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ABSTRACT

Mirror Lake, one of the scenic locations on The Ohio State University's campus, experiences an intense bioturbation event as part of an annual tradition revolving around the rivalry football game against the University of Michigan. This tradition involves thousands of students jumping into the lake over one night in the week leading up to the football game.

Water samples were collected from several locations in the lake before, during, and after the Mirror Lake Jump to determine the impact of this event on lake water chemistry. There were significant and systematic increases in the concentrations of Na^b, K^b, Cl^-, total nitrogen, ammonia, and dissolved organic

carbon (DOC) associated with the jump, especially in the eastern side of the lake where most of the students entered. Over the 3-h period from 10 p.m. to 1 a.m. on the eastern side of the lake, Na^b, K^b, and Cl^- concentrations increased by about 2e4 ppm, 1.5e3 ppm, and 4e6 ppm, respectively. The total nitrogen concentration increased about five to six fold, from 450e500 ppb to 2300e2800 ppb over the height of the event on the eastern side of the lake. Similar increases were observed for DOC, increasing from 3.6 to 18 ppm. This DOC increase was coincident with a 5‰ shift in $d^{13}C$, from a mean of around −28‰ in the early hours of the evening to a maximum of −23‰, implying a large influx of isotopically heavy carbon into the lake. Ammonia concentrations varied substantially from year to year, but always showed a systematic increase in concentration during the event. Smaller changes in major ion and nutrient concentrations were observed in the middle and western side of the lake, where fewer students entered the lake.

The changes in concentration and the timing and spatial distribution of these changes are primarily attributed to anthropogenic input from jumpers in the form of bodily fluids (e.g., evaporated sweat, sebum and urine). Over a single night, these anthropogenic event inputs represent roughly 10% of the annual nitrogen budget of the lake, emphasizing the direct impact humans can have on urban water bodies on short time scales.

1. **Introduction**

Water bodies in urban areas are often subjected to anthropogenic inputs of

nutrients, toxic metals, microorganisms, and other contaminants. Such inputs can include agricultural and lawn fertilizers; automobile, industrial, and pharmaceutical runoff; and recreational inputs (such as swimming, boating) (King and Mace, 1974). Over time, these inputs can result in ecologically detrimental conditions such as eutrophication or anoxia. Mirror Lake, an urban pond on The Ohio State University's campus, is an example of a small water body affected by anthropogenic nutrient input. Mirror Lake is located in the heart of Ohio State's campus and is considered a scenic location. Any unsightly algal growth or malodorous stench arising from nutrient loaded runoff into the lake severely damages the aesthetic qualities of this campus landmark.

1.1. *Background*

Mirror Lake is one of the scenic locations on the Ohio State University's campus and has been a subject of study over the past century (e.g. Marion et al., 2015; Goldsmith et al., 2013; Von Bargen et al., 2010; Herrick, 1984; Hull, 1971; Kraatz, 1921; Stehle, 1920). Early in the history of the university, Mirror Lake was a natural wetland that served as a source of drinking water for the university and the local community. The lake is managed by the University, which has changed the morphology and aerial distribution of the lake over time. During the time of the study, the lake morphology was constrained by brick paving stones along the bottom, and cemented limestone bricks along the sides to prevent erosion. Mirror Lake contains a total volume of approximately 2600 m^3 with a water depth ranging from about 1 m on the east end of the lake to about 2.5 m on the west end of the lake. Water level is maintained by inflow from the

municipal water pump (referred to as the Mirror Lake spring) on the east side of the lake and outflow to an engineered culvert leading to a storm drain on the west side of the lake (Fig. 1). The pump generally operates from March through the end of November, depending on weather conditions, and pumps about 2 million gallons into the lake over these months. Additional water inputs to the lake include rainfall, surface runoff from precipitation and irrigation, and groundwater infiltration. The lake is mixed and aerated by two fountains that circulate water within the lake and generally operate from March through November depending on weather conditions (e.g., ice cover on the lake). These fountains are removed before the event for safety. The lake is drained and cleaned periodically (in August 2009 and 2011 during the study) with high-pressure water hoses to remove physical debris, sediments, and algae from the floor and walls of the structure, but no chemicals are used during this process. After each cleaning, the lake is re-filled with municipal water. Debris, including leaves, is also removed from the lake periodically by the university's grounds crews.

During the time period of the study, the lake was home to dozens of domestic ducks, wild ducks and geese. Due to the physical isolation of the lake from other water bodies, there is limited opportunity for aquatic organisms to colonize the lake, however frogs and turtles are occasionally observed. Goldfish are conspicuous and are probably introduced by the local student population. Numerous micro and mezofauna (such as insect larva and amphipods) were also observed during sampling. A complete characterization of the flora and fauna of the lake was beyond the scope of this study.

Although swimming is prohibited in the area, university archives have noted that

students have entered Mirror Lake as part of evolving school traditions since the early 1900's, which have included "the tossing of freshman into the lake" (Herrick, 1984). The tradition discussed herein of students jumping into Mirror Lake the week before Ohio State plays University of Michigan in football began in 1990 with dozens of students jumping into the lake during a pep rally, however the size of the event has increased over time. During each of our sampling years (2008e2012), we observed roughly four to six thousand people entering the lake, most within an hour period around midnight (local news estimates were as high as 10,000 people participating in the event). The purpose of this study is to analyze the impact of this event on the chemistry and water quality of Mirror Lake.

2. **Methods**

Mirror Lake water samples were collected before, during, and after the events in November 2008 to 2012. The sampling locations and frequency evolved each year based on the results of the previous year and the availability of volunteers to collect samples. Only limited sampling of the event occurred in 2008, when surface water was collected from the spring and surface water was sampled on the east and west sides of the lake before, during, and after the event (Fig. 1). Based on the results of the 2008 analyses, changes to the sampling plan were made in subsequent years to characterize the impact of the disturbance on the lake water chemistry. Spring and east (MLE) and west (MLW) side surface water samples were collected on several occasions in 2009 and 2010 starting about two months before the event. Samples were also collected more frequently during event, from hourly during the time when there were only a few

dozen people jumping in (~8e10 p.m.) to every 30 min when there were hundreds to thousands of students jumping in the lake (~10 p.m.e1 a.m.). In 2010, additional water samples were collected at approximately the midpoint (MLM) of the lake along the southern edge to constrain the effect of 'jumper density' on the change in lake water chemistry. Deep water samples were also collected at MLE, MLM, and MLW before and after the event, although no deep water samples were collected during the event because the use of the long sampling pole would have been a hazard to the researchers and the participants. All surface water lake samples were taken in close proximity to the bank with the exception of the sampling in 2011, when we were able to obtain the assistance of one of the participants to collect water samples from the middle of the lake (MOL) during the height of the event. Fewer water samples were collected in 2012, though additional analyses were performed on these samples. Samples of the spring, Columbus municipal water that feeds the lake, were collected periodically during the study. During the 2008e2011 events, the spring was not actively running the evening of the event; it had been turned off earlier in the day for safety. The spring appeared to be actively flowing for the duration of the 2012 event.

Surface water samples were collected in cleaned LDPE bottles that were rinsed three times with the sample, capped, and then transported back to the laboratory. In 2010, deep water samples were collected with either a new, cleaned, upright dustpan (Oct 24, 2010 samples) to investigate the effect of disturbing bottom sediments on water chemistry, or using a cleaned HDPE bottle secured on the end of a 10 foot PVC pole. The deep water sampler was constructed of a 1 L wide-mouth HDPE Nalgene bottle, a rubber stopper attached to a string, and flexible tubing attaching the rubber stopper to

the bottle.

Temperature, pH, dissolved oxygen, and specific conductivity of surface waters for some samples were measured *in situ* with a ThermoOrion 5 star multi-meter during the 2009 and 2010 events. In later years these parameters were measured on water samples taken back to the laboratory. The electrodes were placed in the water and allowed to equilibrate for several minutes before the measurements were taken. We were unable to measure these parameters on our deepest water samples because the electrode cables were too short. We were also unable to measure these parameters during the height of the jump without risking damage to equipment or injury to our volunteers. During the sampling we made notes of physical characteristics such as water clarity and turbidity, debris in or on the water (mostly leaves), and flora and fauna in the lake and the immediate surrounding area.

