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Cycles of trace elements and isotopes in the ocean – GEOTRACES and beyond

Evaluation of atmospheric dry deposition as a source of nutrients and trace metals to Lake Tahoe[☆]

Chia-Te Chien^{a,b}, Brant Allen^c, Natasha T. Dimova^d, Juan Yang^e, John Reuter^c,
Geoffrey Schladow^c, Adina Paytan^{a,*}

^a Earth & Planetary Sciences Department, University of Santa Cruz, Santa Cruz, CA, USA

^b GEOMAR Helmholtz Centre for Ocean Research Kiel, Kiel, Germany

^c Tahoe Environmental Research Center, University of California, Davis, CA, USA

^d Department of Geological Sciences, University of Alabama, Tuscaloosa, AL 35487, USA

^e School of Marine Science, China University of Geosciences, Beijing, China

ARTICLE INFO

Keywords:

Atmospheric deposition

Lake Tahoe

Trace metals

Pb isotopes

ABSTRACT

Atmospheric deposition can be an important source of nutrients and trace metals to oligotrophic alpine lakes, affecting their biogeochemistry. We measured trace metal concentrations and lead (Pb) isotope ratios in lake water, river water, ground water, and aerosol total suspended particles (TSP), as well as nutrient (NO_3^- , NH_4^+ , PO_4^{3-}) concentrations in TSP in the Tahoe Basin. The contribution of TSP deposition to the lake trace metal budget was assessed. Our results show seasonality in TSP and associated trace metal concentrations with higher concentrations during Oct – April. However, trace metal solubilities are higher during May – Sept, resulting in a higher contribution of soluble trace metals to the lake water. The source of most of the trace metals in TSP in the Lake Tahoe Basin is mineral dust; however, Zn, Cu, and Cd also have an anthropogenic origin. Among major nutrients, NO_3^- concentrations are slightly higher during Oct – April, while NH_4^+ and soluble reactive phosphorus (SRP) are higher during May – Sept. The distributions of trace metal concentrations and Pb isotopic ratios are homogenous throughout the lake water column, suggesting that the residence time of the trace metals in the lake is longer than the lake water mixing time. The contribution of atmospheric TSP deposition to the upper 20 m of lake water trace metal inventory is low, ranging from 0.03% for V to 5.7% for Mn. A triple-isotopes plot of Pb indicates that riverine and groundwater inputs are the major Pb sources, but aerosols still contribute some Pb to the lake.

This article is part of a special issue entitled: Conway GEOTRACES - edited by Tim M. Conway, Tristan Horner, Yves Plancherel, and Aridane G. González.

1. Introduction

Atmospheric deposition is an important source of nutrients and trace metals to remote water bodies like the open-ocean and alpine lakes (Camarero et al., 2009; Duce et al., 1991; Mladenov et al., 2012; Prospero et al., 1996). As a result atmospheric deposition can affect water quality by contributing major and minor nutrients for phytoplankton growth with implications to lake trophic conditions (Morales-Baquero et al., 2006). For example, anthropogenic nitrogen (N) deposition has been linked to increased nitrate (NO_3^-) levels in lakes and to changes in phytoplankton community structure (Saros et al., 2003; Wolfe et al., 2001; Wolfe et al., 2003), as well as changes in nutrient cycling, with negative impacts on lake ecosystems (Driscoll and

Newton, 1985; Greaver et al., 2012). In fact, it has been suggested that an observed decrease in N deposition rates in the last decades contributed to the recovery of community dynamics and species richness in several aquatic ecosystems (Arseneau, 2011; Finlay, 2003) and specific changes were linked to altered lake N:P ratios (Gerson et al., 2016). Trace metals can also have impacts on freshwater organisms. For example Cd concentrations above $0.1 \mu\text{g L}^{-1}$ have been related to reduction in reproductive function (Tarvainen et al., 1997) and Zn above $0.5 \mu\text{g L}^{-1}$ or Mn above $50 \mu\text{g L}^{-1}$ have been deemed harmful to trout (Lydersen et al., 2002; Sayer et al., 1989). Aluminum (Al) at levels $> 50 \mu\text{g L}^{-1}$ may also be toxic to some aquatic organisms (Baker and Schofield, 1982; Lydersen et al., 2002; Schofield and Trojnar, 1980). Copper (Cu) has been shown to inhibit chlorophyll *a* levels,

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* Corresponding author at: Earth & Marine Sciences C308, Mail Stop Ocean Sci., University of California Santa Cruz, 1156 High Street, Santa Cruz, CA 95064, USA.

E-mail address: apaytan@ucsc.edu (A. Paytan).

<https://doi.org/10.1016/j.chemgeo.2019.02.005>

Received 29 April 2018; Received in revised form 22 December 2018; Accepted 4 February 2019

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photosynthesis, and nitrogen fixation of fresh water algae at concentrations of 5–10 $\mu\text{g L}^{-1}$ (Elder and Horne, 1978). Notably, Cd, Zn, Mn and Pb in many lakes are associated with atmospheric deposition particularly related to anthropogenic origins and increases in their concentration in lake water or sediment have been documented in some lakes in Europe (Burton et al., 2013; Rippey et al., 2008). On the other hand, many trace metals are required by organisms for a wide range of metabolic processes (e.g., Fe) and low concentrations of these micro-nutrients can limit or co-limit lake phytoplankton productivity, hence affecting lake biology and ecosystem structure (Sterner et al., 2004).

