MR. Hydrologic setting of wetlands in the Cottonwood Lake area. Stutsman County, North Dakota: US Geological Survey Water-Resources Investigations Report 80-99; 1980.

Wood T, Bormann FH, Voigt GK. Phosphorus cycling in a northern hardwood forest: biological and chemical control. Science. 1984; 223:391–393. [PubMed: 17829887]

Wu YH, Wen YJ, Zhou JX, Wu YY. Phosphorus release from lake sediments: effects of pH, temperature and dissolved oxygen. KSCE J Civ Eng. 2014; 18:323–329.

Yanes C, Alvarez H, Jaffé R. Geochemistry of a tropical lake (Lake Leopoldo) on pseudo-karst topography within the Roraima Group, Guayana Shield, Venezuela. Appl Geochem. 2006; 21:870–886.

Zhang XF, Liu ZW, Gulati RD, Jeppesen E. The effect of benthic algae on phosphorus exchange between sediment and overlying water in shallow lakes: a microcosm study using P-32 as a tracer. Hydrobiologia. 2013; 710:109–116.

Zimmer KD, Hanson MA, Herwig BR, Konsti ML. Thresholds and stability of alternative regimes in shallow prairie-parkland lakes of central North America. Ecosystems. 2009; 12:843–852.

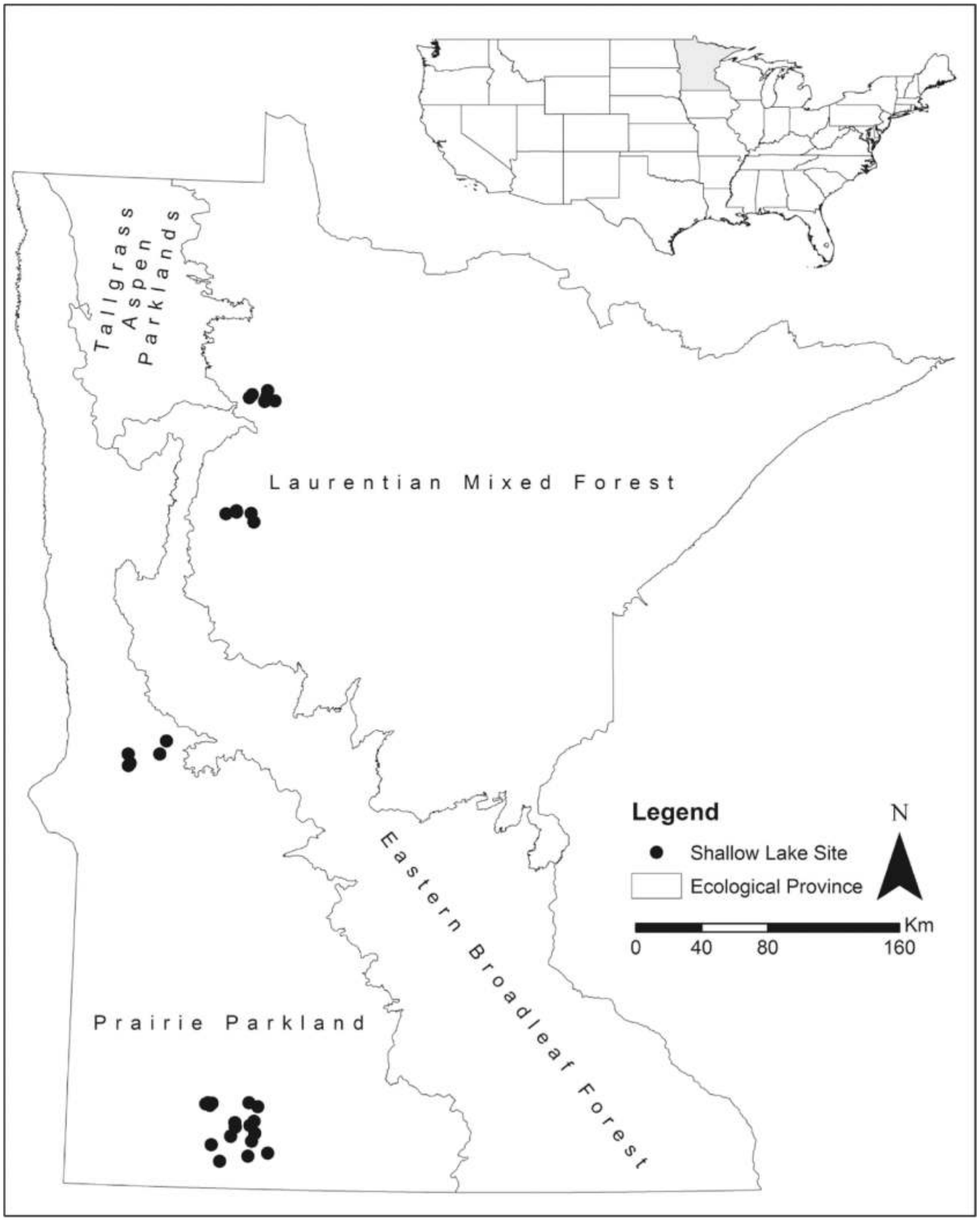

Fig. 1.

Map of Minnesota showing locations of study lakes within the Prairie Parkland and Laurentian Mixed Forest ecological provinces sampled in 2010 and 2011 (reprint from Kissoon et al. 2013)