In order to estimate the impact of the jump on re-suspending sediments from the lake bottom, we collected bottom sediments and water from the east and west sides of the lake using the upright dustpan attached to a long pole. The pan was scraped along the bottom of the lake along the stone pavers, disturbing an area of approximately 2 square feet. Separate water samples were collected in 2010 in order to determine suspended load and the contribution of suspended sediments to the water column chemistry.   The total suspended solids (TSS) were determined gravimetrically using Whatman GF/F 0.7 mm pore size glass microfiber filters. The filters were weighed, a known volume of water was filtered, and then the filters were reweighed after air-drying at 60 °C overnight.
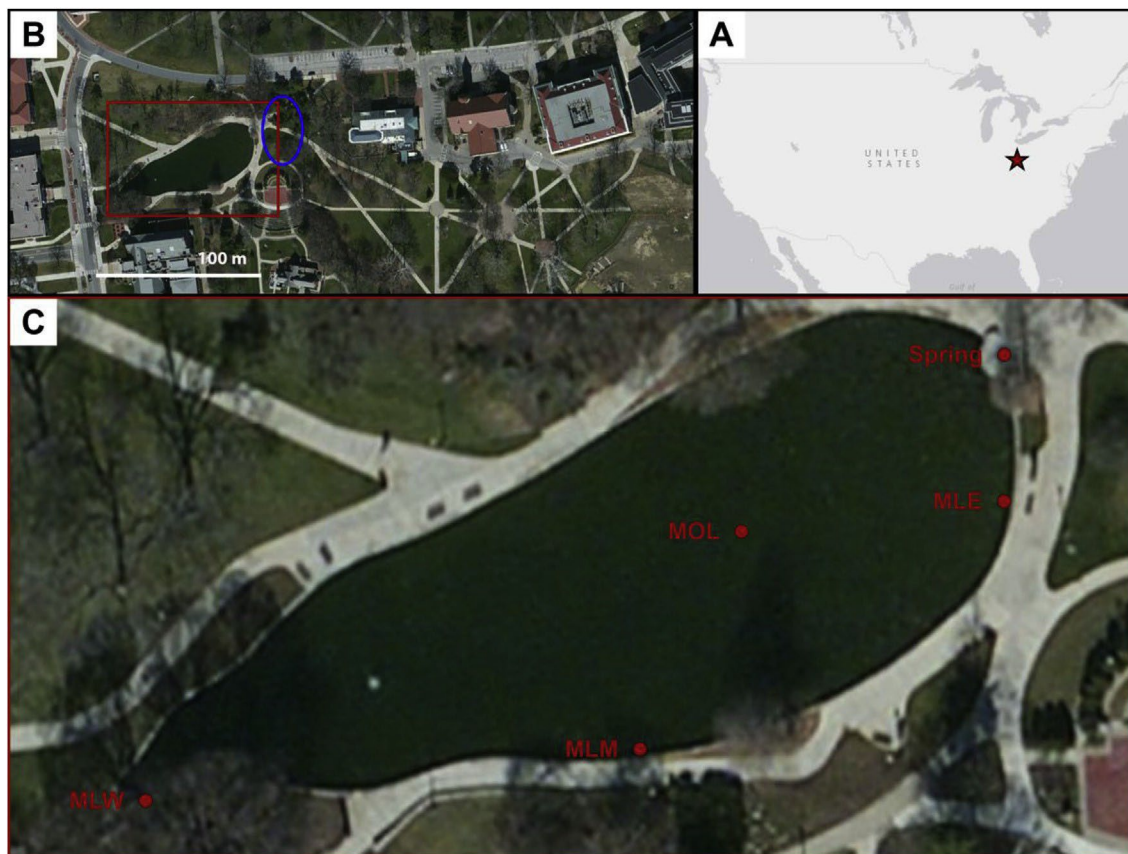
Fig. 1. A) Location of Ohio State (red star) within the continental United States. B) Location of Mirror Lake (red box) on Ohio State's campus with academic buildings, pedestrian walkways, and roads nearby. Sediment and soil samples used in the leach experiment were collected from the area just east of the lake (blue oval) C) Mirror Lake locations (red circles) sampled during this study. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.1. *Chemical analysis*

Water samples were transported back to the laboratory and filtered into clean LDPE bottles using 20 ml plastic syringes and 0.45 mm pore size Whatman syringe filters within hours of collection. Separate aliquots were collected for major ions, nutrients, and dissolved organic carbon. The samples for major ions were stored in the refrigerator until analysis. Nutrient samples were generally stored in the refrigerator and analyzed within several days of collection, although in some years, nutrient samples were stored frozen for several days before analysis. Major cations (Na^+, K+, Mg^{2+},

Ca^{2+}) and anions (Cl$^-$, NO$^-$, SO$_4^{2-}$) were analyzed using a Dionex DX120 Ion Chromatograph following the methods described by Welch et al. (2010). Nutrients, phosphate (PO$_4^{3-}$), total phosphorus (TP), ammonia (NH$_4^+$), nitrate + nitrite (NO$_3^-$ þ NO$_2^-$), total nitrogen (TN), and silica (as SiO$_2$) were measured colorometrically with a Skalar Sanþþ nutrient analyzer following the methods supplied by the manufacturer. Dissolved organic carbon (DOC) and d^{13}C of the DOC was analyzed using an IO Analytical 1030 carbon analyzer attached to a Picarro G1111 cavity ring down spectrometer (CRDS). Aliquots of the major ion samples were acidified with 1% trace metal grade nitric acid and then trace metals were measured using a ThermoFinnigan Element 2 ICP-Sector Field Mass Spectrometer (ICP MS).

2.2. *Leach experiments*

In order to determine the impact of sediment input on the chemistry of the water into the lake during the jump, we collected surface soil samples from several areas around the lake (Fig. 1). Wet samples were leached overnight (1:5 sediment:water wt:wt) in MilliQ ™ deionized water and then filtered. The water samples were then analyzed using the methods described above.

3. **Results**

In each of the five years of this study, the effects of the event on the physical and chemical properties of the lake were similar. Roughly four to six thousand jumpers were seen frolicking in Mirror Lake over the 5-h period between 8 p.m. and 1 a.m. during the 2008-2012 events. The local authorities encouraged the

participants and the researchers to be elsewhere at approximately 12:30 a.m., and people were prohibited from being in or near the lake after 1:00 a.m. A height of activity was observed between 11:00 p.m. and 12:30 a.m., during which time dozens of people per minute were observed jumping into the lake and roughly 100-500 people were in the lake at any given moment. This activity, concentrated in the eastern, shallow side of the lake (MLE), significantly altered the physical and chemical properties of the lake both during the jump and in the day following. The jumpers increased the turbidity of the lake by tracking in dirt and debris when they entered the lake and by disturbing the thin layer of sediments (predominately decaying leaves, alga, and fecal matter from native fauna).

There was a small but systematic change in the major ion compositions of the lake associated with the event, particularly on the shallow eastern side where most of the jumping occurred. This was most apparent in the change in $Na^{\flat}$, $K^{\flat}$ and Cl^- concentrations. However, nutrient levels in the lake, particularly nitrogen species and DOC, increased several times above background levels.

3.1. *Physical properties*

Physical properties (temperature and water clarity) were measured or noted during sampling of the lake water, and these properties varied over time. Water temperature was typically recorded when samples were collected prior to the event and ranged from a high of 20 $^\circ$C during late September to a low of 3 $^\circ$C just before the 2009 event. Small differences in water temperature (~1 $^\circ$C) were measured between surface and deep water or sunny versus shaded side of the lake during the

September and October sampling. Due to the difficulties in using the multimeter during the height of the event, water temperature was not routinely measured. However, in 2009 the water temperature on the east side of the lake increased from 3 to 4 $^{\circ}C$ over approximately 3 h during the event when the air temperature decreased to near freezing, suggesting body heat contributed to the temperature change.

Visual determination of lake water clarity was noted every time water samples were collected but it was not explicitly measured. The bottom of the lake was clearly visible during daylight hours for the MLE (~1 m) and MLM (~1.6 m) sites. The brick paving stones that lined the bottom of the lake and the leaves that fell into the lake from the surrounding trees were easily observable. However, at the deeper (~2.5 m) and shadier MLW site the lake bottom was not visible. The lake bottom sediments that were collected from the shallow and deep sides in 2010 were composed primarily of leaves and decaying algae.

During the events, the water became increasingly turbid due to jumpers tracking dirt and mud into the lake, and from stirring up bottom sediments. This turbidity change was quantified in 2010 by measuring the total suspended solids (TSS) in the lake. Pre-jump TSS levels ranged from ~2 to 4 mg/L throughout the lake and increased to roughly 400 mg/L, 30 mg/L, and 15 mg/L at MLE, MLM, and MLW, respectively (Fig. 2). By the next morning, TSS at MLE had decreased tenfold to ~30 mg/L, TSS at MLM had dropped by half to ~15 mg/L, and TSS in the west side of the lake remained at ~15 mg/L. The observed TSS increase in the east side of the lake would correspond to about 4 g of sediment per 10 x 10 cm square of lake bottom being stirred up into the overlying water column. This amount of material is consistent with pre-jump

observations made using the dustpan to scrape sediments off the bottom, suggesting all the bottom sediments were suspended during the course of the event.

