Water Air Soil Pollut (2012) 223:1415–1427
DOI 10.1007/s11270-011-0954-y

Redox Stratification and Salinization of Three Kettle Lakes in Southwest Michigan, USA

Carla M. Koretsky · Andrew MacLeod · Ryan J. Sibert · Christine Snyder

Received: 6 May 2011 / Accepted: 8 September 2011 / Published online: 21 September 2011

Abstract Redox stratification, especially hypolimnetic anoxia resulting from eutrophication, and salinization resulting from application of salts for road deicing is investigated in three kettle lakes in southwest Michigan. Two of the lakes (Asylum and Woods Lakes) are located in urban Kalamazoo, Michigan, and the third (Brewster Lake) is located in rural Hastings, Michigan. In summer, the water columns of all three lakes are distinctly redox stratified, with anoxic hypolimnia and significant accumulation of reduced solutes (e.g., Mn(II), Fe(II), ammonia) in the lake bottom waters. Extremely elevated conductivity, chloride, sodium, and potassium levels are observed in the urban Asylum and Woods Lakes compared to the rural Brewster Lake, presumably due to runoff of road salt deicers applied in the surrounding watershed. These significant changes in water quality are of concern because they may detrimentally impact lake mixing, biodiversity, and ecosystem function in the urban lakes.

Keywords Anoxia · Anoxic · Eutrophication · Road salt · Saline · Salinization · Stratification · Urban

C. M. Koretsky (✉) · A. MacLeod · R. J. Sibert · C. Snyder
Department of Geosciences, Western Michigan University, Kalamazoo, MI 49008, USA
e-mail: Carla.koretsky@wmich.edu

1 Introduction

Cultural eutrophication of lakes is a major problem in both rural and urban areas due to high loading of nitrogen and especially phosphorous, from fertilizers, detergents, agricultural runoff, septic tanks, and other sources (Wetzel 2001; Schindler et al. 2008). The introduction of high concentrations of these limiting nutrients stimulates organic matter productivity, particularly in summer, leading to algal blooms, increased water column turbidity, and loss of submerged aquatic vegetation. This leads to a decline in dissolved oxygen at depth as organic matter sinks and decays and also due to diminished photosynthesis at depth. Hypoxic (<2 ppm) or anoxic (<0.2 ppm) conditions may develop, leading to fish kills and loss of aquatic biodiversity. In the absence of oxygen, labile organic matter continues to oxidize, coupled to a series of electron acceptors (nitrate, Mn(IV), Fe(III), sulfate), typically used in order of decreasing energetic yield (Stumm and Morgan 1996). Reductive dissolution of Mn(IV) and Fe(III) (hydr)oxide phases releases dissolved Fe(II) and Mn (II) together with adsorbed or co-precipitated phosphorous and trace metals into the water column (Davison 1993). Sulfate reduction produces toxic hydrogen sulfide, and in the absence of these electron acceptors, organic matter degrades via methanogenesis, producing methane. Ammonification releases dissolved ammonia, which may persist and accumulate in the absence of oxygen. The net effect of these processes is development of a hypoxic or anoxic hypolimnion, in which toxic levels of sulfide, ammonia, trace metals, and the absence of oxygen lead to fish kills, loss of aquatic biodiversity, and changes in microbial community structure.

Cultural eutrophication has long been recognized as a threat to aquatic ecosystems. However, significantly less study has been directed at understanding the effects of salt application to roads in areas surrounding urban lakes, although recent studies suggest that this is a growing problem in urban watersheds. For example, Novotny et al. (2008) demonstrated that sodium and chloride levels are 10–25 times higher in urban Minneapolis lakes impacted by road salt-containing runoff compared to non-urban lakes in the same region. Increasing chloride levels have also been observed in lakes in New Hampshire (Rosenberry et al. 1999; Likens and Buso 2010), Wisconsin (McGinley 2008), New York (Godwin et al. 2003), Ontario (Molot and Dillon 2008; Meriano et al. 2009), Michigan (Tuchman et al. 1984; Bridgeman et al. 2000), Norway (Kjensmo 1997), and Sweden (Thunqvist 2004). Given that 66% of the salt used in the USA in 2009 was applied to highways for deicing and that use of salt for road deicing has risen steadily from ~170,000 tons/year in the early 1940s to >15,000,000 tons/year between 2005 and 2009 (Salt Institute 2011), this is perhaps unsurprising. Increased chloride levels can lead to decreases in aquatic biodiversity (Tuchman et al. 1984; Bridgeman et al. 2000; Paul and Meyer 2001; Ramakrishna and Viraraghavan 2005), changes in microbial community structure (Tiquia et al. 2007), increased toxicity of heavy metals (Amrhein et al. 1992; Mayer et al. 1999; Norrstrom 2005; Mayer et al. 2008), and losses of potable freshwater supplies (Kaushal et al. 2005) and may lead to significant changes in the density structure of lakes (Judd 1970; Bubeck et al. 1971; Bubeck and Burton 1989; Bridgeman et al. 2000; Marsalek 2003; Judd et al. 2005; Novotny et al. 2008). Several studies have shown that lakes impacted by road salt input may become monomictic, mixing just once per year, and also show that mixing events are pushed much later into the fall (Judd 1970; Bubeck et al. 1971; Bubeck and Burton 1989; Bridgeman et al. 2000; Marsalek 2003; Judd et al. 2005; Novotny et al. 2008). In theory, with continued road salt input, a dimictic lake could eventually transition to meromixis, in which the water column becomes permanently stratified. In lakes suffering from cultural eutrophication, this is an especially challenging situation because without spring and fall overturn replenishing oxygen to the lake bottom waters, they are likely to become permanently anoxic.

The major objective of this study is to evaluate redox stratification, especially hypolimnetic anoxia resulting from eutrophication, and water column salinization, in urban compared to rural lakes. Three kettle lakes in southwest Michigan were studied during the summer of 2010. Woods Lake and Asylum Lake are located in urban areas and are highly impacted by residential and commercial development of the surrounding land, whereas Brewster Lake is located in a rural setting.

2 Study Sites

Three kettle lakes in southwestern Michigan, USA were for chosen for study. Two of the lakes (Woods Lake and Asylum Lake) are located in Kalamazoo, Michigan, and the third lake (Brewster Lake) is located in Hastings, Michigan (Fig. 1). There is much greater residential and commercial development in the areas surrounding Woods and Asylum Lakes, compared to Brewster Lake, which is in a rural setting (Fig. 2).