Lake Tahoe is a remote subalpine lake situated at an elevation of 1897 m and surrounded by mountains including the Carson Range and the Sierra Nevada (39°05.5'N 120°02.5'W). The unique characteristics of the watershed, including nutrient-poor soils, erosion resistant substrate, and dense forest, minimize terrestrial nutrient inputs from runoff to the lake. These watershed properties, along with the large lake size of 490 km^2 (150 km^3) compared to the size of the watershed (1300 km^2), make Lake Tahoe oligotrophic, resulting in high water clarity. However, the clarity of Lake Tahoe has declined dramatically since the 1960s (TERC, 2016). There is evidence that increasing population, changes in land use and anthropogenic emissions contribute to the decreasing water clarity (Huang et al., 2013; Jassby et al., 1994; Juma et al., 2014). Specifically, atmospheric deposition has been suggested as an important source of nutrients that support phytoplankton growth and affect water quality (Brahney et al., 2014; Morales-Baquero et al., 2006). Accordingly, several studies including the Lake Tahoe Atmospheric Deposition Study (LTADS) by the California Air Resources Board (CARB) have been conducted to monitor gases (Tarnay et al., 2005; Zhang et al., 2002), atmospheric particulate matter (Gertler et al., 2006a; Sahoo et al., 2013; Zhang et al., 2002) and wet deposition (Jassby et al., 1994) at representative sites throughout the Lake Basin. These along with other studies provided important information on total particle deposition (Dolislager et al., 2012; Sahoo et al., 2013; VanCuren et al., 2012) and specifically on N (Jassby et al., 1994; Tarnay et al., 2001) and phosphorus (P) inputs (Dolislager et al., 2012; Jassby et al., 1994) and the distribution of these constituents within atmospheric particulate matter of different size (Dolislager et al., 2012; Tarnay et al., 2001). Other studies focused on organic composition of TSP in the region (Cahill, 2010; Datta et al., 1998). All studies collectively suggested that airborne pollutants which may influence water clarity mainly originate from within the Tahoe Basin (Bytnerowicz et al., 2013; Gertler et al., 2006b).

A bioassay incubation experiment using aerosol TSP addition has been carried out to understand how dry atmospheric deposition may affect phytoplankton growth and ecosystem dynamics in Lake Tahoe (Mackey et al., 2013). This study showed that atmospheric TSP deposition provides nutrients with a high ratio of N:P that favors the growth of picoplankton, thus can increase primary productivity without causing a substantial increase in chlorophyll (Chl *a*) or biomass. The study demonstrated the importance of understanding nutrient inputs from TSP deposition and, more importantly, the fate of TSP after deposition onto the lake surface. However, no detailed study evaluating the contribution of trace metals from TSP deposition relative to other sources has been conducted in Lake Tahoe. Specifically, seasonal changes in water quality may be controlled by temporal changes in TSP sources and their chemical composition (Dolislager et al., 2012). To our knowledge, none of the previous studies in the Tahoe Basin have reported multi-year seasonal variations of nutrients and trace metals in dry atmospheric deposition TSP or evaluated if and how TSP sources change seasonally. Considering the potential impacts of nutrients and trace metals on lakes biogeochemistry and the potential influence of atmospheric deposition (including TSP deposition) on their concentration, it is important to assess the contribution of TSP associated trace metals and nutrients to Lake Tahoe. To fill this gap, we use weekly collected TSP to determine seasonal changes in concentrations and solubility of trace metals and nutrients and calculate deposition rates

and contributions to lake water. We also use this information along with Pb isotopes to shed light on the sources of TSP in the basin (Véron and Church, 1997; Witt et al., 2006).

2. Materials and methods

2.1. Total suspended particles (TSP) collection and treatment

TSP samples were collected between 2005 and 2010. Weekly integrated samples were collected on acid washed quartz fiber filters (10" × 8", Whatman®) using a Graseby Andersen TSP High Volume Sampler. Between November 2005 and May 2007, the sampler was located near the lake at the UC Davis Field Station (Hatchery) away from any local source of disturbance. After May 2007, the sampler was relocated about 300 m south to reduce local impacts due to remodeling at the Hatchery. The TSP sampler was placed 3.2 m above the ground and protected by trees from direct road dust inputs. TSP samples were collected at an airflow rate of 85 $\text{m}^3 \text{h}^{-1}$. All filters were kept frozen until further analyses.

For bulk composition of TSP, a 15 mm × 10 mm sub-sample of each filter was digested by adding 2 mL concentrated HNO_3 and 1 mL HF to the filter in a sealed Teflon beaker and heating on a hotplate at 150 °C overnight. The liquid was then dried down and brought up with 2% HNO_3 for trace metal concentration analysis. To extract the soluble fraction of nutrients and trace metals in TSP samples, a 47 mm circular subsample of each filter was placed on an acid-washed filter tower, and 100 mL of MilliQ water was passed through the sample under gentle vacuum pressure exposing the sample for about 10 s to the water (Buck et al., 2006). A 100 μL of concentrated nitric acid was added to 5 mL of the MilliQ water for trace metal analysis and the rest of the sample was kept frozen for nutrient and ion chromatography analyses. The MilliQ water pH was 7 when it came out of the MilliQ system and similar to that of lake water. We prepared MilliQ water freshly right before the extraction process, thus we expected that the solubility calculated using this treatment is representative of TSP solubility in the lake water. Procedure blanks for the bulk digestion and soluble fraction extraction were obtained by processing blank filters in the same way as other samples and the total processing blanks were subtracted when calculating concentrations.

2.2. Deposition flux estimation

Deposition fluxes of nutrients and trace metals to the lake were calculated based on previous modeling results of TSP deposition fluxes in the Tahoe Basin (Dolislager et al., 2012). We calculated deposition fluxes of each compound or element (F_d) to the lake by multiplying their soluble concentrations (C_s) in the collected TSP sample by the model derived TSP deposition flux (T_d).

$$F_d = C_s \times T_d \quad (1)$$

This calculation is based on an oversimplified assumption that all elements have the same deposition velocity. However, the deposition velocity varies as the square of the particle radius size (Jacobson, 2004). Particle size distributions vary spatially within the Tahoe Basin, and are also different close to the shoreline and at offshore sites (VanCuren et al., 2012). We did not measure the particle size distributions in our samples directly which may introduce considerable uncertainty to our calculated deposition fluxes. Moreover, we note that TSP represents only one fraction of atmospheric deposition and both wet deposition and gas phase reactions are not considered here. Hence our estimates are lower than the total atmospheric deposition contributions to the lake. Despite these limitations, results reported here provide first order estimates which have not been previously available. To address this limitation and for comparison we also applied a fixed deposition rate of 2 cm s^{-1} for TSP, which has been used previously in Lake Tahoe (Mackey et al., 2013) and at coastal and nearshore areas for

coarse particles (Duce et al., 1991) and a rate that is ten times smaller (0.2 cm s^{-1}) that is sometimes used for deposition of fine fraction particles.