3.2. *Major element composition*

The composition of the lake before the event varied from year to year, but some trends were consistent every year the lake was sampled. The total dissolved solids (TDS) of the lake water samples ranged from ~130 to 160 ppm; its composition can be described as a Ca^{2+}-HCO_3^- water, reflecting the limestone lithology of the area. The major ion composition of surface water samples collected at any given time before the event were similar, and variations in concentrations from the east to west side were generally less than the analytical uncertainty for the ion chromatograph (Figs. 3 and 4 and Fig S1 for Na^+, Cl^- and K^+). With the exception of the water samples collected from the deepest part of the lake on the west side (~2.5 m deep), there was little discernible difference in the major element composition between surface and deep water samples, suggesting that the lake was well mixed even though the small temperature differences measured indicate the lake could be thermally stratified. The major element composition of the spring that feeds the lake is generally similar to the lake, but nutrient concentrations are substantially different. The major element composition of the lake does exhibit small changes in composition over time. For example, in 2009 the two month long bi-weekly sampling of the lake before the event showed that major element compositions (Na^+, K+, Mg^{2+}, Ca^{2+}, Cl^- and SO_4^{2-}) could vary by a few parts per million (generally less than 10% of the total concentration) over a period of a few months (Figs. 3 and 4 and Fig S1 for Na^+, Cl^- and K^+). These

differences are likely due to fluctuations in the composition and mass inputs of municipal water (spring), rainfall, and runoff into the lake.

The composition of the lake changed as a result of thousands of people jumping in over several hours. There was little discernible difference in the Mg^{2+}, Ca^{2+}, and SO_4^{2-} concentrations. However, there were significant and systematic changes in the concentrations of Na^+, Cl^- and K^+ associated with the jump (Figs. 3 and 4 and Fig S1).

The most dramatic changes in major ion concentrations during events were observed over the 3 h period from 10 p.m. to 1 a.m. on the eastern side of the lake where Na^+, Cl^- and K^+, increased by about 2-4 ppm, 4-6 ppm, and 1.5-3 ppm, respectively during the 2009-2012 events. The highest concentrations were typically observed around midnight to 12:30 a.m. with decreases observed by 1:00 am when the event is stopped by the university authorities. Surface water samples collected from MLM and from the middle of the lake (MOL) in 2010 and 2011 exhibited smaller but still discernible increases in these ions during the event. There was little change in the surface water composition at MLW by the end of the event (1 a.m. sampling). By morning (8-10 a.m.) the day following the 2009, 2010, and 2011 events, the major element compositions of the surface waters were similar at the MLE and MLW sites, although with higher than pre-event concentrations, suggesting that the solutes added to the lake during the events generally became well mixed throughout the lake overnight. However, by the morning following the 2012 event, the concentrations of Na, K and Cl on the east side of the lake were still significantly higher than those on the west side of the lake, suggesting that, unlike previous years, the lake had not completely mixed overnight. The 12 h changes in the Na^+, Cl^-, and K^+ concentrations

during all years of the event were greater than the variation that was observed over a period of weeks to months prior to the events in 2009 and 2010, especially in the east side of the lake.
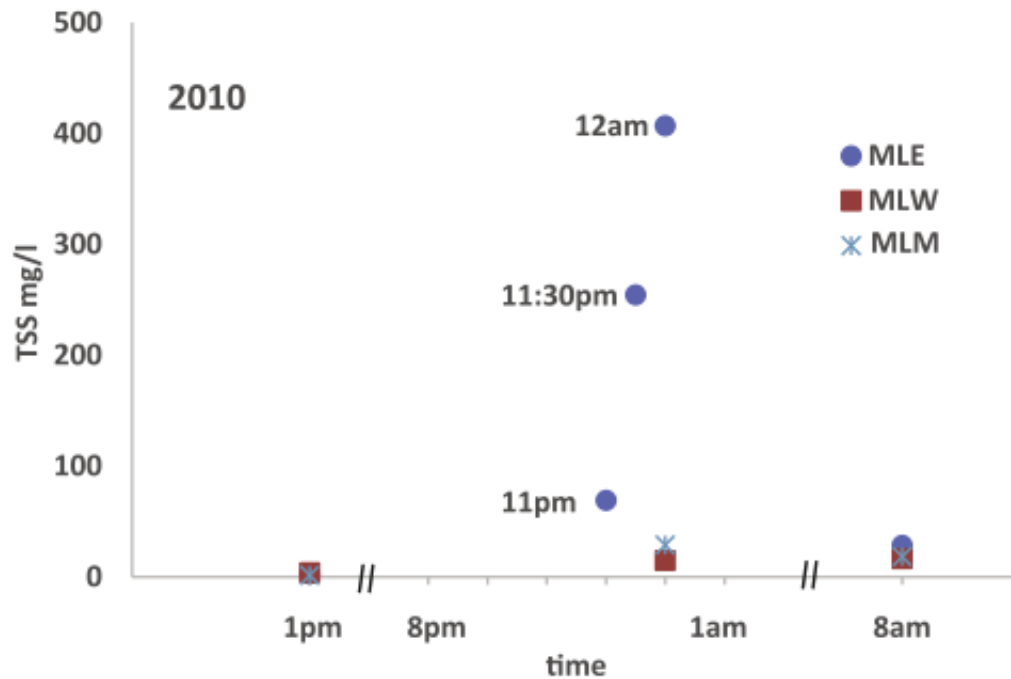

Fig. 2. Total suspended solids (TSS) measured during the Mirror Lake jump 2010.

3.3. *Nutrient composition*

The event had a profound impact on the nitrogen geochemistry of Mirror Lake. Preliminary sampling in 2008 illustrated that the event affected the total nitrogen (TN) and ammonia levels in the lake (Fig. 5). This effect was greatest at MLE during the most active part of the jump and almost negligible at MLW. The next day, concentrations at MLE and MLW were similar, increasing about 50% from values measured at the same time the day before. These elevated concentrations persisted for at least one week following the 2008 event.

More detailed and systematic sampling of the event from years 2009e2012 further elucidated the impact of the jump on the nitrogen chemistry of the lake. The
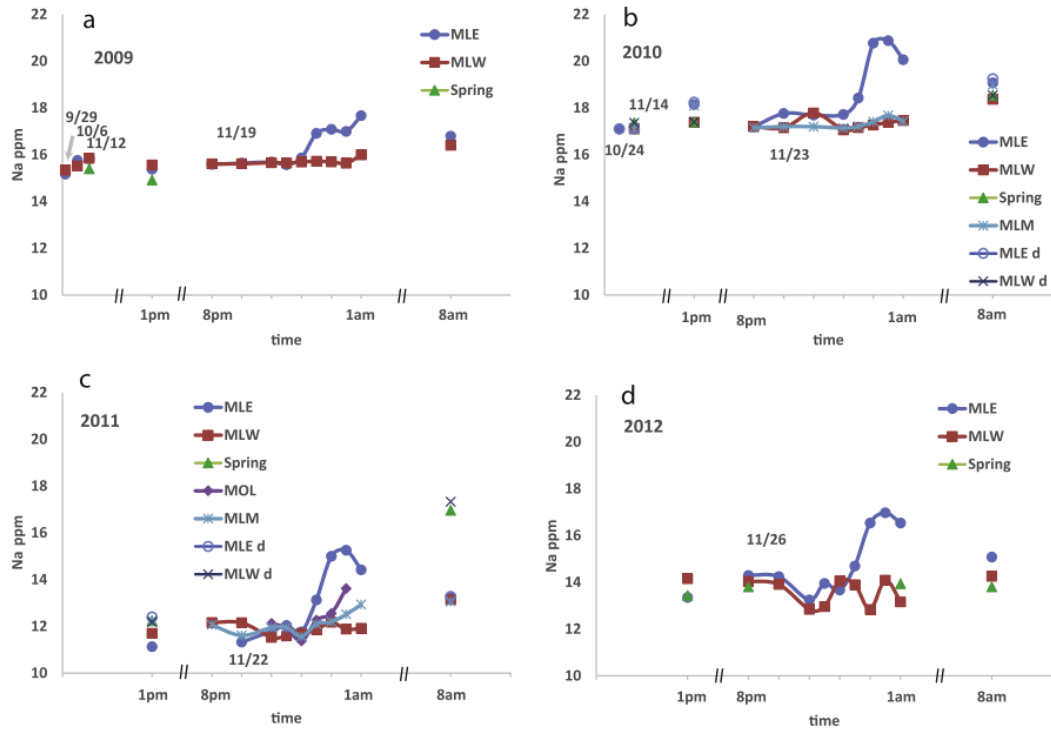
Fig. 3. Sodium concentrations (ppm Na) in Mirror Lake in a) 2009; b) 2010; c) 2011; and d) 2012. Sodium concentrations for samples collected earlier in the autumn (SepeNov) in 2009 and 2010 are plotted for reference.
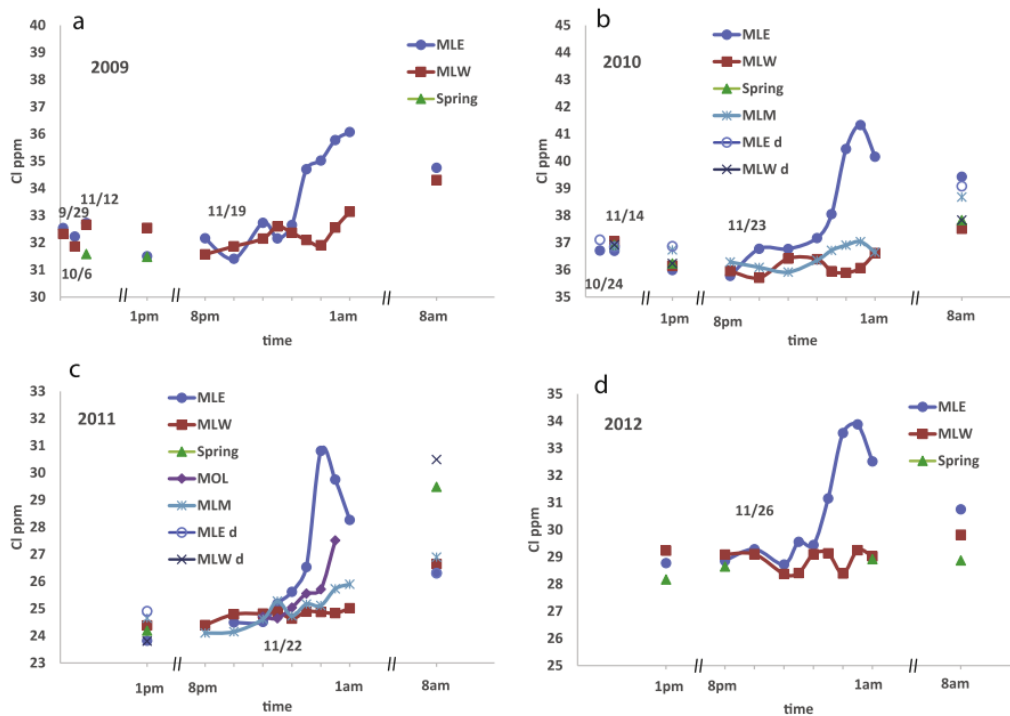