Woods Lake has a surface area of approximately 9.7 ha and a maximum depth of ~14 m. The soils surrounding the lake are classified as urban land–Oshtemo complex, with 12–25% slopes. The parent material is coarse-loam over sandy outwash (USDA 2011). The lake has no natural surface water inflows or outflows, and piezometer data suggest that the lake loses water to the underlying groundwater aquifer (Kieser and Associates 1997). However, for more than three decades, five storm water drains have channeled surface runoff from the surrounding watershed (~80.5 ha comprised of ~78% residential, 16% wooded, and 6% commercial development) directly into the lake (Kieser and Associates 1997). This has led to a variety of water quality issues in the lake, including growth of nuisance weeds, diminished water clarity, increased sedimentation, and input of nutrients (Kieser and Associates 1997). For this reason, in 2002–2003, the City of Kalamazoo implemented a number of strategies to control phosphorous input into the lake. Discharge from two

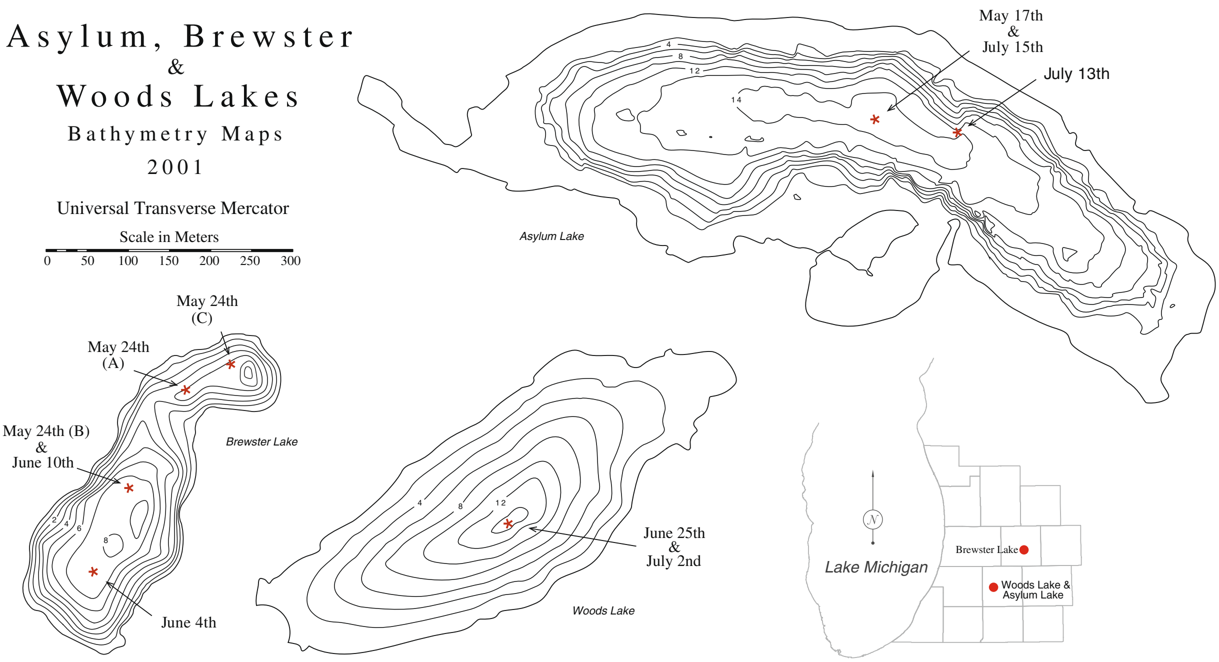

Fig. 1 Bathymetric maps of **a** Woods Lake (Kieser and Associates 1997), **b** Asylum Lake (Western Michigan University Facilities Management, personal communication), and **c** Brewster Lake (Honsowitz and Roher 2005) with sampling sites noted

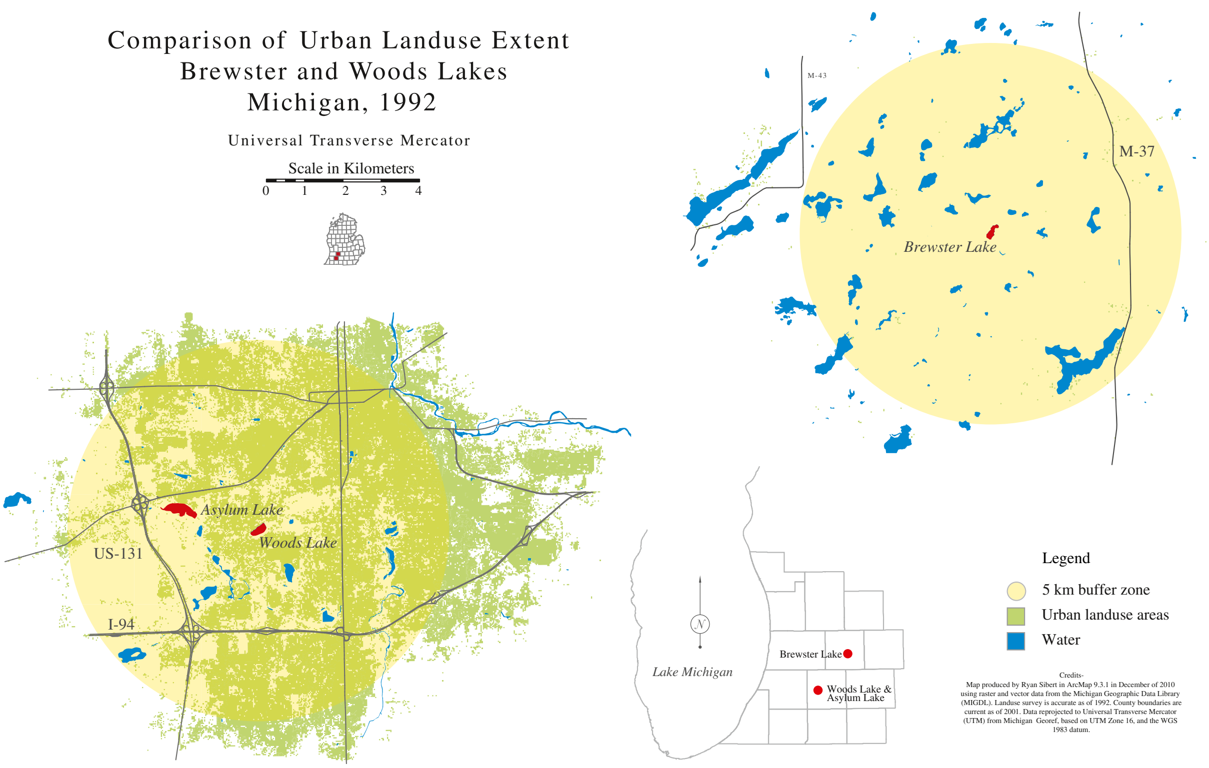

Fig. 2 Comparison of urban land use extent in the areas surrounding Woods, Asylum, and Brewster Lakes. Land use in the 5-km zone surrounding Brewster is primarily forested (~53%) and farmland (~39%) with <3.5% urban or roads

storm water sewers thought to be responsible for the bulk of the phosphorous, and sediment inputs into the lake were rerouted through a detention pond and wetland area with a sediment forebay and infiltration trench in 2002 (Boyer and Kieser 2008).

Asylum Lake has a surface area of ~19.8 ha, a maximum depth of ~15.8 m, and a mean depth of ~7.2 m with no natural surface water inflow (Kalamazoo Nature Center 2002). It has been significantly impacted by human activities, including orchards and farms located close to the lake beginning in the late nineteenth century, and subsequent construction and use of a state asylum (Kalamazoo State Hospital Colony Farm) on the property surrounding the lake from ~1888 to the late 1960s (Kalamazoo Nature Center 2002). Other human impacts on the lake include a dump in a gully just to the south of the lake; a City of Kalamazoo leaf composting area just to the southwest of the lake; a city sewer line just to the north of the lake (relocated to higher ground in 1992); storm drainage from surrounding residential areas, especially a high traffic state highway just to the west; septic drainage from a small trailer park to the northwest of the lake (now linked to city sanitary sewer system); and an earthen dam with a 7.3-m culvert on the east end of the lake, probably built in the 1870s (Kalamazoo Nature Center 2002), which allows some outflow of water to Little Asylum Lake, located just to the east of Asylum Lake. The lake is currently buffered by wetlands to the west and nature preserve areas (meadows and forest) to the south, with residential development mostly on the north side of the lake. The lake is fed by groundwater, which flows from west to east (Sauck and Barcelona 1992). Soils to the north and east of the lake are comprised of the same urban–Oshtemo complex as is present around Woods Lake. To the southwest of the lake is the Oshtemo sandy loam with 12–18% slope, and due south of Asylum Lake, the soils are Kalamazoo loam with 6–12% slopes. To the southeast of the lake lies a combination of Oshtemo sandy loam with 18–35% slopes and a minor amount of ponded Houghton and Sebewa soils, with 0–2% slopes and parent material of herbaceous organics and loamy soils over sandy and gravelly outwash (USDA 2011).