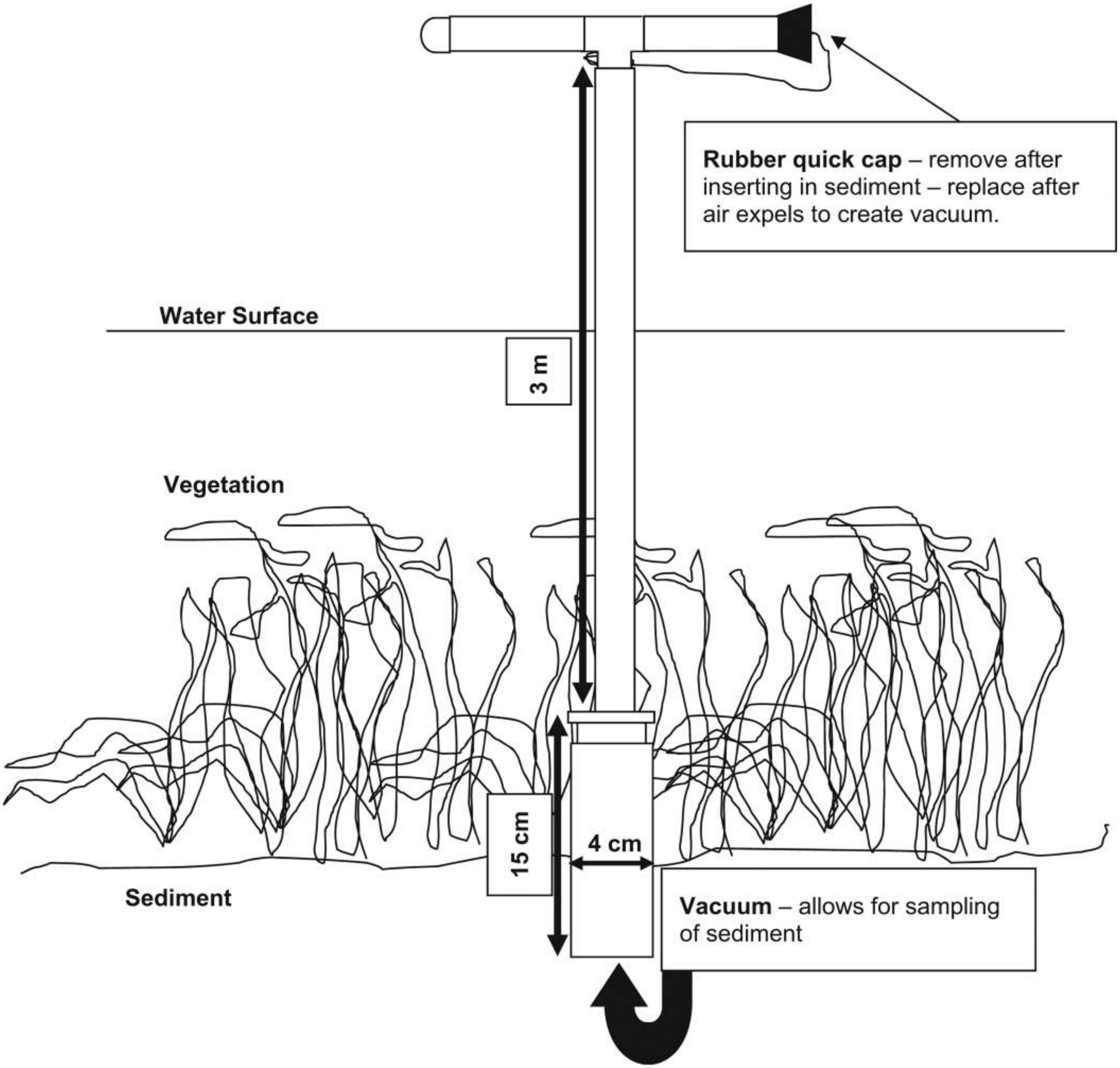

Fig. 2.

Sediment corer for sampling sediments in shallow lakes (adapted from Madsen et al. 2007, reprinted from Kissoon et al. 2013)