Fig. 4. Chloride concentrations (ppm Cl) in Mirror Lake in a) 2009; b) 2010; c) 2011; and d) 2012. Chloride concentrations for samples collected earlier in the autumn (SepeNov) in 2009 and 2010 are plotted for reference.

TN values before the 2009e2012 events were consistent with concentrations found before the 2008 event, ranging from 400 to 500 ppb N. There was little variation in TN in the weeks prior to the event in 2009 and 2010 (Fig. 6a and b). Little spatial or depth variation was observed for any sampling time prior to the event in any of the years sampled. However, the TN values in the spring ranged from 800 to 1000 ppb, approximately double that of the lake water over the sampling period.

Before the event, ammonia and nitrate concentrations were considerably lower than TN values for the lake and varied substantially over time, as would be expected due to variations in biological activity (Fig. 7 and Fig S2). In 2009, ammonia concentrations in the early autumn (SepteOct) were roughly 50 ppb, but in the week preceding the event, ammonia concentrations had dropped to only a few ppb (Fig. 7a). In 2010, ammonia concentrations ranged from 0 to 20 ppb before the event (Fig. 7b). Deep water samples taken in 2010 showed ammonia values similar to those found in surface waters except for in the deepest sample taken from the bottom of the west side of the lake (~2.5 m), where ammonia values were about 100 ppb, and the sample smelled sulfidic. There was also elevated ammonia in the supernatant of a debris sample collected from the bottom of the lake near MLE in 2010 compared to the undisturbed overlying water (~50 ppb compared to ~20 ppb, respectively). There was no long term sampling of the lake prior to the 2011 and 2012 events. However, the ammonia concentrations of the surface water before the 2011 and 2012 events were similar to those measured during the long-term sampling of the previous years (a few to a few tens ppb NH_3) (Fig. 7c and d). Ammonia in the spring was only a few ppb during the sampling period.

Nitrate values in the spring ranged from 550 to 900 ppb over the sampling period, indicating that the TN values are roughly 80-90% nitrate (Figure S2). Nitrate levels in the lake prior to the event varied considerably more than TN or ammonia. For example, in the two months before the 2009 event, nitrate concentrations in the surface water increased from a few ppb to a few 10's ppb and then decreased to undetectable levels in the evening of the event. However, nitrate values in the lake were much higher in 2010, ranging from 150 to 200 ppb, and there was a small but systematic spatial trend with elevated nitrate measured at MLE (close to the spring) compared to MLW. The overall higher nitrate values measured in 2010 probably reflect the increased aeration and draining and cleaning the lake earlier in the summer, thus inhibiting denitrification. The nitrate concentrations measured in the lake waters prior to the event in 2011 and 2012 were generally lower than those measured in 2010.

There were substantial changes in nutrient concentrations from pre-event values associated with event. Although the general trends observed were similar from year to year, the absolute values and the timing of these changes differed somewhat. The most profound chemical changes measured during the events were seen in the TN and ammonia concentrations. These changes were greatest at MLE, coincident with the distribution of jumpers in the lake.

The TN concentrations at MLE increased approximately 5-6 fold from a baseline of 450-500 ppb, to 2300-2800 ppb over the 2 h period at the height of the 2009-2012 events (11 p.m.-1 a.m.) (Fig. 6). The peak in TN was measured at about 12:30 (except in 2009 when the peak occurred at 1 a.m.) and then decreased roughly 20% by the 1 a.m. sampling time when the students were forbidden from being in

the lake. There were much smaller in- creases in TN at the MLM and MOL sites (Fig. 6b and c) reflecting the smaller number of participants frolicking in these areas of the lake. Although the participants were not allowed to enter the water on the west side, by 1 a.m. the TN values in the west side of the lake were elevated, indicating that the nutrient enriched water plume had mixed over to the west side. By the morning following the 2009-2011 events, the TN values in the west side of the lake had increased twofold to around 1000 ppb, and TN values in the east side of the lake were similar or higher around 1000-1500 ppb, indicating that the lake had mixed overnight. The TN observed at MLW in 2012 was slightly lower than at MLE, indicating incomplete mixing that year. The 12-h increase in nitrogen concentration observed overnight for the 2009-2012 events corresponds to the addition of approximately 1.3 kg of nitrogen to the lake during the event.
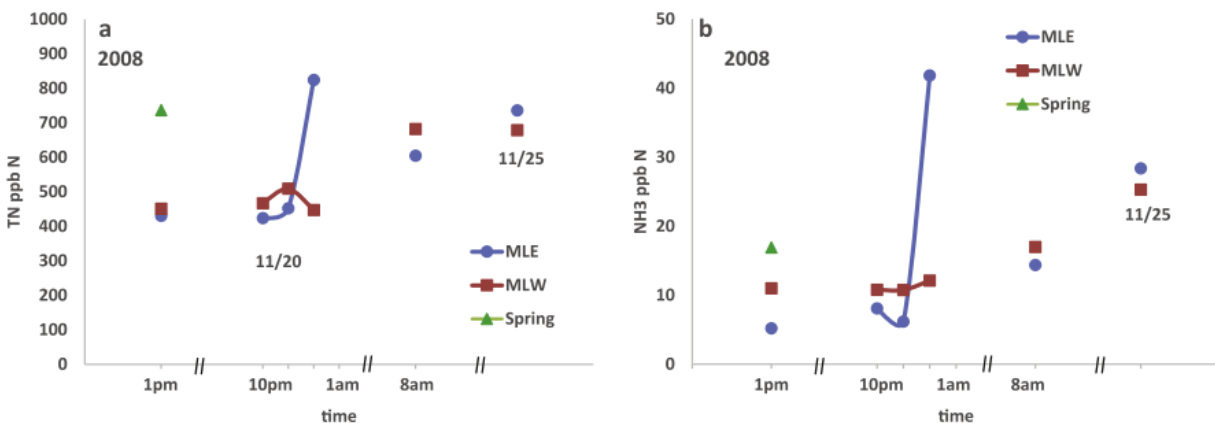

Fig. 5. a) Total nitrogen (ppb N) and b) ammonia (ppb N) during the Mirror Lake jump in 2008.