2.3. Lake water collection

Water depth profile samples from Lake Tahoe were collected seven times at different seasons between the Spring of 2013 and Summer 2016. Van Dorn bottles (Wildco Beta Plus acrylic 2.2 L, with no metal parts that touch the sample) were used for water collection at depths of 50, 100, 150, 200, 250, 300, 350, 400 and 450 m and a one-liter HDPE bottle attached to a 2.5 m long plastic rod was used to collect surface water samples. Samples were collected at the Mid-lake Tahoe Profile (MLTP) station (39.09231° N ; $120.00275^\circ \text{ W}$). From each depth, one-liter of water was dispensed into an acid-washed sample rinsed LDPE bottle for trace metals and Pb isotope analyses as described in Chien et al. (2017). Groundwater samples were obtained from two wells at the Lake Tahoe fire station and three wells at the Hatchery, and river water samples were collected from Third Creek, Trout Creek, Upper Truckee River, Ward Creek, Incline Creek, Blackwood Creek and General Creek. All water samples were filtered with acid washed $0.45 \mu\text{m}$ filters (SupaPore) before nutrient, trace metal and Pb isotope analyses. Samples for trace metal and Pb isotopes analyses were acidified to $\text{pH} < 2$ with concentrated double distilled nitric acid. MilliQ water blanks were also collected and analyzed similarly. TSP and water sampling location sites are shown in Fig. 1.

2.4. Nutrients, ions, trace metals and Pb isotopes analyses

Nitrate+nitrite ($\text{NO}_3^- + \text{NO}_2^-$), ammonium (NH_4^+) and soluble

reactive phosphorus (SRP) in the soluble fractions of TSP samples were analyzed using a nutrient autoanalyzer (QuikChem 8000 Flow Injection Analyzer). Detection limits of $\text{NO}_3^- + \text{NO}_2^-$, ammonium and SRP are $0.29 \mu\text{mol N L}^{-1}$, $0.53 \mu\text{mol N L}^{-1}$ and $0.1 \mu\text{mol P L}^{-1}$, respectively. Formate (CHOO^-), acetate ($\text{C}_2\text{H}_3\text{O}_2^-$), chloride (Cl^-), sulfate (SO_4^{4-}) and oxalate ($\text{C}_2\text{O}_4^{2-}$) were separated and eluted using a $4 \times 250 \text{ mm}$ AS18 column (DIONEX) with a KOH eluent and analyzed by Ion Chromatography (IC) using a DIONEX ICS-2000 system.

Due to low trace metal concentrations in the lake water, about 200 mL of each water sample was first dried down on a hotplate and then reconstituted with 10 mL 2% HNO_3 for concentration analyses (20-fold concentration increase). TSP total and soluble trace metal concentrations, and lake, river and groundwater trace metal concentrations of Al, V, Cr, Mn, Fe, Co, Ni, Cu, Cd, and Pb were analyzed by a High Resolution Inductively Coupled Plasma Mass Spectrometry (Element XR) with triple detector mode. Na, Mg, Ca, P, Zn, Sr, Ti, and U were also measured in bulk TSP and in the TSP soluble fraction samples, while total concentration of Ba was determined only in bulk TSP samples. Low resolution mode was used for Cd, Ba, Pb and U and medium resolution for the rest of the elements. Instrument calibration was done using gravimetrically prepared multi-element standards in the range of concentrations represented by our samples. The coefficient of determination of calibration (RSQ) of the calibration curves for the different elements were better than 0.99, which indicates that interferences were negligible, if any. The blanks for lake water, TSP bulk and soluble fractions are listed in Table S2. Details of trace metal analysis can be found in Chien et al. (2016).

In order to separate Pb from the different sample matrices, 500 mL from each water sample and the digested TSP samples were dried down and re-dissolved in 100 μL of concentrated HBr (Optima grade, Fisher

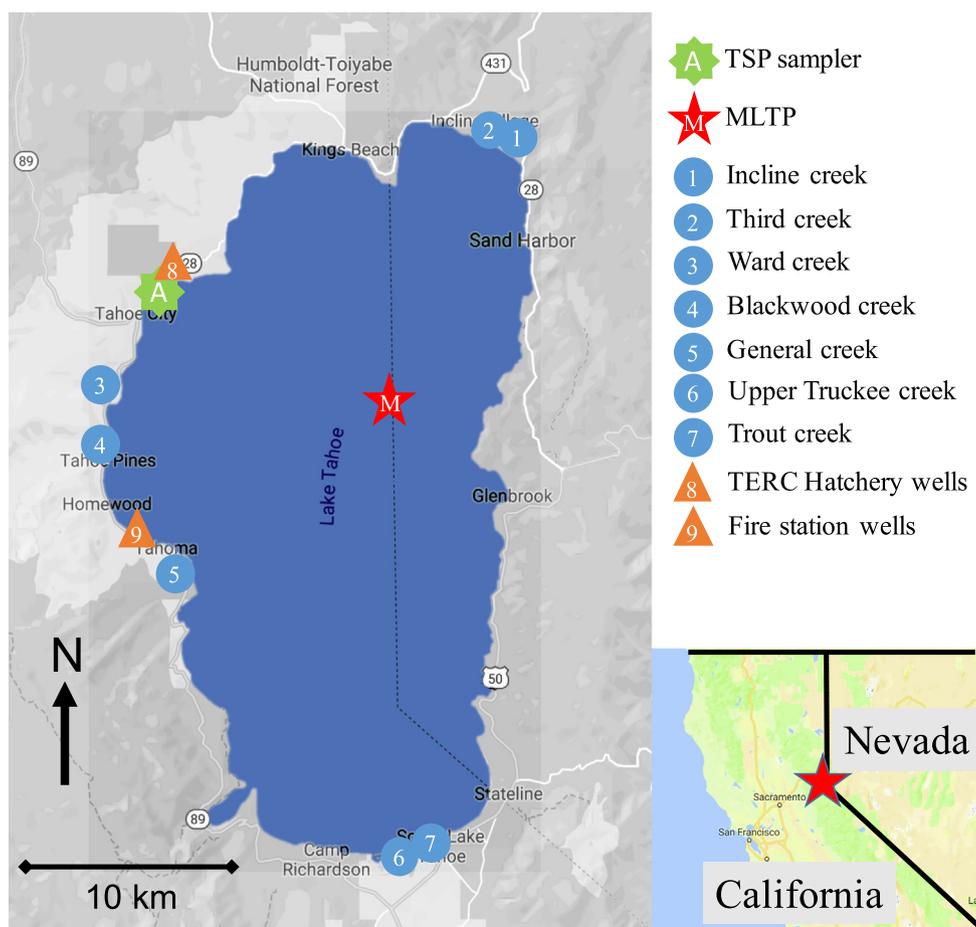


Fig. 1. Map showing the location of Lake Tahoe and the sampling sites for TSP, river water, groundwater and lake water samples.