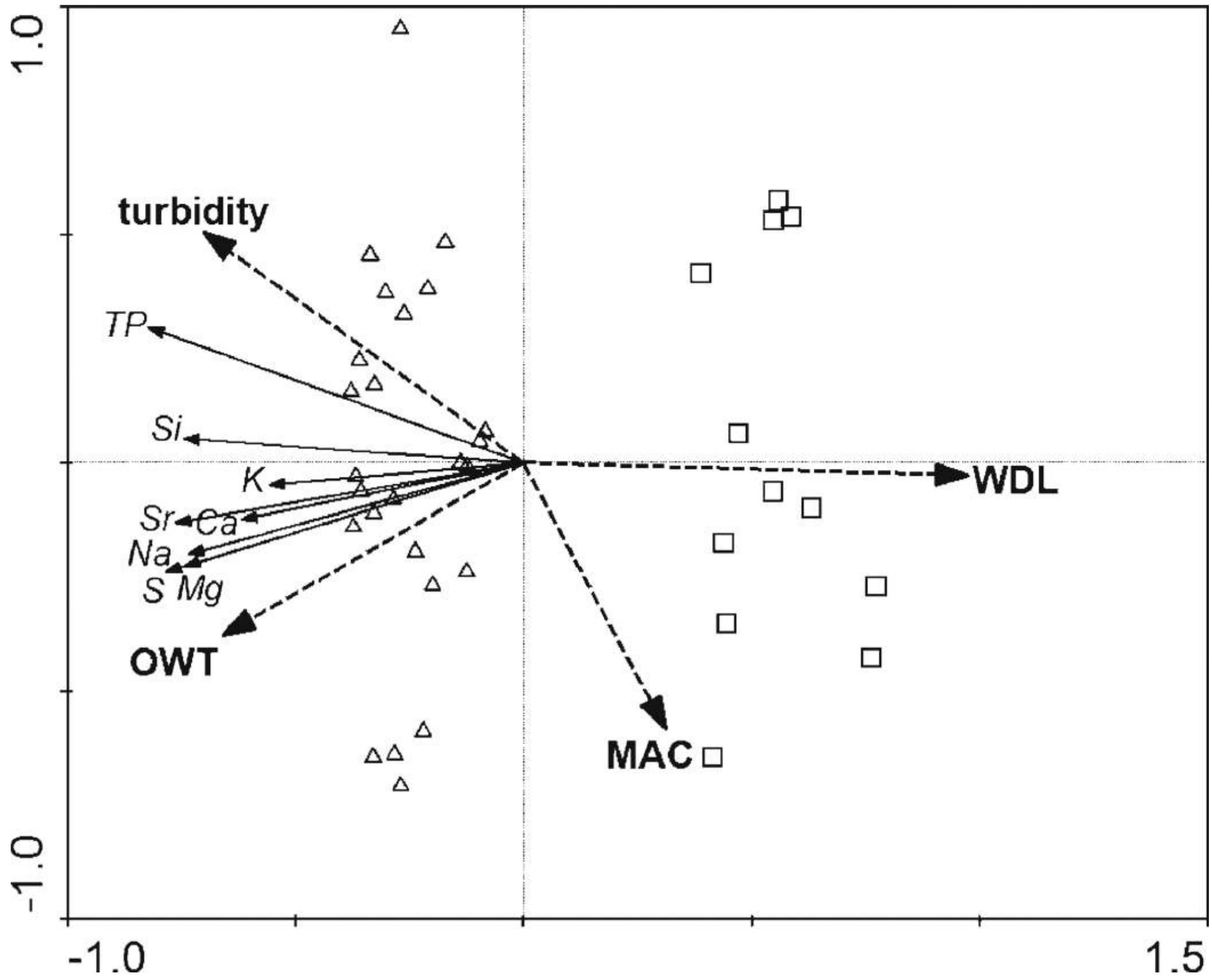

Fig. 3.

Ordination plot of RDA of water chemistry variables constrained by environmental variables (environmental variables (in bold): percent woodland (WDL), turbidity, open water area (OWT), total macrophyte cover (MAC); provinces: Prairie Parkland (Δ), Laurentian Mixed Forest (□); water chemistry variables: chemical elements)