Similar trends were observed for ammonia, although ammonia concentrations generally began to increase earlier in the evening than TN, and ammonia concentrations were lower and more variable than TN (Fig. 7). In 2010, ammonia in the east side of the lake increased roughly threefold from about 10 to 30 ppb

between 8p.m. and 11 p.m. No such increase was observed during the 2009 sampling. A roughly tenfold ammonia increase was observed during the 2009 and 2010 events between 11 p.m. and 1 a.m., the height of jumping activity. The 2010 sampling showed a higher ammonia peak concentration than was seen in 2009, about 350 ppb compared to about 200 ppb. The largest peak in ammonia during the study period, around 600 ppb, was observed in 2011, coincident with the highest peak in TN
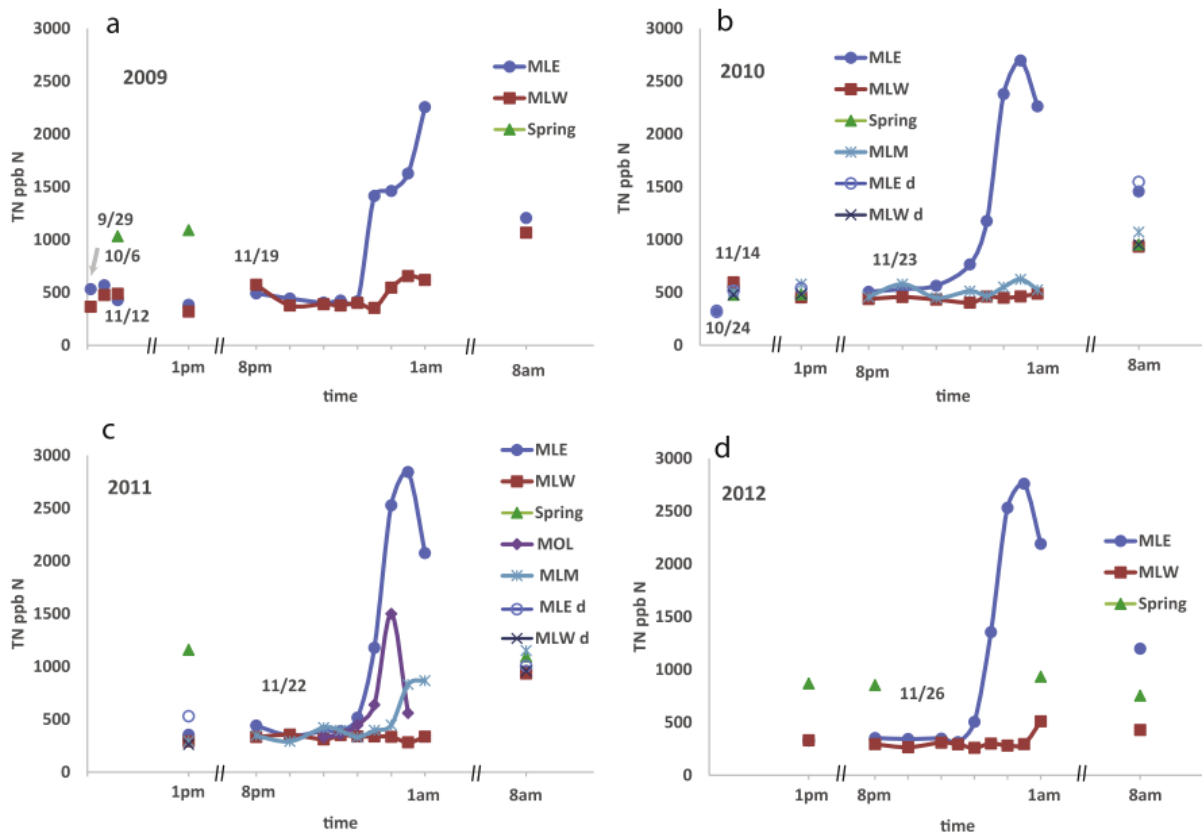

Fig. 6. Total nitrogen (TN) concentrations (ppb N) in Mirror Lake in a) 2009; b) 2010; c) 2011; and d) 2012. TN concentrations for samples collected earlier in the autumn (SepeNov) in 2009 and 2010 are plotted for reference.

(~2800 ppb) and with elevated ammonia concentrations measured in some of the deeper water samples. It is not clear if the elevated ammonia concentration in the shallow part of the lake in the early evening of the 2011 event represents a nutrient rich stratified layer or if we had sampled an area that was recently disturbed by one of

the participants. In 2012, the peak ammonia concentration was lower than previous years (80 ppb). Similar to what was observed for TN, ammonia concentrations decreased at MLE after the peak of the event and increased at MLW overnight as the lake mixed. Ammonia accounts for roughly 5-10% of the TN increase at MLE during the 2009 event, around 15-20% of the TN increase observed at MLE during the 2010 and 2011 event, but only about 3% of the TN increase at MLE in 2012.

No significant systematic change in nitrate was observed during the events from 2009 to 2012 (Figure S2). The 2009 nitrate concentrations were much lower and more variable than measured for the following years. In general, nitrate concentrations measured at the MLE site were higher and more variable than for the MLW site due to the close proximity of the high nitrate spring waters.
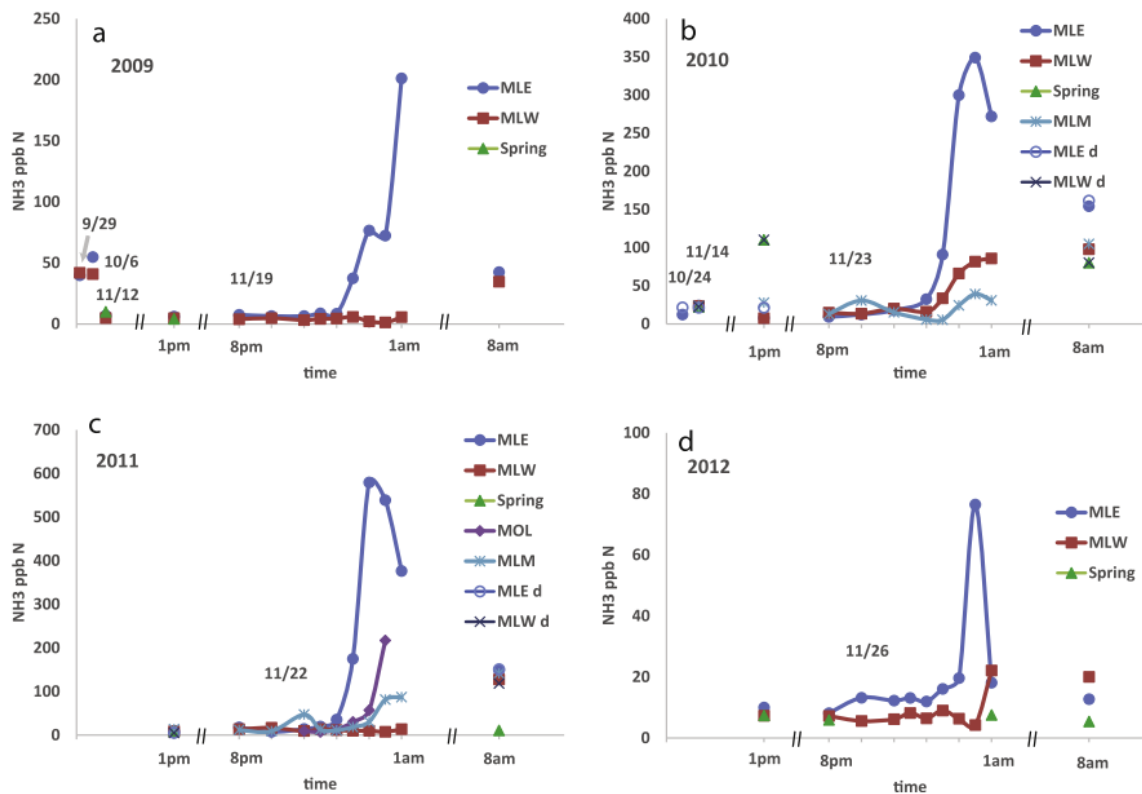

Fig. 7. Ammonia concentrations (ppb N) in Mirror Lake in a) 2009; b) 2010; c) 2011; and d) 2012. Ammonia concentrations for samples collected earlier in the autumn (SepeNov) in 2009 and 2010 are plotted for reference.

Although silica, orthophosphate, and total phosphate were measured for all the samples, there was little change in the concentrations of these species associated with the event, and little horizontal or vertical variability at any given sampling time. Silica concentrations varied each year, ranging from roughly 1-4 ppm. Total phosphate concentrations in the lake were high, ranging from approximately 1 to 2.5 ppm. Orthophosphate values are also elevated, about 200-1000 ppb.

Measurements of dissolved organic carbon (DOC) concentration and isotopic composition ($\delta^{13}C$) of the DOC were conducted for the 2012 event. At MLE, DOC values increased from 3.6 ppm C during the early hours of the evening up to 18 ppm C at midnight (Fig. 8). This was coincident with a 5‰ change in $\delta^{13}C$, from a mean of around –28‰ in the early hours of the evening to a maximum of -23‰, suggesting a large influx of isotopically heavy carbon into the lake. Over the night following the 2012 event, DOC values at MLE decreased with a small increase in DOC at MLW. However, DOC concentrations and isotopic compositions were different, indicating that the lake had not mixed overnight. This is consistent with observations of the major ions (Na, K, and Cl), TN, and ammonia, which were all still elevated at MLE the day after the 2012 event.