Brewster Lake has a surface area of ~5.3 ha and a maximum depth of ~8.5 m with no natural surface water inflow and a shallow, intermittent outflow to Cedar Creek to the south (Holderread and Aljobeh 2008). It is located approximately 50 km to the north of Woods and Asylum Lakes, in rural Hastings, Michigan. The lake is currently owned by, and located on the property of, the Pierce Cedar Creek Institute (PCCI), a nature center and biological station. The surrounding 270 ha comprising PCCI consist of ~40% forest, 5% wetland, and 13% upland forest and fields. The land adjacent to Brewster Lake has been not been used for industrial or agricultural activities since at least 1952 (Honsowitz and Roher 2005). The lake is entirely surrounded by Houghton muck soils, which are poorly drained, organic-rich soils with 0–1% slopes. Beyond the Houghton muck lie Tekenink fine sandy loam with 18–40% slopes, Marlette loam with 18–40% slopes, Perrinton loam with 6–12% slopes, and Coloma loamy sand with 6–12% slopes, all of which have loamy till or sandy outwash parent materials (USDA 2011).

3 Materials and Methods

Water column profiles were measured on multiple dates at each lake. At Brewster Lake, three sites were sampled on 24 May 2010, one site was sampled on 4 June 2010, and one site was sampled on 10 June 2010. The profiles were chosen to form a transect across the lake, with three of the profiles (June 4, 10, May 24B) measured at the deepest points found using a sonar depth finder and two additional profiles measured at shallower sites (Fig. 1). Woods Lake was sampled at approximately the same location, located in the deepest portion of the lake, on 25 June 2010 and on 2 July 2010. Profiles were measured at Asylum Lake on 17 May, 13 July, and 15 July 2010, close to the center of the lake in the deepest waters.

A YSI multiprobe sonde was used to collect in situ pH, temperature, conductivity, and dissolved oxygen profiles at a depth resolution of 0.5 m from the lake surface to the lake bottom for all sampling trips, except on May 17 at Asylum Lake. On this sampling trip, a salinity meter was used to measure samples retrieved from the water column on-board the canoe. A Van Dorn vertical water sampler (Aquatic Research Instruments, Inc.) was lowered from the side of a rowboat or canoe, to retrieve water samples at depth intervals of 1 m. Four water samples (~25 mL each) were collected at each depth from a single Van Dorn draw. These were immediately filtered through 0.45-

μm syringe filters. Two replicates were preserved with two drops of concentrated nitric acid, and two replicates were left unacidified and tightly capped. All analyses described below were completed on both replicates; the reported data are averages of the two replicate measurements.

Samples were returned to laboratories located at Western Michigan University in Kalamazoo, Michigan (near Woods and Asylum Lakes) or PCCI in Hastings, Michigan (near Brewster Lake) immediately after water sampling was complete. Samples that were not analyzed immediately for alkalinity, Fe(II), Mn(II), and ammonia were kept in a refrigerator; samples to be analyzed for chloride were typically frozen and thawed completely prior to analysis. Within 1 day of sampling and typically within several hours of sampling, total alkalinity, and dissolved ammonia, Fe(II) and Mn(II) were measured using UV/Vis spectrophotometric methods. Alkalinity was measured using unacidified fresh samples, according to the method described by Sarazin et al. (1999). Ammonium was measured using unacidified samples according to the indophenol blue method described in Grasshoff et al. (1983). Dissolved ferrous iron (FeII) and manganese (MnII) were analyzed using acidified and unacidified samples, respectively, with matrix matched calibration standards, according to the methods of Viollier et al. (2000) and Grasshoff et al. (1983), respectively. Unacidified samples were used to measure chloride with a Dionex ion chromatograph. Acidified samples were used to measure major elements (sodium, potassium, magnesium, and calcium) within 2 weeks of sampling with a Perkin Elmer Optima 2100DV inductively coupled plasma optical emission spectrometer (ICP-OES). All ICP-OES samples and calibration standards were prepared with internal standards (1,000 ppb Y).

4 Results and Discussion

4.1 Temperature, Dissolved Oxygen, and pH

Temperature in the well-mixed epilimnia (upper 2–3 m) of all three lakes depends primarily on sampling date; higher temperatures are generally recorded later in summer, coincident with increases in ambient air temperature (Fig. 3a). The sharp decrease in temperature in all three lakes delineates the metalimnia between 2 and 7.5 m depths; temperatures are constant with depth in the deeper waters of the hypolimnia (below 7.5–10 m depth).

Dissolved oxygen is saturated or supersaturated and changes little with depth in the shallow epilimnia of the three lakes. It decreases rapidly in the metalimnia, and all three lakes are anoxic in the hypolimnia (Fig. 3b). A subsurface maximum in dissolved oxygen is observed between 2.5 and 4.5 m depth in all three lakes. Dissolved oxygen concentrations in these subsurface maxima are much larger in Asylum Lake then Brewster or Woods Lakes, reaching nearly 200% saturation. Photosynthetic production of oxygen,

$$CO_2 + H_2O = CH_2O + O_2 \quad (1)$$

where "CH_2O" represents organic matter, is the most likely source of this subsurface peak in oxygen levels. This is further confirmed by the subsurface maxima in pH that occur at the same depths as oxygen maxima in all three lakes (Fig. 3c) because as photosynthesis consumes carbon dioxide, acidity is also consumed:

$$CO_2 + H_2O = H_2CO_3 = H^+ + HCO_3^- \quad (2)$$

Below the subsurface maxima in dissolved oxygen, pH decreases with depth in all three lakes (Fig. 3c). This is likely the result of downward mixing and diffusion of oxygen and its subsequent consumption via aerobic respiration and reoxidation of more reduced solutes (e.g., Mn(II), Fe(II), sulfide, or ammonia) diffusing upward from the anoxic bottom waters.

Decreasing oxygen and pH with depth has been reported in other lakes located in Kalamazoo and Barry Counties in southwest Michigan (Table 1). Water quality data collected by the Michigan Department of Natural Resources and the Michigan Department of Environmental Quality demonstrate that, during summer, lakes located in this region typically become hypoxic below ~3–7.5 m (SWIMS 2011). pH values in the bottom waters of lakes in this area range between ~6.6 and 7.4 with surface pH values of ~7.5–9.0. Thus, the dissolved oxygen and pH profiles measured in Asylum, Woods, and Brewster Lakes appear to be typical of lakes in southwest Michigan.