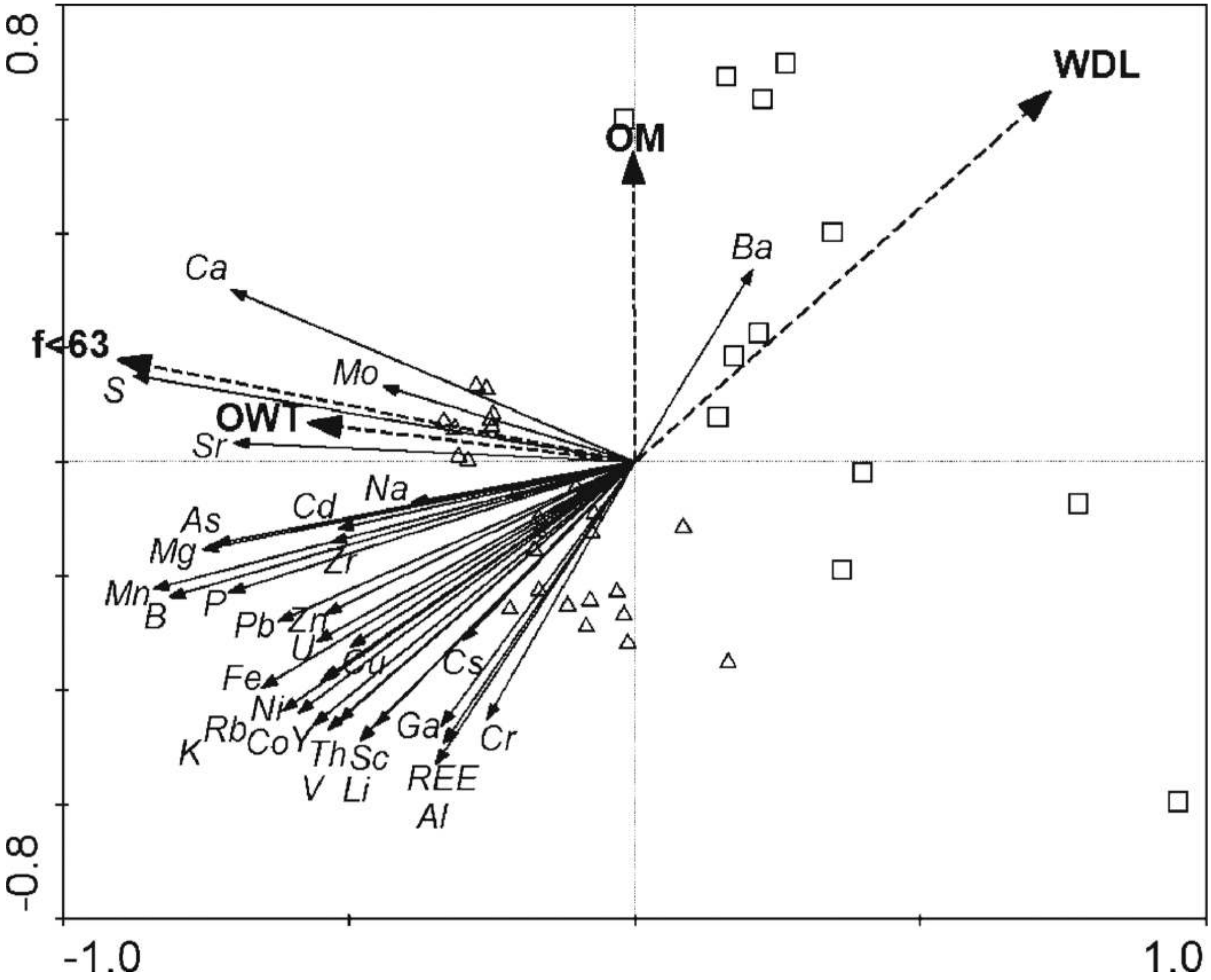

Fig. 4.

Ordination plot of RDA of sediment chemistry variables constrained by environmental variables (environmental variables (in bold): fraction of sediment smaller than 63 m (*f*<63), percent woodland (WDL), open water area (OWT), organic matter (OM); sediment chemistry variables: chemical elements, rare earth elements (REE); provinces: Prairie Parkland (Δ), Laurentian Mixed Forest (□))

Table 1

Average±standard deviation for environmental variables for each ecological province

Variables		**Prairie Parkland (*n*=26)**	**Laurentian Mixed Forest (*n*=12)**
Water	pH	8.8±0.5	7.6±0.7
	Turbidity (NTU)	24±25	2.4±2.5
	Chl-a (μgl^{-1})	69±81	5.4±4.8
Sediment	Organic matter (% dry sediment)	10±5	25±16
	f<63 μm (% dry sediment)	91±15	67±28
Within-lake	Submerged plant cover (%)	57±48	67±46
	Basin area (ha)	24±17	6±3
	Open water area (ha)	20±15	4±2
	Emergent vegetation area (ha)	5±7	2±3
Watershed	Lake watershed area (ha)	335±350	74±71
	Lake watershed:basin area	16±17	14±18
	%grassland	21±24	5±7
	% shrubland	0.9±2	2±4
	% woodland	2±2	84±10
	% corn and soybeans	34±21	0±0
	% hay and grains	29±23	0±0
	% total agriculture	65±24	0±0

Table 2

Average±standard deviation for water element concentrations in each ecological province and significance of differences (probability) in water element concentrations between provinces and among lakes within provinces as determined by Nested ANOVA (element concentrations in μmol l^{-1}, NS indicates non-significance, $p<0.01$)

Elements	**Average±standard deviation**		**Source of variation**	
	Prairie Parkland	**Laurentian Mixed Forest**	**Province**	**Lake(Province)**
	***n*=26**	***n*=12**	**Probability**	
Ca	1012±332	472±333	0.000	0.000
K	113±51	55±27	0.000	0.000
Mg	1309±287	319±204	0.000	0.000
Na	260±100	40±21	0.000	0.000
S	376±322	9.3±1.7	0.000	0.000
Si	2.4±0.9	0.27±0.18	0.000	0.000
Sr	479±252	103±124	0.000	0.000
TP	5.2±3.9	0.52±0.56	0.001	NS

Table 3

Average±standard deviation for sediment element concentrations in each ecological province and significance of differences (probability) in sediment element concentrations between provinces and among lakes within provinces as determined by Nested ANOVA (element concentrations in μmol g^{-1}, except where indicated by † for nmol g^{-1} and ‡ for mmol g^{-1}, NS indicates non-significance, $p<0.01$)