3.4. **Trace element composition**

Trace elements were analyzed on samples collected from the MLE site from the 2012 event. Most of the elements measured did not show any appreciable change in concentration over the event (data not shown), however, others exhibited a systematic increase in concentration with trends that were similar to those observed

for Na, K, Cl, TN or DOC (Figure S3). For example, dissolved Rb concentrations increased about threefold over 2 h, from approximately 1 ppbe3 ppb from 10 p.m. to midnight, followed by a decrease in concentration to approximately 1.5 ppb the next day. The similarity in the trends for Rb, Na and Cl and the behavior of these elements suggest a similar source. Dissolved Fe and Mn exhibit similar trends to the soluble salts, with concentrations increasing approximately five fold over 2 h. However, Fe and Mn probably have a different source than the Na and Cl, likely reflecting the resuspension of the thin layer of sediments on the lake bottom. The concentrations of B and Sr vary over the course of the event, although both exhibit a peak in concentration towards the end of the event, and a small but measurable increase in concentration overnight suggesting an input in these elements as a result of the event.

3.5. *Sediment-solute experiments*

The impact of the potential input of solutes, either from tracking soil and dirt into the lake during the jump, or by suspension of the *in situ* sediments in the lake on the lake water chemistry was estimated by two experiments. Samples of dirt and soils were collected from an area near the east side of the lake (Fig. 1) and leached using a 1:5 (wt:wt) solid-water ratio to estimate the release of solutes from dirt that was tracked into the lake during the event. Results of the leach experiments are listed in Table 1. Total salt content of these experiments ranged from about 40 to 70 ppm TDS but salt composition varied substantially among the five samples analyzed. Nutrient concentrations in solutions ranged over an order of magnitude from ~600 to 6000 ppb P as phosphate, ~20 to 800 ppb N as ammonia, and ~800 to 10,000

ppb N as TN.

In the second experiment, the impact of re-suspended bottom sediments was estimated by disturbing the sediments from the shallow east side of the lake and the deeper west end of the lake with the dustpan and collecting the sediment water slurry and overlying water. The sediment contribution was then estimated by the differences in water chemistry between the undisturbed water sample and the slurry. The contribution of solutes from the sediments to the overlying water was negligible for most of the species measured, however ammonia nitrogen, and total nitrogen were approximately 30 ppb higher in the sediment slurry on the east side, and 200-250 ppb N higher on the west side, than in the overlying water.

4.   Discussion

Five years of data show that the annual tradition of jumping into Ohio State's Mirror Lake before the Ohio State v. Michigan football game profoundly affects the chemistry of the lake during and after the event. The impact on the TN concentration in the lake is dramatic, as TN increases four to six fold during the jump in the east side of the lake. This nitrogen input then mixes throughout the lake overnight and increases the TN of the total lake approximately twofold by the next morning. Although ammonia concentrations vary significantly from year to year, changes in ammonia observed during the event resemble those seen in TN but are insufficient to account for the whole of the TN increase. The DOC concentration increased six-fold, along with an approximately 5‰ increase in $\delta^{13}C$, suggesting a large input of carbon to the lake. The change in concentrations of Na, Cl, and K (and Rb) also follow the

observed TN trend, suggesting a link among N, Na, Cl, and K inputs. In contrast, there was no systematic increase in other nutrient or major ion species measured associated with the event.

Observed changes in lake water chemistry during the event are due to: 1) jumpers stirring up the bottom sediment, increasing the concentration of solutes in the overlying water; 2) jumpers tracked in dirt and salts from the surrounding area that then dissolve in the lake; 3) anthropogenic input from jumpers in the form of bodily fluids (e.g., skin surface fluids such as sweat or sebum, and urine) or solubilization of other compounds from the skin surface or dissolution of personal care products like perfumes, lotions, make up or soap residues. Input from these sources could vary from year to year due to variations in lake cleaning schedule, temperature, and the number of participants.
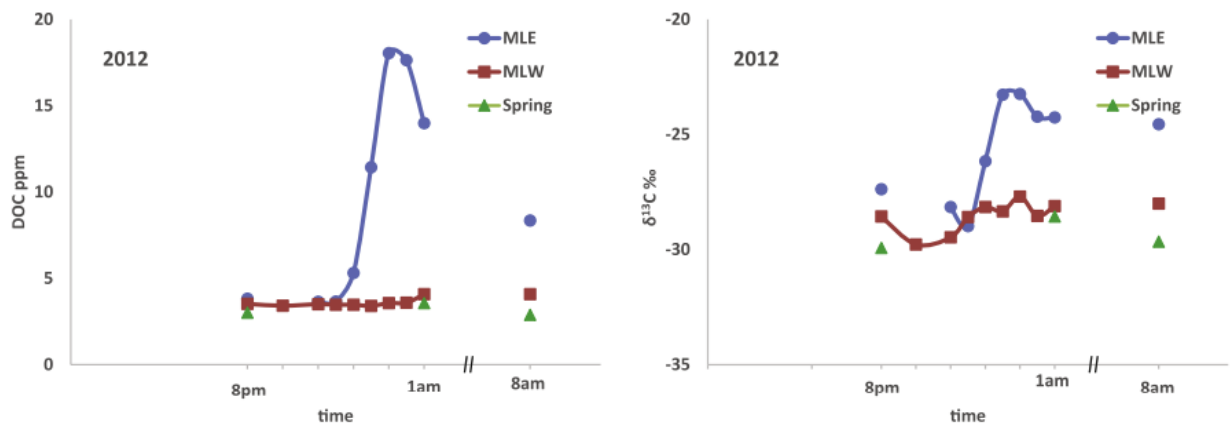

Fig. 8. Dissolved organic carbon (DOC) concentrations (ppm C) and d^{13}C of the DOC from Mirror Lake in 2012.

Table 1
Results of experiments. Five samples of soils and sediments were collected from the area surrounding the lake and leached with MilliQ water (1:5 solid:water).

Sample	Cl	SO$_4$	Na	K	Mg	Ca	PO$_4$	NH$_3$	TN
	ppm	ppm	ppm	ppm	ppm	ppm	ppb P	ppb N	ppb N
1	2.97	28.6	10.0	0.33	4.62	25.6	868	117	2450
2	9.09	1.54	19.9	1.84	1.84	13.6	3020	110	784
3	5.19	6.22	8.61	3.56	2.62	12.0	5800	769	10 600
4	5.93	0.76	26.9	4.67	0.91	8.08	1430	70	1460
5	4.18	24.2	6.77	16.30	nd	20.1	559	19	758

4.1. *Bottom sediments as a source of nutrients and solutes*

In order to constrain the input of nutrients and major ions into the overlying water column from disturbance of the lake's bottom sediments, sediment-water slurries were collected from the bot- tom of the lake about a month before the 2010 event. Although the amount of sediment covering the bottom of the lake was not measured directly, it can be inferred from the lake's maintenance schedule and from visual observations that the amount of sediment in the bottom of the lake was different during each sample year. The lake had not been cleaned for several years prior to the 2008 event, during which time the lake was home to dozens of domestic ducks. None of the brick pavers lining the bottom was visible in 2008 and the lake likely contained the greatest amount of bottom sediment compared to later years.

If the disturbance of bottom sediments is the major factor contributing to the nutrient increases observed during the event, then it is expected that the changes measured during the 2008 event would exhibit the greatest increase in TN and ammonia compared to later years. However, TN and ammonia increases observed in 2008 were ~400 ppb and ~30 ppb respectively, much less than increases observed in subsequent years (2009-2012) which were ~2000 ppb TN and ~60-600 ppb ammonia, respectively. As the lake was completely drained and cleaned four months prior to the

2009 event, there was much less detritus covering the bottom than was seen before the 2010 event. Yet the observed TN and ammonia trends from 2009 and 2010 years are comparably similar, suggesting resuspension of the bottom sediments was not a significant source of solutes to the overlying water.