Scientific) three times. Pb was separated using AG1-X8 resin (adapted from Kamber and Gladu (2009)). Briefly, the matrix of the samples was eluted with 1 N HBr and the Pb fraction was eluted by 6 N double distilled HNO₃, this eluent was then dried down and brought up with 2% HNO₃ to ~2 ppb for analyses. Pb separation and trace metal pre-treatments were done in the clean room in the Keck lab of UCSC. Accuracy of the procedure was evaluated by preparing and analyzing three 50 ng aliquots of NIST SRM-981 as unknowns and results showed that isotope fractionation and contamination was negligible (Table S1).

To determine Pb isotopic composition, analyses were carried out on a Thermo Element XR HR-ICP-MS in the Marine Analytical Laboratory at UC Santa Cruz following the method developed by (Zurbrick et al., 2013). ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb and ²⁰⁸Pb were analyzed and ²⁰⁰Hg and ²⁰²Hg were also monitored for isobaric interference correction on ²⁰⁴Pb. Pb isotopes in the samples were corrected by bracketing to NIST SRM-981 values; NIST SRM-981 was analyzed between every five samples. Typically, a 2 ppb Pb solution resulted in a signal of about 4×10^6 counts per second on ²⁰⁸Pb, external precision (2σ) for ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁷Pb are 5.7‰, 3.7‰ and 2.2‰, respectively (based on 33 NIST SRM-981 analyses).

2.5. Groundwater discharge assessment

We have implemented a radon (²²²Rn)-based tracer approach for assessing groundwater discharge for a better estimation of Pb input from groundwater to the lake. In August 2013, we carried a high-resolution ²²²Rn boat survey along the west shore of Lake Tahoe to measure ²²²Rn concentrations in surface water. Radon measurements were carried out with a three-detector system (RAD AQUA, Duridge, Inc.) as described in Dimova et al. (2009). A map of the groundwater 'hot spots' distribution throughout the west shore was constructed (Fig. S1). We then use the same instrumentation and measured ²²²Rn concentrations at the identified hot spots for several hours to obtain a representative ²²²Rn measurement of the surface/lake water at these sites. Radon concentrations in groundwater collected from wells were also measured to obtain representative groundwater end-member values and a ²²²Rn mass-balance model that was used to calculate groundwater seepage rates (cm/day) using the approach described at Dimova and Burnett (2011).

3. Results and discussion

3.1. Temporal variation in TSP concentrations and in their chemical composition

Between December 2005 to February 2010, TSP concentrations in the air at the Tahoe Basin ranged between 2.7 and 76 $\mu\text{g m}^{-3}$ of air, with an average and standard deviation of $26.3 \pm 14.2 \mu\text{g m}^{-3}$ (Table S3 and Fig. 2). In general, TSP concentrations in the Tahoe Basin air

were higher in the cold periods during late Fall to early Spring (October to April) than in the warm periods during late Spring to early Fall (May to September). Average seasonal concentrations were $29.8 \pm 16.1 \mu\text{g m}^{-3}$ and $20.6 \pm 7.6 \mu\text{g m}^{-3}$, in winter and summer, respectively (Table S3). Variations in atmospheric mixing layer thickness due to differences in sensible heat in the different seasons has been suggested as the cause for seasonal differences in air pollution gases such as CO and SO₂ and in particulate matter concentration (Tang et al., 2015). Specifically, during the warm season when the mixing layer thickness is larger, particulate matter concentrations are lower because the vertical diffusion capability of the atmosphere is higher; in contrast, in the cold season the diffusion capability is lower since the mixing layer height is reduced. Similar mixing layer thickness trend was estimated for Sandy Way at the northwest of Tahoe Basin (CARB, 2006).

The concentrations of bulk metals in the TSP samples are listed in Table S3. Aluminum (Al) has the highest mean concentration ($1329 \pm 920 \text{ ng m}^{-3}$) among the trace metals, followed by Fe ($776 \pm 495 \text{ ng m}^{-3}$) and Ca ($698 \pm 480 \text{ ng m}^{-3}$). The metal with the lowest concentration is Cd ($0.029 \pm 0.025 \text{ ng m}^{-3}$). Similar to TSP concentrations in the air, most trace metals concentrations were also higher in the cold periods (October to April) and lower in the warmer periods (May to September). For example, average concentrations of Al were $1697 \pm 1042 \text{ ng m}^{-3}$ and $823 \pm 294 \text{ ng m}^{-3}$ in the cold and warmer periods, respectively. However, Zn and Cd do not follow this seasonal trend, suggesting they have different sources than the other trace metals (Table S3 and Fig. 3A). The contribution of crustal material (mineral dust) to the trace metals in TSP can be determined by correlating to Al and assuming Al mostly originates from crustal materials. Indeed, some of the elements were highly correlated with Al, including Ti, Fe, Sr, Co, Ca, V, Mg, Mn, K, Na, and U (correlation coefficient > 0.93, $n = 69$), indicating a common source for these elements, primarily from mineral dust originating from the local soil and upper crust. However, Ba, Cu, Zn, and Cd were poorly correlated with Al (correlation coefficient < 0.45) suggesting dominance by non-lithogenic anthropogenic sources, while Ni, Pb, Cr and P, show correlation coefficients between 0.6 and 0.8, suggesting mixed origin (anthropogenic sources in addition to natural mineral dust). These elements can come from tires (Pb, Zn, and Cu) (McKenzie et al., 2009), vehicle emission (Cd, Pb, Zn and Cu) (Bilos et al., 2001), road dust from non-exhaust activities (Ni, Cr, Zn, Ba) (Pant and Harrison, 2013), fertilizer use (Cd, Cr, P, Pb and Ni) (Mortvedt, 1995; Tipping et al., 2014) and industry (Pb, Ni, Cd, Cr, Cu, and Zn) (Chen et al., 2005). Biomass burning is another source of trace metals and can contain Cr, Ni, Cu, Zn, P and Ba (Anderson et al., 2010; Chang-Graham et al., 2011), while firewood burning can be a source of Zn, P, and Ba (Anderson et al., 2010; Kleeman et al., 1999). Considering the limited industrial and agriculture activities within the basin, vehicle emissions, road dust, and wood and biomass burning are the most likely sources. However, further studies need to be carried out to identify the specific sources for