Elements	**Average±standard deviation**		**Source of variation**	
	Prairie Parkland	**Laurentian Mixed Province**	**Province**	**Lake(Province)**
	***n*=26**	***n*=12**	**Probability**	
Al	466±186	242±183	0.000	0.000
As†	0.08±0.03	0.03±0.05	0.000	0.000
B	2.0±0.8	0.72±0.49	0.000	0.000
Ba	0.39±0.32	0.74±0.53	0.000	0.000
Ca‡	1127±591	1826±2610	0.000	0.000
Cd†	0.004±0.002	0.003±0.002	0.000	0.000
Co†	0.12±0.03	0.06±0.03	0.000	0.000
Cr	0.39±0.14	0.23±0.18	0.000	0.000
Cs†	0.005±0.002	0.004±0.002	0.000	0.000
Cu	0.24±0.08	0.14±0.11	0.000	0.000
Fe	287±109	132±91	0.000	0.000
Ga†	0.05±0.02	0.03±0.02	0.000	0.000
K	44±15	18±12	0.000	0.000
Li	1.8±0.7	0.72±0.46	0.000	0.000
Mg	287±145	129±51	0.000	0.000
Mn	9.8±4.6	2.9±1.7	0.000	0.000
Mo†	0.02±0.01	0.02±0.01	NS	0.000
Na	10±6	7.3±4.8	0.000	0.000
Ni	0.34±0.11	0.19±0.10	0.000	0.000
P	24±6	17±8	0.000	0.000
Pb†	0.06±0.03	0.03±0.03	0.000	0.000
Rb†	0.19±0.06	0.11±0.08	0.000	0.000
S	250±151	80±51	0.000	0.000
Sc†	0.06±0.02	0.02±0.02	0.000	0.000
Sr	1.1±0.7	0.5±0.5	0.000	0.000
Th†	0.01±0.004	0.005±0.003	0.000	0.000
U†	0.02±0.01	0.003±0.002	0.000	0.000
V	0.83±0.31	0.32±0.21	0.000	0.000
Y†	0.1±0.03	0.04±0.03	0.000	0.000
Zn	0.99±0.31	0.64±0.52	0.000	0.000
Zr†	0.05±0.02	0.03±0.02	0.000	0.000
Ce†	0.21±0.06	0.12±0.08	0.000	0.000
Dy†	0.01±0.004	0.005±0.003	0.000	0.000

Elements	Average±standard deviation		Source of variation	
	Prairie Parkland	Laurentian Mixed Province	Province	Lake(Province)
	n=26	*n*=12	Probability	
Gd†	0.02±0.005	0.007±0.005	0.000	0.000
La†	0.10±0.03	0.06±0.04	0.000	0.000
Nd†	0.10±0.03	0.05±0.03	0.000	0.000
Pr†	0.03±0.01	0.01±0.01	0.000	0.000
Sm†	0.02±0.01	0.009±0.006	0.000	0.000

Table 4

Results of global RDA models of water and sediment chemistry using environmental variables and pRDA models of water and sediment chemistry using environmental variables and covariables (determined by manual forward selection procedures with Monte Carlo permutation tests (999 permutations) according to ter Braak and Šmilauer (2002) ($p<0.05$), variance proportions calculated according to Borcard et al (1992))

Species matrix	Variance class	Variables	%Variance explained	p-value	%Variance explained	p-value
Water chemistry			RDA		pRDA	
	Environmental	%Woodland	57.6	0.001	0.1	0.231
		Turbidity	5.2	0.023	6.2	0.021
		Open water area	2.2	0.020	2.3	0.040
		Macrophyte cover	0.2	0.039	1.9	0.084
	Covariable	Province			2.1	0.120
	Covariance				54.8	
	Total		65.2		67.4	
Sediment chemistry	Environmental	*f*<63	52.1	0.001	26.1	0.001
		%Woodland	9.3	0.001	0.4	0.286
		Open water area	1.7	0.005	3.1	0.002
		Organic matter	1.1	0.023	1.5	0.016
	Covariable	Province			1.3	0.301
	Covariance				33.1	
	Total		64.2		65.5	