4.2 Alkalinity and Carbonate Speciation

Total alkalinity, which is likely dominated by carbonate alkalinity in these lake column waters, increases

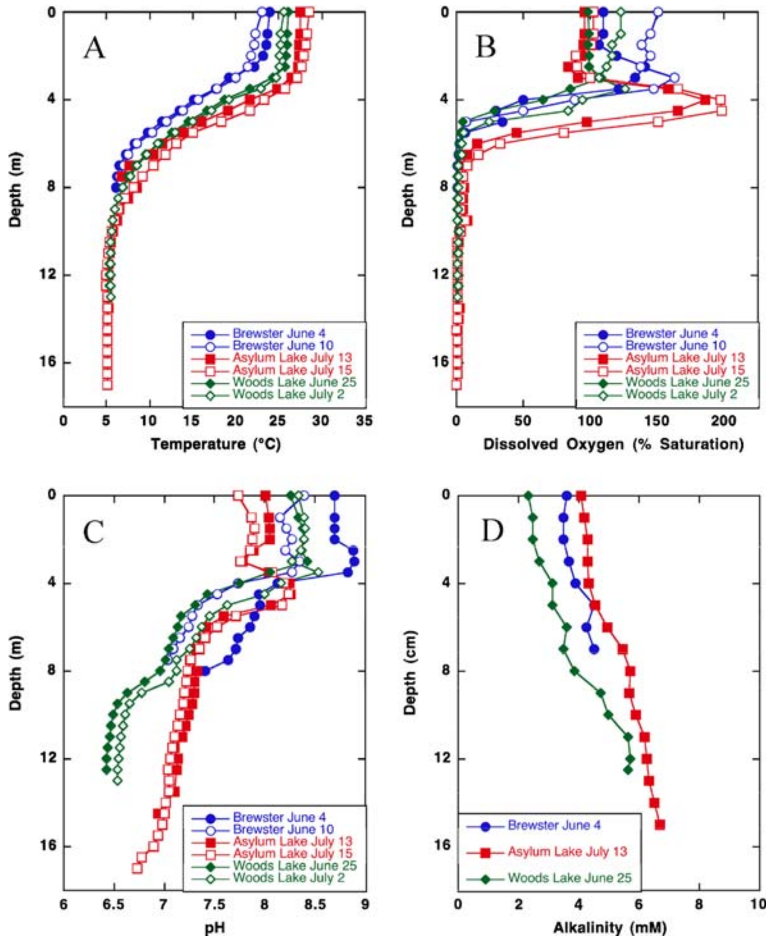

Fig. 3 **a** Temperature, **b** dissolved oxygen, **c** pH, and **d** total alkalinity profiles at Brewster Lake (*circles*), Asylum Lake (*squares*), and Woods Lake (*diamonds*)

gradually with depth in all three lakes (Fig. 3d). Carbonate alkalinity is produced by anaerobic respiration (aerobic respiration does not produce alkalinity) and carbonate mineral dissolution (e.g., Koretsky et al. 2007). The quantity of carbonate alkalinity produced by anaerobic respiration depends on the terminal electron acceptor: respiration of one mole of carbon via Mn(IV), Fe(III), or sulfate respiration produces 4, 8, or 1 mol of carbonate alkalinity, respectively (Koretsky et al. 2007). The higher alkalinity at Asylum Lake likely reflects greater organic matter productivity, as is suggested by the very large subsurface dissolved oxygen peak compared to the other lakes. The increase in alkalinity with depth in the three lakes is probably the result of anaerobic respiration of organic matter, although dissolution of carbonates could also contribute alkalinity.

Speciation calculations were completed to assess changes in carbonate mineral saturation in the lake column waters as a function of depth. Saturation indices (log of the ion activity product divided by the mineral solubility product) were calculated with the software JCHESS (Van der Lee and de Windt 2000) using the default thermodynamic database (based on the EQ3 database). A saturation index greater than zero indicates supersaturation, whereas a saturation index less than zero indicates undersaturation, of the lake water with respect to the mineral. At each depth, measured pH and concentrations of cations (Mg, Ca, Na, K, Fe(II), Mn(II), NH_3), chloride, and total carbonate were used to assess the saturation state of a suite of minerals including aragonite, dolomite, calcite, rhodochrosite, and siderite. For these calculations, total carbonate levels were assumed to be equal to the measured total alkalinity concentrations.

Table 1 DO and pH data as a function of depth for several lakes in Kalamazoo County, Michigan (location of Asylum and Woods Lakes) and Barry County, Michigan (location of Brewster Lake)

Lake, date sampled, county	Depth (m)	Temperature (C)	DO (mg/L)	pH	Total specific conductance (μS/cm)
Austin Lake, August 1, 2005, Kalamazoo County	0.3	27.5	8.4	9.0	371
	1.1	27.5	8.6	9.0	372
	2.0	27.0	9.0	9.1	371
Clear Lake, August 12, 2003, Barry County	0.6	24.0	7.5	7.5	86
	3.7	23.0	1.3	6.9	88
	4.9	18.5	0.3	6.6	106
Crooked Lake, August 19, 2004, Barry County	0.9	22.0	8.4	8.3	329
	5.8	20.5	3.6	7.6	334
	13.1	11.0	0.4	7.4	377
Duncan Lake, August 12, 2003, Barry County	1.5	24.5	8.8	8.1	474
	4.0	21.0	0.9	7.4	519
	15.5	6.5	0.5	7.0	613
Leach Lake, August 11, 2003, Barry County	0.9	25.5	8.0	8.2	369
	4.6	18.5	1.3	7.4	424
	10.1	6.5	0.4	7.1	446
Long Lake, August 12, 2003, Kalamazoo County	0.9	24.5	8.1	8.1	307
	7.3	9.5	0.9	7.2	359
	12.2	6.0	0.5	7.0	367
Sherman Lake, August 5, 2004, Kalamazoo County	0.9	25.5	8.5	8.4	179
	7.3	18.5	1.3	6.8	211
	9.1	14.0	0.7	6.9	253
Thornapple Lake, August 11, 2003, Barry County	0.6	24.0	11.5	8.0	497
	3.0	21.5	0.5	7.2	565
	6.1	14.0	0.2	7.1	678
Whitford Lake, August 5, 2004, Kalamazoo County	0.9	25.0	7.6	7.8	360
	6.1	19.0	1.6	7.3	420
	8.5	11.5	0.9	7.3	459

Data were compiled from the Surface Water Information Management System (SWIMS) (2011)

DO dissolved oxygen

The speciation calculations demonstrate that calcite, aragonite, and dolomite are supersaturated in the epilimnion of Asylum Lake (Fig. 4). Supersaturation with respect to calcite and physical evidence of calcite precipitation has been observed in the epilimnia of many other lakes of southern Michigan (e.g., Hamilton et al. 2009). Saturation indices of all three minerals decrease in the metalimnion at Asylum Lake, reaching values close to saturation with respect to aragonite and in the hypolimnion. In the epilimnion of Woods Lake, calcite and aragonite are slightly supersaturated, becoming increasingly undersaturated with depth. The saturation index profiles at Woods and Asylum Lake are consistent with precipitation of calcite in the epilimnia and dissolution of calcite occurring in the deeper lake waters. This calcite dissolution may contribute to the increased alkalinity with depth observed at Woods and Asylum Lakes (Fig. 3d). Dolomite, which is typically near saturation in the groundwaters of southwest Michigan (Szramek et al. 2004), remains undersaturated, as observed in other lakes in southern Michigan (Hamilton et al. 2009). Although total alkalinity is slightly higher at Brewster Lake compared to Woods