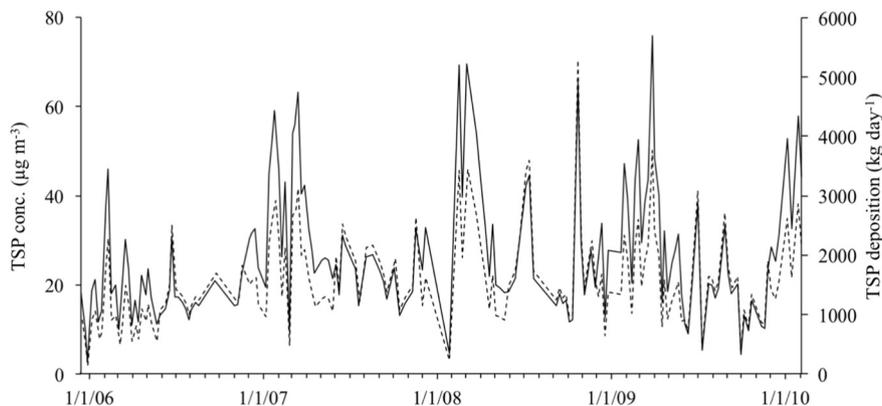


Fig. 2. TSP concentration ($\mu\text{g m}^{-3}$, solid line) and calculated deposition flux to Lake Tahoe (kg day^{-1} , dash line) from 12/12/2005 to 2/2/2010.

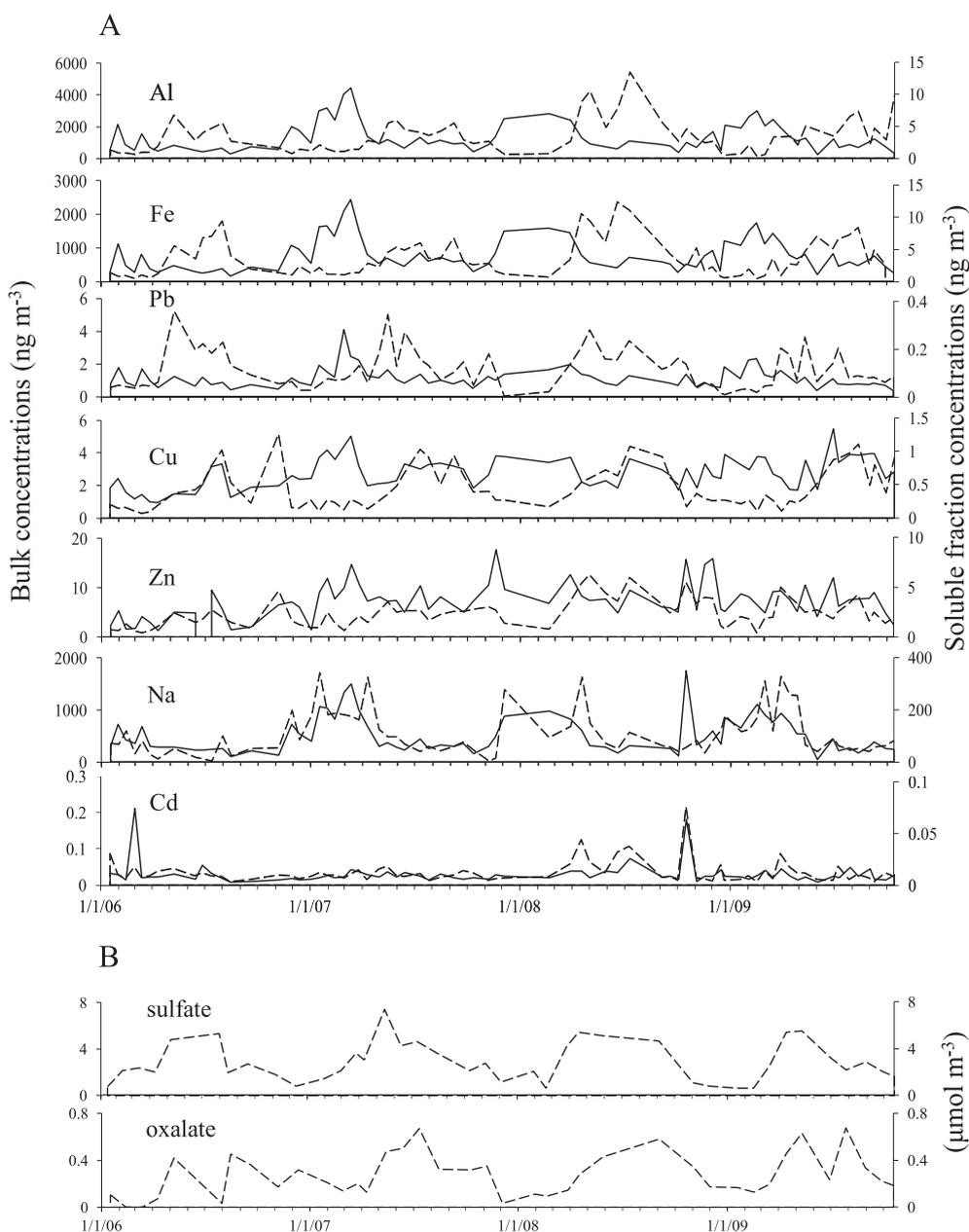


Fig. 3. (A) Bulk trace metal (solid lines, scales are on the left) and soluble fraction (dash lines, scales are on the right) concentrations in TSP (ng m^{-3}). (B) Soluble ion concentrations ($\mu\text{mol m}^{-3}$). The concentrations were normalized to air volume collected.

each of these elements within the basin.