Table 5

Pearson correlations for turbidity, LOI, *f*<63 μm, chlorophyll*a* concentrations and element concentrations in lake water

	Chl-a	**Turbidity**	**pH**	**OM**	***f*<63**	**TP**
Chl-a		0.919		−0.561		
OM		−0.515	−0.677			
TP	0.744	0.716	0.701	−0.775		
K						0.530
Mg	0.511		0.500	−0.508	0.522	0.558
Na						
S	0.526			−0.571		0.588
Si	0.583	0.638			0.577	
Sr	0.546	0.518		−0.58		0.625

Correlations with $r \geq 0.500$ (that explain 25 % or more variation) are shown ($p<0.01$)

Table 6

Pearson correlations for chlorophyll-*a* concentrations (Chl-a), turbidity, and pH in water; OM, *f*<63 μm, and element concentrations in lake water against element concentrations in sediment (correlations with *r* ≥0.500 (that explain 25 % or more variation) are shown (*p*<0.01), element_w: elements in water, element_s: elements in sediment)

	Chl-a	**Turbidity**	**pH**	**OM**	***f*<63**	**TP_w**	**Ca_w**	**K_w**	**Mg_w**	**Na_w**	**S_w**	**Si_w**	**Sr_w**
Al_s			0.535			0.694							0.532
As_s	0.571	0.520	0.514		0.603	0.691	0.600		0.703	0.596	0.662	0.566	0.730
B_s					0.667		0.677	0.541	0.791	0.788	0.732	0.641	0.737
Ca_s					0.707		0.632		0.631			0.514	
Ce_s	0.520		0.640	−0.555		0.727							0.529
Co_s	0.600	0.526	0.569			0.718			0.541		0.561		0.636
Cr_s			0.593	−0.532		0.693							0.518
Cs_s						0.507							
Cu_s			0.531			0.601					0.539		0.576
Dy_s	0.573	0.509	0.6	−0.558		0.743			0.558		0.600		0.684
Fe_s	0.592	0.516	0.648	−0.537		0.799			0.589		0.615		0.656
Ga_s			0.564	−0.511		0.691					0.503		0.586
Gd_s	0.556		0.609	−0.556		0.735			0.520		0.57		0.649
K_s	0.567		0.531			0.682		0.618	0.643	0.634	0.705		0.698
La_s			0.638	−0.55		0.712							0.519
Li_s	0.572		0.638	−0.609		0.767			0.588	0.557	0.706		0.750
Mg_s	0.560		0.561		0.510	0.610	0.621	0.739	0.868	0.811	0.798	0.552	0.747
Mn_s					0.703				0.539	0.568		0.586	
Na_s										0.519			
Nd_s	0.531		0.624	−0.565		0.732					0.508		0.581
Ni_s	0.535		0.634			0.721			0.524		0.588		0.644
P_s					0.590								
Pb_s					0.525								0.523
Pr_s	0.512		0.622	−0.554		0.721							0.554
Rb_s	0.508		0.515			0.627			0.512		0.569		0.634
S_s					0.749							0.539	

	Chl-a	Turbidity	pH	OM	*f*<63	TP_w	Ca_w	K_w	Mg_w	Na_w	S_w	Si_w	Sr_w
Sc_s	0.554		0.580	−0.590		0.718			0.545		0.600		0.687
Sm_s	0.539		0.612	−0.560		0.732					0.540		0.621
Sr_s					0.580		0.602	0.509	0.737	0.749	0.749	0.513	0.727
Th_s	0.609	0.562	0.596	−0.641		0.702	0.603		0.671	0.528	0.653	0.515	0.740
U_s							0.532		0.642	0.610	0.67		0.724
V_s	0.564		0.634	−0.564		0.751			0.576		0.637		0.698
Y_s	0.551		0.613	−0.537		0.746			0.575		0.626		0.699