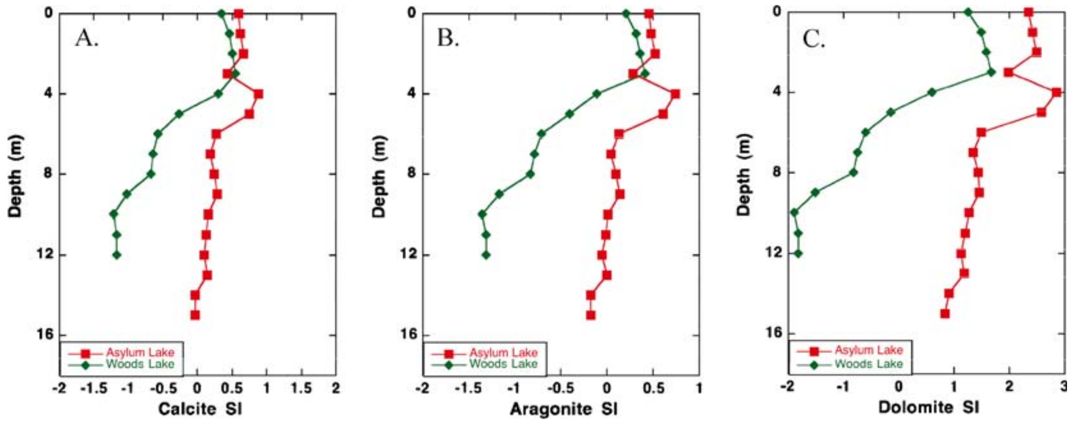

Fig. 4 Saturation indices of **a** calcite, **b** aragonite, and **c** dolomite calculated using datasets from July 13 at Asylum Lake (*squares*) and from June 25 and July 2 at Woods Lake (*diamonds*)

Lake, carbonate minerals are significantly undersaturated (SI<−3) throughout the water column and therefore are unlikely to contribute to the observed changes in alkalinity with depth.

4.3 Redox Stratification

Redox stratification is evident in the water columns of all three lakes (Fig. 5). Reduction of Mn(IV) (hydr) oxides produces dissolved Mn(II) at depths as shallow as 4 m at Woods Lake, accumulating to greater than 50 μM by 9 m depth (Fig. 5a). Dissolved Fe(II), produced from reduction dissolution of Fe(III) (hydr) oxides, appears slightly deeper in the lake column, with concentrations increasing dramatically below 8 m depth and exceeding 200 μM by 12 m depth (Fig. 5b). In the anoxic portion of the water column, ammonification is the likely source of dissolved ammonia, which also increases rapidly with depth, reaching nearly 700 μM at 12 m depth (Fig. 5c). Accumulation of high levels of dissolved Mn(II) occurs at even shallower depths in Brewster Lake (Fig. 5a), although there is little or no Fe(II) in the lake column (Fig. 5b). Ammonium levels increase below 4 m at Brewster Lake, reaching ~200 μM at 7 m depth (Fig. 5c). Similarly, at Asylum Lake, both Mn(II) and ammonia increase with depth in the anoxic hypolimnia, but Fe(II) is absent (Fig. 5).

The measured profiles demonstrate anaerobic respiration in the water columns of all three lakes. At Woods and Asylum Lakes, production of organic matter is undoubtedly stimulated by the anthropogenic addition of nitrogen and phosphorous from fertilizers; detergents, leaky septic tanks, and yard debris

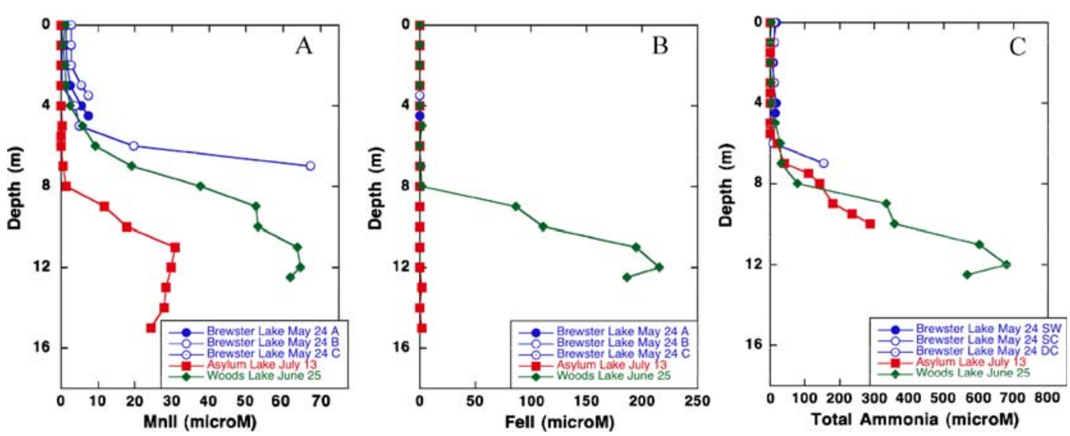

Fig. 5 **a** Fe(II), **c** Mn(II), and **d** total NH_3 profiles at Brewster Lake (*circles*), Asylum Lake (*squares*), and Woods Lake (*diamonds*)

may also play a role, both by directly contributing labile organic matter and also by supplying limiting nutrients that stimulate enhanced organic matter productivity (e.g., Kieser and Associates 1997). Of the three lakes, Asylum Lake has the least accumulation of dissolved Mn(II) and Fe(II), in spite of the very large subsurface maxima in dissolved oxygen which suggests greater photosynthetic activity compared to the other lakes. A distinct sulfidic odor could be detected in the anoxic waters. Sulfide production could result in stripping of dissolved Fe(II) from the lake column at Asylum Lake, but this cannot be confirmed because dissolved sulfide was not analyzed. Another possibility is that Woods Lake is much more impacted by surface water runoff than Asylum Lake, both due to the direct discharge of the storm water sewers into the lake and because of the sharp slopes (up to 24% gradient) located on the east side of the lake (Kieser and Associates 1997). Although the composition of the soils surrounding Woods and Asylum Lakes are similar, a greater quantity of Fe oxide-rich particulates might be flushed into Woods Lake, resulting in greater accumulation of dissolved Fe(II) in the lake column.

Brewster Lake, while much less impacted by anthropogenic activities than the two urban lakes, nonetheless displays rapid loss of dissolved oxygen and significant accumulation of dissolved Mn with depth. The Houghton muck soils surrounding Brewster Lake may provide a natural source of organic matter, stimulating primary productivity and summertime development of anoxia in the lake column. Hypoxia or anoxia has been noted during summer in the water columns of other lakes located in rural Barry County (Table 1). Although some of these lakes are likely more impacted by residential development (e.g., leaky septic tanks, runoff from yards) and agricultural activities (e.g., runoff of animal wastes and fertilizers) than the relatively isolated Brewster Lake, some are also surrounded by mostly undeveloped areas and, like Brewster Lake, become hypoxic or anoxic in summer.