Enrichment factors (EFs) can also be used to evaluate the source of various elements in the TSP. EF for each element is described as:

$$EF = \frac{\left(\frac{\text{Element}}{\text{Al}}\right)_{\text{TSP}}}{\left(\frac{\text{Element}}{\text{Al}}\right)_{\text{crust}}} \quad (2)$$

where $(\text{Element}/\text{Al})_{\text{TSP}}$ is the mass concentration ratio of the trace element to Al in the collected TSP samples and $(\text{Element}/\text{Al})_{\text{crust}}$ is the ratio in the upper continental crust (Taylor and McLennan, 1985) (Fig. 4). EFs that are close to one indicate that the specific constituent in the TSP originated primarily from the upper continental crust (e.g., mineral dust, soil). Higher EF suggests additional sources, specifically from anthropogenic activities, biogenic materials or wildfires. We calculated EFs using the average composition of upper continental crust as well as the composition of Californian soils and regional volcanic rocks (Table 1). In our samples, V, Co, and Fe have low EFs with average

values lower than two, indicative of a mineral dust source, while the enrichment factor of Zn, Cu and Cd is higher than five, indicating that anthropogenic inputs contributed to these elements. Overall metal EF of TSP collected in Tahoe Basin are low, typically < 10 while in urban polluted areas EFs are much higher and can be > 100 (Balasubramanian and Qian, 2004; Sarti et al., 2015). Even in areas dominated by mineral dust, like the Gulf of Aqaba, higher EFs were observed (Chen et al., 2008). The low EF suggests that anthropogenic impacts are low in this region. Differences in EF between the warm (May to September) and cold periods (October to April) suggest a seasonal change in the relative contribution of the sources of these elements to the TSP load. Specifically, Zn, Cu, Ni, and Cd have EF $> 50\%$ higher during the warm periods than in the cold periods (Table 1) implying that the relative contribution from anthropogenic sources, such as transportation-related activity, is higher between May and September.

We also applied a principal component analysis (PCA) to the TSP

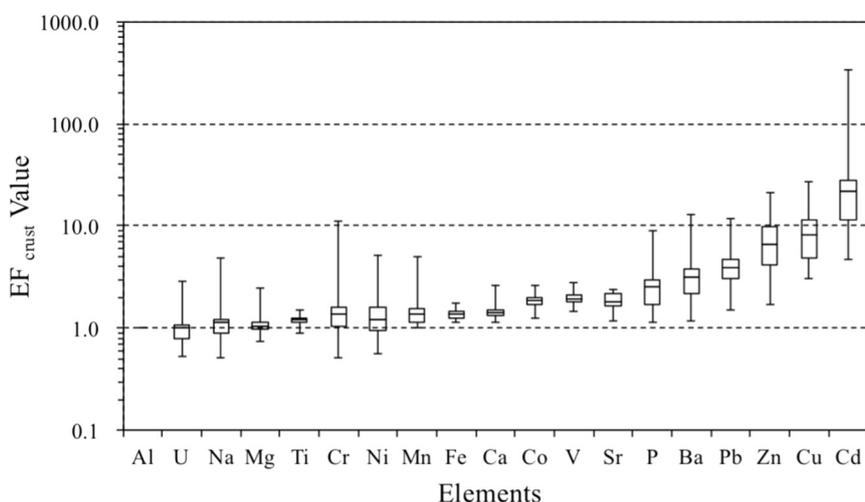


Fig. 4. Enrichment factor values (relative to Al in the upper crust) for various trace elements in TSP collected in Tahoe Basin. The bottom and the top of each box are located at the 25th and 75th percentiles, central horizontal line is drawn at the sample median.

bulk metals composition (Table 2). Overall, the majority of the metals have a common source (or combination of sources) based on their strong association with the first factor. The common source is likely mineral dust based on the low EFs of these metals and the high correlations between these metals and Al. High loading of Cd in factor 2 (likely vehicle emissions) and Cu and Zn in factor 3 (likely biomass burning) indicate these metals are dominated by distinct anthropogenic sources as mentioned previously.

3.2. Total suspended particles metals soluble fraction

When considering nutrient and metal inputs to lakes, the soluble fraction of these nutrients and metals in the TSP is what affects the water chemistry and biology. The soluble fractions (soluble concentration/total concentration) of the various trace metals are largely controlled by their solubilities. For example, although the average bulk

concentration of Al is 1329 ng m^{-3} , the average concentration of the soluble Al fraction is only 3.3 ng m^{-3} , which is 0.25% of the bulk concentration, consistent with the low solubility of Al in mineral dust (Trapp et al., 2010). On the other hand, the average bulk concentration of Zn (7.1 ng m^{-3}) is 180 times smaller than the Al bulk concentration, but the average concentration of soluble Zn (2.4 ng m^{-3} ; > 30% of the bulk) is only slightly lower than that of soluble Al. The soluble fractions of most trace metals in the TSP we analyzed are higher during the warm periods (May to September) (Table S3 and Fig. 3). This could be due to changes in the TSP sources between seasons and source dependent solubility stemming from changes in composition (Sarti et al., 2015). Alternatively, it is possible that chemical transformations in the TSP that depend on seasonally changing conditions such as relative humidity, temperatures, or presence of volatile organic acids affect the solubilities. The latter explanation is more likely the cause for the seasonal changes in solubility in our samples, because the small

Table 1

Element to Al Ratios in the upper continental crust, California soil, Lake Tahoe–Reno region volcanic rocks and the calculated enrichment factors based on average upper crust (EF upper crust), Californian soil (EF soil) and the volcanic rocks for trace elements in TSP collected in this study. EF upper crust in warm and cold periods and their differences are also listed, bold numbers indicate difference larger than 50%. Note that from P to Cd ratios the Element/Al ratios reported are multiplied by 1000.