An estimate of the contribution of bottom sediment disturbance on the nutrient chemistry of the lake was obtained in 2010 by comparing the TSS and nutrients of slurry samples collected a month before the event with the TSS and nutrients in samples taken during the event. Ammonia concentrations in sediment- slurry samples were ~30 ppb higher in the east side of the lake and ~200-250 ppb higher in the deep (and likely suboxic to anoxic) west side of the lake than undisturbed samples taken from the same locations. Sediment-slurry samples contained about 275 mg/ L TSS in the east side of the lake and 600 mg/L TSS in the west side of the lake. There was little change in the TSS in the west side of the lake (MLW) during the event, but the TSS in the east side of the lake (MLE) increased to 400 mg/L. Given the total ammonia concentrations in sediment-slurry samples, the observed TSS trends would contribute only one-fifth of the total ammonia increase observed in the east side of the lake in 2010 and a negligible amount of the ammonia increase seen in the west side of the lake. No significant difference was observed in major ion chemistry between sediment- slurry samples and undisturbed samples, suggesting that the resuspension of bottom sediments contributes little, if any, to the changes in Na, Cl, and K observed.

However, it is likely that the disturbance of the bottom sediments was the source of the redox sensitive elements Fe and Mn, either as dissolved reduced Fe^{2+} and Mn^{2+}, or as colloidal Fe and Mn hydroxides.

Soil and salt contribution

Another potential source of nutrients and solutes to the lake is the tracking in of dirt and salts into the lake by jumpers. This input was estimated by comparing TSS data gathered during the 2010 event with results obtained from leach experiments of soils and dirt surrounding the lake (Table 1). If the TSS increase observed was solely the result of surrounding sediments tracked into the lake, and the highest concentration seen in the leach samples was representative of the whole, then ammonia and TN would only increase by about 2 and 20 ppb, respectively, during the event, much less than the increases seen in sediment-slurry samples discussed above and negligible compared to the actual changes observed during the event. This would only correspond to a less than 0.1 ppm increase in major ion concentrations.

However, there is some evidence of solute input into the lake from the soles of the jumpers' feet. In 2010, the Na and Cl concentrations in the east side of the lake increase measurably early in the evening, 1.5 ppm increase in Na + Cl, which corresponds to 1.5 kg of NaCl tracked into the east side of the lake between 8 and 9 p.m. (Figs. 3b and 5b). This increase in NaCl concentrations earlier in the evening was not noted in other years, and likely represents the input from the salt and brine applied to surrounding walkways before the 2010 event to mitigate icy conditions, a procedure that was not observed other years of the study. The total increases in Na and Cl observed during the height of the event in 2010 could result from roughly 8 kg of NaCl dissolved into the east side of the lake (assuming 1000 m^3), a reasonable estimate given the amount of brine applied to walkways surrounding the area before the event. However, Na and Cl also increased substantially at the height of the event during the

other years when there was no brine was applied, suggesting brine was not the only source of salt. It is also unlikely that there was a significant amount of potassium, nitrogen, and ammonia in the brine, suggesting another source of ion and nutrient input was responsible for the changes observed.

4.3. *Input from sweat and urine*

Anthropogenic pollution, primarily from the jumpers' urine, sweat, soluble compounds from skin such as sebum, or personal care products is likely the main contribution to the observed changes in lake water chemistry. Studies on swimming pool chemistry suggest that swimmers contribute significant amounts of inorganic solutes, organic carbon, and nitrogen to the water (e.g., Jmaiff Blackstock et al., 2017; Lian et al., 2014; Keuten et al., 2012, 2014; Wojtowicz, 2001; Gunkel and Jessen, 1986) as a result of their activity. Others suggest that urine represents the major source of anthropogenic ammonia and TN contribution to the pool water (Wojtowicz, 2001; Gunkel and Jessen, 1986). The potential contribution due to urine was estimated from the change in TN at MLE from pre-event levels to the height of the activity and average urine compositions from the literature (Udert et al., 2006; Wojtowicz, 2001; Gunkel and Jessen, 1986).

Urine is a complex mixture of organic compounds and inorganic solutes. The average nitrogen concentration of fresh urine is approximately 9 g/L, of which, approximately 85% is urea, 5% is ammonia and the rest is other organic nitrogen compounds, primarily amino acids, creatinine, and uric acid (Udert et al., 2006). Our results showed that the TN concentration of the east side of the lake (~1000 m^3

volume) increased approximately 2000 ppb during the height of the event. If all the nitrogen was derived from urine, this would correspond to approximately 200 L of urine entering the lake, or assuming approximately 5000 participants, 40 ml per person. This urine input per bather is similar to the volumes estimated (~30-35 ml) by Gunkel and Jensen (1986) for nitrogen contamination in swimming pools. If all of the increase in ammonia is derived from urine, then this would correspond to about 100 ppb N as ammonia. The increases in ammonia observed in 2009 and 2012 are consistent with calculated inputs from urine. How- ever, the ammonia concentrations measured in 2010 and 2011 were approximately three-to five-fold greater than expected if urine was the lone source. The organic compounds in urine, particularly urea, can degrade to ammonia in aqueous solutions, (Alexandrova and Jorgensen, 2007; Udert et al., 2006; Warner, 1942), so the elevated levels of ammonia could be due, at least in part, to sample degradation before analysis (i.e., urea degradation). Based on average composition, urine alone could only account for roughly one-third of the total increases in Na, Cl, and K observed throughout the study, and only 10% of the DOC. Thus, another source of these solutes to the lake during the event must exist.

Input of soluble compounds from skin, particularly sweat (either active sweating during the event or the dried residue left on the skin from a normal days activity) or sebum (lipids or other organic compounds secreted by skin), represents another significant source of anthropogenic solutes to the lake water (Keuten et al., 2012, 2014). The composition of sweat is extremely variable, and depends on multiple factors comprising diet, hydration, gender, age, and extent and duration of exercise (Keuten et al., 2012; Harvey et al., 2010; Baker et al., 2009, 2011; Bates and Miller,

2008; Stefaniak and Harvey., 2006; Cheng et al., 2005; Patterson et al., 2000; Palacios et al., 2003; Shirreffs and Maughan, 1997; Fukumoto et al., 1988). The measured composition of sweat can also vary depending on collection method used, as some collection methods, such as rinsing skin surfaces can collect some fraction of the sebum or other soluble skin surface compounds. We chose to use values from studies that were most similar to the ways in which the jumpers would have contributed sweat and sebum to the lake, i.e. rinsing studies, and therefore expect our calculations to account for those inputs as adequately as possible. Harvey et al. (2010) tabulated the mean, minimum, and maximum concentrations of dozens of inorganic and organic species in human sweat. We calculated the composition of major constituents in sweat from the tabulation of Harvey et al. (2010), considering all compounds that had a reported median composition greater than 10^{-4} M. Results of this calculation show that sweat can be described as a solution of Na, Cl, K, DOC, and TN with concentrations of 0.71, 0.81, 0.24, 49, and 9.3 g/L respectively. The median inorganic solute content of sweat is similar to the ratios we measured for the increases in Na and Cl during the event. However, the change in K concentration during the event was approximately 2-3 times greater than would be predicted from the median sweat composition alone.

Increases in the sum of Na þ Cl in the eastern side of the lake from the pre-event levels to maximum concentrations measured at the height of the jump range from a low of 6.5 to a high of 9 ppm Na þ Cl for the 2009-2012 events (Table 2). Given that the major changes are observed on the east side of the lake (~1000 m^3) where ~ 90% of the participants jump in, this corresponds to ~6.5e9 kg salt

added to the water. This amount of salt would correspond to the solubilization of ~4000-6000 L of evaporated sweat from the participant's skin, or approximately 0.8-1.2 L per participant based on the median salt content of sweat from Harvey et al. (2010), Cheng et al. (2005) tabulated the concentrations of a smaller number of components in sweat and determined a characteristic salt (predominately NaCl) concentration that was three times higher than the median values tabulated by Harvey et al. (2010). The Cheng et al. (2005) values would correspond to the dissolution of ~0.27-0.4 L of evaporated sweat per participant. Given typical sweat rates for fluid and solutes, salt content of skin surfaces (Bates and Miller, 2008) ranges from several hundreds of milligrams to grams per person. Therefore, it is feasible to attribute the increase in inorganic salt concentration in the lake to the dissolution of solutes from the participants' skin.

Similarly, the potential contribution of evaporated sweat on the jumper's skin to the changes in TN, ammonia, and DOC observed in lake water can be estimated from published data. Harvey et al. (2010) noted that the median values calculated for vitamins (thia- mine, riboflavin, pantothenic acid, niacin, and pyroxidine) are heavily influenced by an older summary data set from Kuno (1956). When the Kuno (1956) data set is omitted, the median concentrations of these compounds are about 6 orders of magnitude lower, and therefore would represent a negligible contribution to the in- crease in DOC and TN. The revised sweat composition would have median concentrations of ~1 g/L DOC and ~0.5 g/L TN. Potential contributions of TN and DOC from residual sweat were calculated from the measured change in Na þ Cl and median sweat composition. There is reasonably good agreement between the

measured and predicted changes in TN; predicted TN values are approximately 1-26% greater than measured values. Measured DOC change was approximately 3 times the calculated value from dissolution of evaporated sweat (Table 2). However, it should be noted that considerable uncertainty exists in the estimated sweat composition from Harvey et al. (2010) and the values used represent a median concentration for components whose reported measured concentrations can vary by orders of magnitude. If the sweat composition from Cheng et al. (2005) is used, then DOC concentrations estimated from increases in Na + Cl would be only 4 ppm, similar to the DOC predicted using the Harvey et al. (2010) values.