Accumulation of dissolved Fe(II), Mn(II), and ammonia associated with anaerobic respiration has also been reported in Third Sister Lake, located in southeastern Michigan a few miles to the west of Ann Arbor, Michigan (Judd et al. 2005). Third Sister Lake is a kettle lake (3.85 ha), which, like Woods and Asylum Lakes, is located in an urbanized setting. In spring, Mn(II) levels at Third Sister Lake have been reported to reach 85 μM, with Fe(II) concentrations of up to 150 μM, by 15 m depth, comparable to the concentrations measured in the bottom waters of Woods Lake. Ammonia levels are likewise reported to increase with depth at Third Sister Lake, reaching ~960 μM in the bottom waters. The similarity in the chemistry of these lakes suggests that the geochemistry of Woods and Asylum Lakes is typical of kettle lakes in suburban or urban environments of this region.

4.4 Lake Salinization

Although Woods, Brewster, and Asylum Lakes have similar temperature profiles and all exhibit distinct redox stratification in the water column with anoxic hypolimnia, there are clear differences between urban Woods and Asylum Lake and rural Brewster Lake with respect to conductivity, chloride, and sodium profiles (Fig. 6). In the epilimnia and metalimnia, conductivity is the greatest at Asylum Lake and the lowest at Brewster Lake (Fig. 6a). Conductivity increases gradually with depth at Asylum and Brewster Lakes and increases rapidly in the metalimnion of Woods Lake, reaching levels equivalent to those at Asylum Lake in the hypolimnion (Fig. 6a). Differences in chloride and sodium profiles are even more dramatic: Chloride and sodium levels in urban Woods and Asylum Lakes are similar and reach concentrations more than 100 times greater than those observed in rural Brewster Lake (Fig. 6b, c). Chloride levels in the deepest waters of Woods Lake exceed suggested chronic toxicity thresholds of 230 ppm (Environment Canada 2001). Correlations between conductivity and sodium or chloride are very strong at Asylum and Woods Lakes and much weaker at Brewster Lake, as expected if the major source of sodium and chloride to the urban lakes is road salt (Fig. 7). These data demonstrate the significant impact of urban land use, specifically the use of road salt as a deicer, on the water quality of the two urban lakes.

The distinct differences in the shapes of the conductivity curves at Asylum and Woods Lake most likely reflect differences in both the salinity sources and the hydrology of the two lakes. The greater conductivity and concentrations of sodium and chloride at the surface of Asylum Lake probably reflect the close proximity of a heavily trafficked state

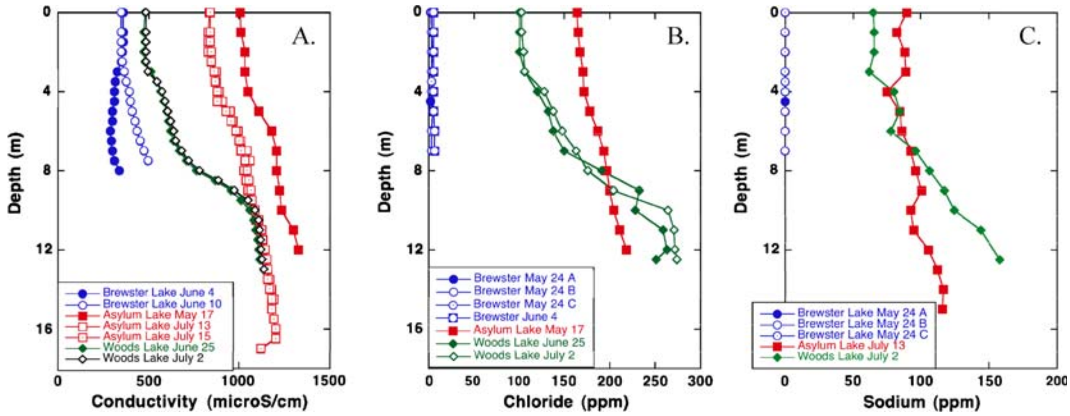

Fig. 6 **a** Conductivity, **b** chloride, and **c** sodium profiles at Brewster Lake (*circles*), Asylum Lake (*squares*), and Woods Lake (*diamonds*). Note: Conductivity profile for Asylum Lake (May 17) converted from parts per million to micro-Siemens per centimeter assuming a conversion factor of 0.59

highway (US 131) located directly to the west of the lake. Prior studies suggest that salt from US 131 flows into the lake with the shallow groundwater and that salt is lost from the lake via surface and groundwater outflow on the east side of the lake (Sauck and Barcelona 1992). The greater accumulation of salinity with depth at Woods Lake may reflect slower discharge compared to Asylum Lake. Residence times of water in Woods Lake are not well-known, but the available data suggest that there is only slow leakage of water from the lake to the underlying aquifer (Kieser and Associates 1997).

The specific conductivity, sodium, and chloride levels measured in Woods and Asylum Lakes are within the ranges reported for other urban lakes. For example, Judd et al. (2005) report specific conductivity values of 1,100–1,800 μS/cm, Na levels of ~140–260 ppm, and Cl concentrations of ~220–445 ppm in Third Sister Lake, located in southeast Michigan. Early studies of Third Sister Lake suggest that mean chloride levels increased from ~19–260 ppm between 1981 and 1999. Novotny et al. (2008) report mean chloride levels of 132 and 186 ppm in the top and bottom waters of urban lakes in Minnesota, with mean sodium concentrations of 73 and 105 ppm and mean specific conductivities of 745 and 988 μS/cm. Investigators in Minnesota (Novotny et al. 2008), Michigan (Bridgeman et al. 2000), New Hampshire (Rosenberry et al. 1999; Likens and Buso 2010), Norway (Kjensmo 1997), and Sweden (Thunqvist 2003) all report increasing levels of chloride or specific conductance in urban lakes and strong correlations between specific conductivity and chloride levels. Taken together, these data suggest that

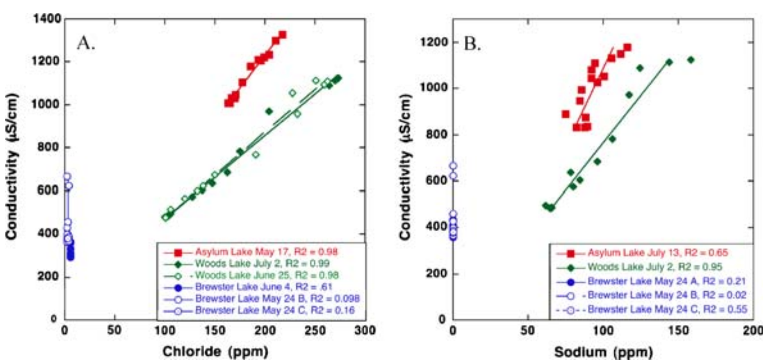

Fig. 7 Conductivity versus **a** chloride and **b** sodium profiles at Brewster Lake (*circles*), Asylum Lake (*squares*), and Woods Lake (*diamonds*). Note: Conductivity profile for Asylum Lake (May 17) converted from parts per million to micro-Siemens per centimeter assuming a conversion factor of 0.59

salinization of urban lakes due to road salt application is a widespread problem that continues to increase with time. Specific conductivity levels measured at Brewster Lake are similar to those observed in other rural lakes in this region (e.g., Table 1). The much lower conductivity levels in these lakes relative to lakes in urban settings suggest that these lakes have, so far, been much less impacted by road salt deicers.