Element	Element/Al ratios			Calculated enrichment factors			
	California soil, Bradford et al., 1996	Lake Tahoe–Reno region volcanic rocks, Cousens et al., 2008	Upper crust, Taylor and McLennan, 1985	EF _{California soil}	EF _{volcanic rocks}	EF _{upper crust}	
						Warm – Cold Cold	
Al	1	1	1	1	1	1	0%
Fe	0.51	0.42	0.44	1.17	0.72	1.35	10%
Na	0.22	0.20	0.36	1.61	1.42	0.97	–17%
Mg	0.14	0.45	0.17	1.33	0.41	1.07	11%
Ca	0.20	0.79	0.37	2.65	0.66	1.41	–6%
Ti	0.06	0.09	0.04	0.87	0.66	1.20	5%
P	5.6	13.3	12	4.42	1.88	2.11	34%
Mn	8.8	13.8	7.5	1.13	0.72	1.33	42%
Ba	7.0	10.9	6.8	2.79	1.78	2.88	49%
Sr	1.8	8.3	4.4	5.00	1.05	1.98	–24%
Zn	2.04	-	0.88	3.20	-	7.42	51%
V	1.53	2.04	0.75	0.96	0.72	1.96	12%
Cr	1.67	0.83	0.44	0.34	0.68	1.29	18%
Cu	0.39	-	0.31	6.33	-	8.18	78%
Ni	0.78	0.30	0.25	0.40	1.05	1.30	56%
Pb	0.33	0.09	0.25	2.88	10.04	3.87	35%
Co	0.20	-	0.12	1.06	-	1.80	16%
U	0.06	-	0.03	0.43	-	0.86	29%
Cd	0.0049	-	0.0012	4.29	-	17.14	51%

Table 2

The rotated principal component matrix of annual TSP metals in Lake Tahoe, factor loadings larger than 0.5 are highlighted in bold.

	F1	F2	F3
Na	0.880	0.273	-0.233
Mg	0.981	0.079	-0.119
Al	0.980	-0.107	-0.091
P	0.858	0.001	-0.038
Ca	0.987	-0.005	-0.111
Ti	0.980	-0.129	-0.056
V	0.982	-0.126	-0.039
Cr	0.861	-0.018	-0.002
Mn	0.909	-0.008	0.052
Fe	0.984	-0.116	-0.037
Co	0.978	-0.139	-0.058
Ni	0.906	-0.045	0.163
Sr	0.963	-0.139	-0.131
Ba	0.732	0.021	0.248
Pb	0.857	-0.041	-0.216
U	0.939	0.200	-0.024
Cu	0.656	0.121	0.633
Zn	0.543	0.408	0.532
Cd	0.022	0.918	-0.300

differences in EFs (< 10%) for most of the elements throughout the year is suggestive of a similar source; hence, change in sources is not the major cause of the significant seasonal variations in solubility (> 100%, Table 1). Specifically, the low pH history of the TSP can increase the solubility of trace metals such as Al, Fe, and Mn (Spokes and Jickells, 1995). Other studies also observed increases of TSP Fe solubility related to sulfate content (Li et al., 2017; Tang et al., 2015) or sulfate together with nitrate or oxalate (Buck et al., 2006), both of which reduce the TSP pH as they form sulfuric and nitric acids. Indeed, in our samples sulfate concentrations and the concentrations of several volatile organic acids (particularly oxalate) are higher during May to September (Fig. 3B). Interestingly, the seasonal differences in solubility for Na, Zn and Cd are smaller than for the other elements. This could be because these elements have relatively high solubility overall (41.4%, 33.8% and 22.3% for Cd, Zn, and Na, respectively) hence the relative changes due to seasonal atmospheric conditions are muted. Our data also suggest low seasonal differences for Na. This is likely due to an extra source of Na in winter from salting of the road, reducing the seasonal differences. Indeed Cl⁻ concentrations in our samples are also higher in the winter (Table S3) suggesting a road salting source as there is no other apparent source for Cl⁻ in TSP.

Annual average concentrations of soluble NO₃⁻ + NO₂⁻, NH₄⁺ and SRP are 1.71 ± 0.86 μmol m⁻³, 2.93 ± 2.23 μmol m⁻³ and 0.05 ± 0.03 μmol m⁻³, with an average N to P ratio of 117 ± 71 (Table S3). Major nutrients extracted from the TSP samples also show seasonal patterns (Fig. 5). Overall, NO₃⁻ + NO₂⁻ is slightly higher in the cold periods (1.93 ± 0.92 μmol m⁻³) than in the warm periods (1.38 ± 0.66 μmol m⁻³), but the difference is not statistically significant. In contrast, NH₄⁺ and SRP are higher during the warm periods (May to September; 4.75 ± 1.95 μmol m⁻³ and 0.08 ± 0.02 μmol m⁻³, respectively) than in the cold periods (October to April; 1.68 ± 1.39 μmol m⁻³ and 0.03 ± 0.02 μmol m⁻³, respectively). Similar to the metals, the causes for the seasonal variability could be seasonal changes in the TSP sources and/or processes in the atmosphere that impact the solubility of these nutrients. Based on the seasonal variability in the EFs and solubility for P (EF changes by 34% between warm and cold periods and solubility is 215% higher in May through September than in October through April) we conclude that, like for the other elements we measured, it is the seasonal meteorological parameters and processes in the atmosphere that are affecting the solubility of phosphate and likely NH₄⁺. On the other hand, NO₃⁻ + NO₂⁻ solubility in water is high (~60%; Chen et al., 2007). Hence the seasonal differences seen were small. The annual average N:P

ratio of 117 is higher than the ratio of 16 N:1P that phytoplankton generally need for growth. This ratio is even higher, reaching an average of 141 during the cold periods (October to April), likely due to the lower solubility of P in the cold season as mentioned above. This finding is consistent with the report of Mackey et al. (2013) which was based on a smaller number of samples. Moreover, a N:P ratio of nutrients contributed from atmospheric deposition would be even higher when considering nitrogen deposition from gas phase inputs such as HNO₃ and NH₃, which were not included in this study. These N phases are major sources of N deposited into Lake Tahoe (CARB, 2006) and can account for 50% of total inorganic atmospheric N input. The high N:P ratio in atmospheric deposition could impact the N:P ratio in lake water thus influencing the growth of phytoplankton in Lake Tahoe. Indeed, a nutrient addition experiment indicated that phytoplankton tend to be P limited during October through April when atmospheric N:P in the Tahoe Basin is higher (Goldman et al., 1993).