Table 2

Comparison of change in solute chemistry of the lake to median sweat composition calculated from Harvey et al. (2010). Predicted values are calculated from the ratio of TN or DOC to Na + Cl in sweat.

	Na + Cl (ppm) increase	TN (ppm) measured	TN (ppm) predicted	DOC (ppm) measured	DOC (ppm) predicted
Sweat	1.52	0.5		1	
2009	6.5	1.85	2.1		
2010	7.8	2.2	2.6		
2011	9.2	2.4	3.0		
2012	7.7	2.5	2.5	14	5

In another study, Keuten et al. (2012) used shower experiments to investigate the initial anthropogenic pollutant release (sum of residual evaporated sweat, sebum, or other soluble compounds on skin surfaces) to swimming pool water and determined an average initial release of 211 mg TOC and 46 mg TN per person, though values could vary by an order of magnitude for different individuals. The same jumper density assumptions as were used for the salt contributions (5000 participants jumping into a

volume of 1000 m^3) were used to estimate DOC and TN increase from the Keuten et al. (2012) numbers. These calculated releases would contribute only a small fraction to the observed changes in DOC and TN, approximately 1 ppm DOC and 230 ppb TN. In a subsequent study, Keuten et al. (2014) determined the anthropogenic input of DOC and TN per swimmer for the initial release (rapid dissolution of organic compounds from sweat and sebum that is on the participants' skin), continual release (dissolution of sweat actively produced as a result of swimming activity and sebum secreted to restore the skins lipid film) and incidental release (primarily urination) of 659 mg DOC and 204 mg TN. These inputs would correspond to an increase of approximately 3.3 ppm DOC and 1000 ppb TN, still only a fraction of the measured changes that occur in the shallow end of Mirror Lake during the jump. There is good agreement between the measured and estimated increases in salts and TN that can be attributed to the dissolution of evaporated sweat from the participants' skin surfaces, but these calculations, along with the estimates of DOC and TN pollutant release per jumper based on the data from Keuten et al. (2012; 2014) under- estimate the changes in DOC, suggesting another source contributes to the change in water chemistry. DOC was not measured in the sediment disturbance experiments since the instrument was unavailable at the time of the experiments, but some fraction of the increase in DOC likely comes from re-suspended sediments. The large shift in the carbon isotopic composition of DOC from δ^{13}C of –28‰ before the event to –23‰ at the height of the event is consistent with an anthropogenic input. Grottoli and Matsui (unpub) routinely measure the isotopic composition of hair and fingernails of Ohio State students as part of the isotope biogeochemistry class. The δ^{13}C measurements of

dozens of students typically range from ~-17 to –19‰, reflecting a diet derived from C3 plants. If the δ¹³C of DOC associated with the re-suspended sediments has the same isotopic composition as the pre-event DOC in the surface water, then we can estimate the contribution from these sources using a simple mass balance:

$$DOC_{lake} * \delta^{13}C_{lake} + DOC_{ss} * \delta^{13}C_{ss} + DOC_{ant} * \delta^{13}C_{ant}$$
$$= DOC_{event} * \delta^{13}C_{event}$$

where *lake* refers to the initial DOC concentration and isotopic composition, *ss* refers to the contribution to DOC from suspended sediments, *ant* refers to the contribution to DOC from anthropo- genic pollutants (predominately sweat, sebum and urine), and *event* refers to the composition and concentration of DOC measured at the height of the event. Results of these calculations indicate that ~9 ppm C is derived from the participants, and ~5 ppm C is derived from DOC from the bottom sediments. An increase of 9 ppm from the participants is roughly double the DOC input estimated from either the dissolution of evaporated sweat or sebum, suggesting either uncertainty in the median composition of soluble organics released from skin surfaces or urine derived from the literature values or substantial unidentified sources of DOC such as solubilized soap residues, perfumes, lotions, and spilled beverages. The morning after the events there were dozens of empty beverage containers observed floating in the lake, along with more discarded on the grounds nearby, suggesting that spilled beverages may also contribute to the measured DOC.

Nirel and Revaclier (1999) found that Rb/Sr ratios in river water can be used to infer contamination from sewage treatment plants. This technique works best in waters with much greater Sr than Rb as were found in this study. We found a roughly

three-fold increase in Rb/Sr ratios during the event coincident with increases in TN, DOC, Na þ Cl, and K. The Rb/Sr changes support an anthropogenic source of pollutants to the lake similar to what would come out of a sewage treatment plant (e.g., human effluents and solubilized soaps, perfumes, and lotions).

4.4. *Impact of the event on the annual N budget of Mirror Lake*

The Mirror Lake jump has a profound impact on the nitrogen content of the lake, contributing approximately 1.3 kg N in a single night. This event input is a small, but important fraction of the annual TN flux to the system from the spring, rainfall, and local flora and fauna. The greatest nitrogen input comes from the spring that feeds the lake. If we assume that the nitrogen concentrations measured in the spring water samples (~1000 ppb N, primarily as NO_3^-) represent typical concentrations and an annual flow rate of approximately two million gallons per year, then the total nitrogen input from the spring would be about 8 kg N per year. There was no significant precipitation during the evening of any of the events, so the observed change in salts and nutrients cannot be attributed to precipitation, even though rain and snow can be a significant source of nitrogen to the lake. Annual average rainfall for Columbus over the 5 years of the study was 0.94 m (weather.gov). The average inorganic N (NO_2^-, NO_3^-, and NH_3) content of ~200 precipitation samples collected during 2014-2016 from three sites located within 5 km of the study areas was 930 ppb N (Carey et al., 2016; Carey and Welch, unpub). If this is representative of the rainfall at Mirror Lake, then approximately 2 kg N enters the lake through direct rainfall annually. The rainfall contribution might be even greater if contributions from

overland flow during rain events are considered.

Estimates of nitrogen flux from biogenic sources are more difficult to constrain. The lake is located in a small hollow surrounded by trees, and leaf litter could represent a significant source of nitrogen to system. Leaves are clearly observed floating on the lake surface during the autumn months, but many of these are removed by the groundskeepers. Based on our visual inspection of the system and analyses of sediments and detritus at the bottom of the lake during water sampling, we estimate that about half the lake bottom is covered in leaves. Several leaves were collected from the area and weighed to determine a leaf mass/surface area of 2 g/ 100 cm^2, thus it would require approximately 220 kg of leaves to cover half the lakes surface area. Melillo et al. (1982) tabulated nitrogen content of leaf litter from several hardwood species, and average nitrogen content of leaf tissues is ~1%. Therefore, the nitrogen flux from leaves falling into the lake is about 2.2 kg N, although the solubility and thus chemical impact of this nitrogen on this surface water is unclear. However, sediment slurry samples from the bottom of the lake show that detrital contributions of nutrients to the surface water may be negligible.

The potential contribution of nitrogen from waterfowl was obvious from the abundant fecal droppings surrounding the lake but the actual analysis of duck feces was beyond the scope of this study. Sasmal et al. (2010) estimated the impact of duck droppings on pond productivity in a fish farm and determined that duck output was approximately 20 g/day dry weight of a material containing about 5% nitrogen, which corresponds to a flux of 1 g nitrogen per duck per day or 365 g N per duck per year. The abundance of water fowl at Mirror Lake varies throughout the year, but

anywhere from a few to a few dozen can be observed at any given time. If we assume roughly half of the fecal nitrogen is deposited into the lake and a consistent population of ten to twenty ducks, then we calculate an annual flux of ~1.5-3 kg N to the lake from duck excrement. This estimate disregards any recycling of lake nitrogen by the ducks, and so actual inputs may be lower and closer to the inputs observed from the Mirror Lake jump.

About 14 kg N enters the lake per year outside of the night of the jump. The 1.3 kg N contributed to the lake during the jump represents about 10% of reasonable estimates of the annual nitrogen budget of the lake.

5. **Conclusions**

The Mirror lake jump has a profound impact on the chemistry of the lake, resulting in an increase in inorganic TDS (particularly Na, K, and Cl), TN, ammonia, and DOC. Mass balance calculations show that although some of the change in the overlying water composition can be attributed to resuspension of sediments, the larger contribution is direct anthropogenic pollution, primarily the inadvertent release of urine from the participants and the dissolution of salts and DOC from skin surfaces. Thus, this study suggests that direct inputs of contaminants (i.e., dissolution of skin surface compounds from sweat and sebum, urine, etc.) from humans can have an immediate impact on recreational bodies of water.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.apgeochem.2017.03.004.

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