4.5 Major Elements (Potassium, Magnesium, Calcium)

Dissolved potassium levels are similar at Woods and Asylum Lakes and, as for sodium and chloride, are much greater than at Brewster Lake (Fig. 8a). Potassium substitutes readily for sodium in halite (Deer et al. 1996); thus, the elevated potassium levels at Woods and Asylum Lakes could be a result of road salt input. Another possibility is that runoff impacted by fertilizer with high levels of potassium impacts the urban lakes to a much greater extent than Brewster Lake. Calcium levels are variable in the three lakes, with the highest concentrations in Asylum Lake and the lowest at Brewster Lake (Fig. 8b). This could reflect differences in the soil geochemistry at these three sites. However, a more likely source of the difference is again road salt, particularly given the similarity in soil types surrounding Woods and Asylum Lakes. Calcium chloride deicers are sometimes used by the Michigan Department of Transportation (Grand Rapids Press 2007), which is responsible for clearing US 131 to the west of Asylum Lake. Likewise, the elevated magnesium levels in Asylum Lake compared to Brewster and Woods Lakes (Fig. 8c) could be the result of application of calcium magnesium acetate road deicer, or perhaps has been contributed by other anthropogenic sources near the lake (e.g., leaf compost pile, septic tanks, orchards). It is also possible that ion exchange in the sediments near the urban lakes contributes elevated magnesium and calcium in response to the flow-through of high concentrations of sodium. For example, Judd et al. (2005) report that calcium and potassium levels doubled in Third Sister Lake between 1981 and 2004, which they attribute to cation exchange on clay minerals between these elements and sodium.

5 Conclusions

Rural Brewster Lake and urban Woods and Asylum Lakes are all anoxic below 5–7 m depth and show distinct redox stratification in the water column, with significant accumulation of reduced solutes (e.g., Mn(II), Fe(II), ammonia) in the lake bottom waters. Asylum and Woods Lakes, however, have much higher specific conductivity, chloride, sodium, calcium, and potassium levels compared to Brewster Lake. Chloride, sodium, and potassium levels are elevated by 100 times or more in the urban lakes compared to the rural lake, with chloride levels sometimes exceeding chronic toxicity levels. The much increased concentrations of these solutes in urban lakes reflect greater input by anthropogenic activities, specifically application of road deicers in the surrounding water-

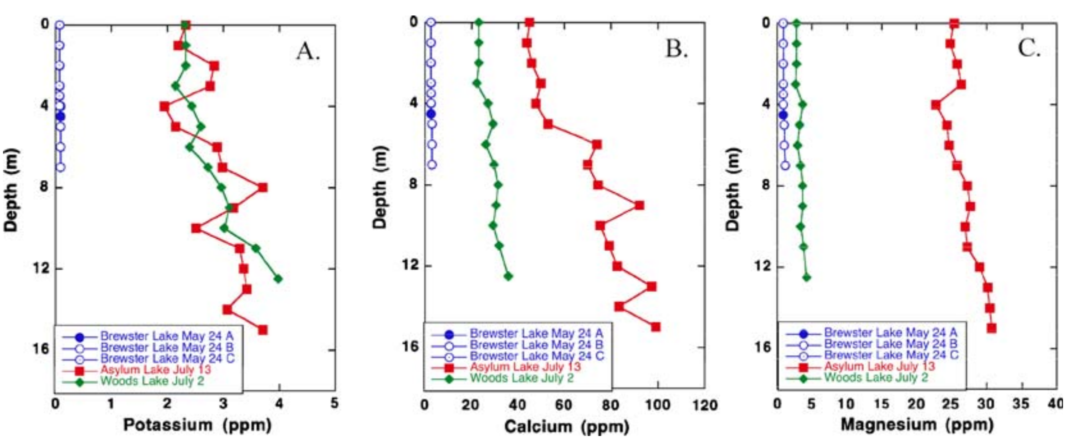

Fig. 8 Total **a** potassium, **b** calcium and **c** magnesium profiles at Brewster Lake (*circles*), Asylum Lake (*squares*), and Woods Lake (*diamonds*)

sheds. Although this study considered only summer lake column geochemistry, it is likely that the elevated salinity observed in these urban lakes diminishes or delays lake mixing in fall and spring. This is expected to have detrimental effects on the aquatic ecosystems of these eutrophic lakes because mixing introduces oxygenated water to the anoxic bottom waters. Without such mixing, or with diminished or delayed mixing, the lake column could become permanently stratified with persistent anoxia in the deepest waters. This is expected to further exacerbate eutrophication in these lakes because permanent anoxia in the bottom waters will reduce binding of phosphorous in the lake sediments, although the lack of physical mixing may slow replenishment of phosphorous from the bottom waters to the surface waters. Further study, including detailed seasonal and yearly sampling of urban kettle lakes like these, will be required to establish the influence of elevated salt levels on lake mixing and ecosystem function.

Acknowledgments Funding support from the Pierce Cedar Creek Institute URGE program, the National Science Foundation CAREER program (NSF-EAR 0348435), and the National Science Foundation Geosciences Education program (NSF-GEO 0807578) is gratefully acknowledged. Logistical support from PCCI staff, especially Matt Dykstra, is much appreciated. We also wish to thank Thomas Reich, Michelle Barger, Sara Snyder, and Greg Sawatzki for their assistance with laboratory and field work. We also appreciate comments from the editor and two anonymous reviewers, which greatly improved this paper.

References

Amrhein, C., Strong, J. E., & Mosher, P. A. (1992). Effect of deicing salts on metal and organic matter mobilization in roadside soils. *Environmental Science and Technology, 26*, 703–709.

Boyer, B., & Kieser, M. (2008). Technical memorandum re: Kalamazoo foundation grant, Woods Lake-Kensington Stormwater Monitoring Summary.

Bridgeman, T. B., Wallace, C. D., Carter, G. S., Carvajal, R., Schiersari, L. C., Aslam, S., et al. (2000). A limnological survey of Third Sister Lake, Michigan with historical comparisons. *Journal of Lake and Reservoir Management, 16*, 253–267.

Bubeck, R. C., Diment, W. H., Deck, B. L., Baldwin, A. L., & Lipton, S. D. (1971). Runoff of deicing salt: Effect on Irondequoit Bay Rochester, New York. *Science, 172*, 1128–1132.

Bubeck, R.C., & Burton, R.S. (1989). Changes in chloride concentrations, mixing patterns, and stratification characteristics of Irondequoit Bay, Monroe Country, New York, after decreased use of road-deicing salts, 1974–1984. Water Resources Investigation, 87-4223. Reston: USGS.

Davison, W. (1993). Iron and manganese in lakes. *Earth Science Reviews, 34*, 119–163.

Deer, W. A., Howie, R. A., & Zussman, J. (1996). *An introduction to the rock-forming minerals* (2nd ed.). London: Prentice Hall.

Canada, E. (2001). *Priority substance list assessment report: Road salts* (p. 171). Gatineau: Environment Canada.

Godwin, K. S., Hafner, S. D., & Buff, M. F. (2003). Long-term trends in sodium and chloride in the Mohawk River, New York: The effect of fifty years of road-salt application. *Environmental Pollution, 124*, 273–281.

Grand Rapids Press (2007). MDOT using beets to de-ice roads. December 11, 1007.

Grasshoff, K., Ehrhardt, M., & Kremling, K. (1983). *Methods of seawater analysis* (2nd ed.). Germany: Verlag Chemie.

Hamilton, S. K., Bruesewitz, D. A., Horst, G. P., Weed, D. B., & Sarnelle, O. (2009). Biogenic calcite–phosphorus precipitation as a negative feedback to lake eutrophication. *Canadian Journal of Fisheries and Aquatic Sciences, 66*, 343–350.

Holderread, A.T., & Aljobeh, Z. (2008). Water quality and hydrology in the Cedar Creek watershed within the PCCI property. Pierce Cedar Creek Institute URGE final report. Available at: http://www.cedarcreekinstitute.org/bfs/urge/research_findings/.

Honsowitz, A., & Roher, T.K. (2005). Bathymetric mapping and baseline limnological study of Brewster Lake, Barry County, Michigan. Pierce Cedar Creek Institute URGE final report. Available at: http://www.cedarcreekinstitute.org/bfs/urge/research_findings/.

Judd, J. H. (1970). Lake stratification caused by runoff from street deicing. *Water Research, 4*, 521–532.

Judd, K. E., Adams, H. E., Bsoch, N. S., Kostrezewski, J. M., Scott, C. E., Schultz, B. M., et al. (2005). A case history: Effects of mixing regime on nutrient dynamics and community structure in Third Sister Lake, Michigan during late winter and early spring 2003. *Lake and Reservoir Management, 21*, 316–329.

Kalamazoo Nature Center (2002) Western Michigan University: Asylum Lake Property. Historical uses and land cover, natural features inventory, and habitat enhancement recommendations. Report to the Asylum Lake Preservation Council. www.wmich.edu/asylumlake/.

Kaushal, S. S., Groffman, P. M., Likens, G. E., Belt, K. T., Stack, W. P., Kelly, V. R., et al. (2005). Increased salinization of fresh water in the northeastern United States. *Proceedings of the National Academy of Sciences, 102*, 13517–13520.

Kieser & Associates. (1997). *Woods lake water quality study. Report for the City of Kalamazoo, Michigan*. Kalamazoo: Kieser & Associates.

Kjensmo, J. (1997). The influence of road salts on the salinity and the meromictic stability of Lake Svinsjoen, southeastern Norway. *Hydrobiologia, 347*, 151–158.

Koretsky, C. M., Haveman, M., Beuving, L., Cuellar, A., Shattuck, T., & Wagner, W. (2007). Spatial variation of redox and trace metal geochemistry in a minerotrophic fen. *Biogeochemistry, 86*, 33–62.

Likens, G. E., & Buso, D. C. (2010). Salinization of Mirror Lake by road salt. *Water, Air, and Soil Pollution, 205*, 205–214.

Marsalek, J. (2003). Road salts in urban stormwater: An emerging issue in stormwater management in cold climates. *Water Science and Technology, 48*, 61–70.

Mayer, T., Snodgrass, W. J., & Morin, D. (1999). Spatial characterization of the occurrence of road salts and their environmental concentrations as chlorides in Canadian surface waters and benthic sediments. *Water Quality Research Journal of Canada, 34*, 545–574.

Mayer, T., Rochfort, Q., Borgmann, U., & Snodgrass, W. (2008). Geochemistry and toxicity of sediment porewater in a salt-impacted urban stormwater detention pond. *Environmental Pollution, 156*, 143–151.

McGinley, P. M. (2008). Modeling the influence of land use on groundwater chloride loading to lakes. *Lake and Reservoir Management, 24*, 112–121.

Meriano, M., Eyles, N., & Howard, K. W. F. (2009). Hydrogeological impacts of road salt from Canada's busiest highway on a Lake Ontario watershed (Frenchman's Bay) and lagoon, City of Pickering. *Journal of Contaminant Hydrology, 107*, 66–81.

Molot, L. A., & Dillon, P. J. (2008). Long-term trends in catchment export and lake concentrations of base cations in the Dorset study area, central Ontario. *Canadian Journal of Fisheries and Aquatic Science, 65*, 809–820.

Norrstrom, A. C. (2005). Metal mobility by de-icing salt from an infiltration trench for highway runoff. *Applied Geochemistry, 20*, 1907–1919.

Novotny, E. V., Murphy, D., & Stefan, H. G. (2008). Increase of urban lake salinity by road deicing salt. *Science of the Total Environment, 406*, 131–144.

Paul, M. J., & Meyer, J. L. (2001). Streams in the urban landscape. *Annual Reviews in Ecology System, 32*, 333–365.

Ramakrishna, D. M., & Viraraghavan, T. (2005). Environmental impact of chemical deicers—a review. *Water, Air, and Soil Pollution, 166*, 49–63.

Rosenberry, D. O., Bukaveckas, P. A., Buso, D. C., Likens, G. E., Shapiro, A. M., & Winter, T. C. (1999). Movement of road salt to a small New Hampshire lake. *Water, Air, and Soil Pollution, 109*, 179–206.

Salt Institute (2011). www.saltinstitute.org.

Sarazin, G., Michard, G., & Prevot, F. (1999). A rapid and accurate spectroscopic method for alkalinity measurements in sea water samples. *Water Research, 1*, 290–294.

Sauck, W.A., & Barcelona, M.J. (1992). Final project report: Long-term hydrogeological research and education test site, Western Michigan University.

Schindler, D. W., Hecky, R. E., Findlay, D. L., Stainton, M. P., Parker, B. R., Paterson, M. J., et al. (2008). Eutrophication of lakes cannot be controlled by reducing nitrogen input: results of a 37-year whole-ecosystem experiment. *Proceedings of the National Academy of Science, 105*, 11254–11258.

Stumm, W., & Morgan, J. J. (1996). *Aquatic chemistry* (3rd ed.). New York: Wiley-Interscience.

Surface Water Information Management System (SWIMS), Department of Environmental Quality, Department of Natural Resources, Michigan. (2011). www.mcgi.state.mi.us/miswims/, visited March 2011.

Szramek, K., Walter, L. M., & McCall, P. (2004). Arsenic mobility in groundwater/surface water systems in carbonate-rich Pleistocene glacial drift aquifers. *Applied Geochemistry, 19*, 1137–1155.

Thunqvist, E. L. (2003) Increased chloride concentration in a lake due to deicing salt application. *Water Science and Technology, 48*, 51–59.

Thunqvist, E. L. (2004). Regional increase of mean chloride concentration in water due to the application of deicing salt. *Science of the Total Environment, 325*, 29–37.

Tiquia, S. M., Davis, D., Hadid, H., Kasparian, S., Ismail, M., Sahly, R., et al. (2007). Halophilic and halotolerant bacteria from river waters and shallow groundwater along the Rouge River of southeastern Michigan. *Environmental Technology, 28*, 297–307.

Tuchman, M. L., Stoermer, E. F., & Carney, H. J. (1984). Effects of increased salinity on the diatom assemblage in Fonda Lake, Michigan. *Hydrobiologia, 109*, 179–188.

USDA Natural Resources Conservation Service Web Soil Survey. (2011). http://websoilsurvey.nrcs.usda.gov, visited March 2011.

Van der Lee, J., & De Windt, L. (2000). *CHESS tutorial and cookbook. User's guide Nr. LHM/RD/99/05 Fontainebleau*. France: CIG-Ecole des Mines de Paris.

Viollier, E., Inglett, P. W., Hunter, K., Roychoudhury, A. N., & Van Cappellen, P. (2000). The ferrozine method revisited: Fe(II)/Fe(III) determination in natural waters. *Applied Geochemistry, 15*, 785–790.

Wetzel, R. G. (2001). *Limnology: Lake and river ecosystems* (3rd ed.). San Diego: Academic.