3.3. Nutrients and trace elements fluxes from TSP to the lake

Cumulative average (based on the different years) seasonal TSP deposition to lake Tahoe is 2.8 × 10⁵ kg for December to May and 3.1 × 10⁵ kg for June to November and the average annual flux is 5.9 × 10⁵ kg yr⁻¹. TSP and associated nutrients and trace elements fluxes are listed in Table 3. The difference in TSP deposition between the warm and cold periods is small, however, when considering the solubility, the overall soluble fraction input to the lake is higher during the warm season. TSP deposition calculated using the deposition velocity from Dolislager et al. (2012) (5.9 × 10⁵ kg yr⁻¹) is much lower than that obtained using a rate of 2 cm s⁻¹ (8.2 × 10⁶ kg yr⁻¹) and slightly lower than the deposition calculated using 0.2 cm s⁻¹ as the deposition velocity (8.2 × 10⁵ kg yr⁻¹). The TSP deposition velocity modeled by Dolislager et al. (2012) is low compared to deposition velocities estimated for other locations. For example, a velocity of 0.34–1.5 cm s⁻¹ is the range reported for calculating metals deposition in Los Angeles (Lim et al., 2006), between 0.22 and 13 cm s⁻¹ is used at Burnaby Lake Canada (Brewer and Belzer, 2001) and from 0.0062 cm s⁻¹ to 5.4 cm s⁻¹ with an average of 0.2 cm s⁻¹ in used some Great lakes (Pirrone et al., 1995; Zufall et al., 1998). The range represents the range of particle sizes that various metals are associated with. Most of the trace metals in our samples have low EFs (EF < 10) indicating their association with mineral dust. Duce et al. (1991) suggested that dry deposition velocities for mineral TSP range from 0.3 to 3 cm s⁻¹ with an average 0.4 cm s⁻¹, a value that is more than twice the modeled velocity of Dolislager et al. (2012). Hence, our calculations may be conservative estimates.

3.4. Lake water trace metal concentrations

The most striking feature of the TSP samples collected in Tahoe Basin is the seasonal variation of trace metal solubilities and corresponding higher soluble trace metal fluxes in the spring and summer between May and September, despite higher TSP concentrations in winter (October to April). This finding is important because Lake Tahoe's water experiences stratification during the warm season (June – November) and previous studies indicated that during the stratification seasons, high N:P input from TSP deposition could alter the N:P in the surface lake water (Mackey et al., 2013). This poses the question whether TSP associated trace metal inputs to the lake during stratification also alter Lake Tahoe's surface water trace metal composition. To address this question, we collected lake water samples in 2013 and 2016 at different seasons and analyzed them for trace metals. Although the water samples were collected during in different years than the TSP samples (2005–2010), the trends of higher deposition in the summer is repeatedly seen across the five years of TSP sampling and stratification is also a known annual seasonal feature in the lake (TERC, 2016), thus we assumed these trends are representative of the respective seasons

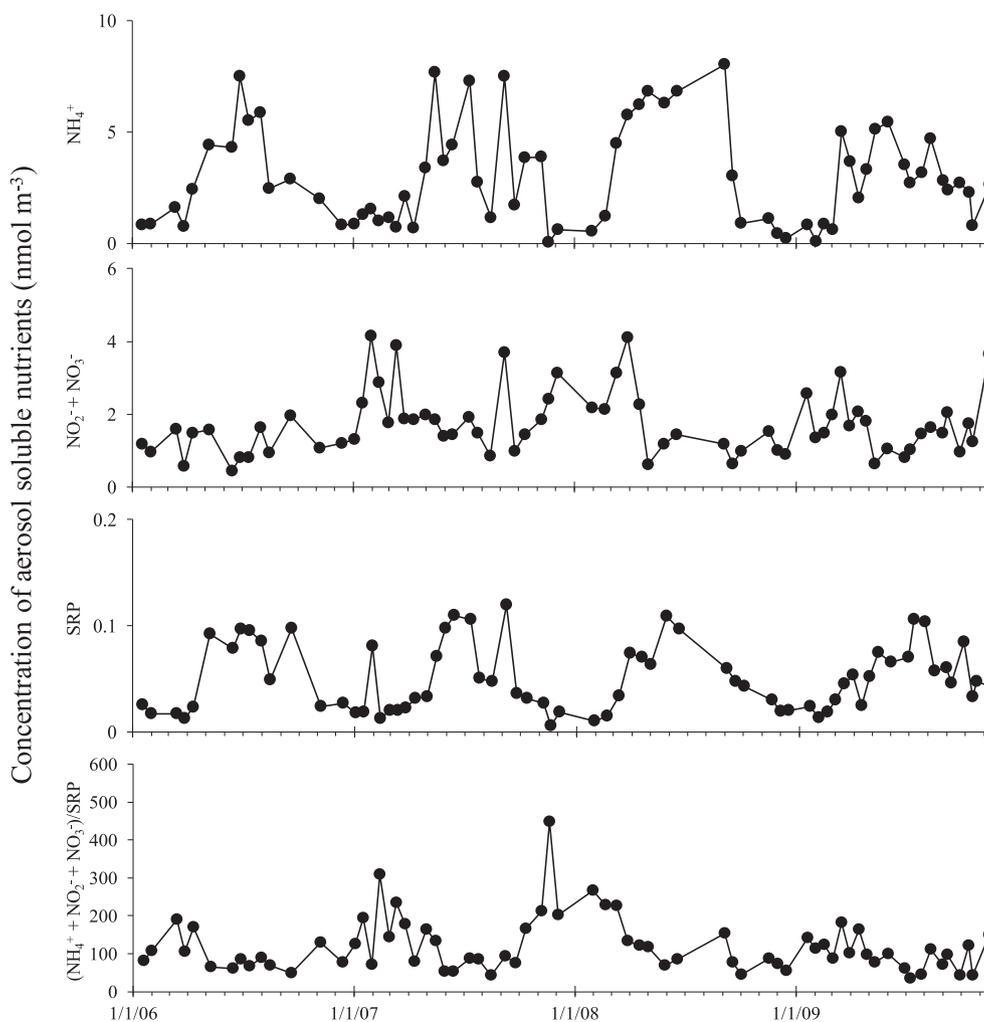


Fig. 5. NH_4^+ , $\text{NO}_2^- + \text{NO}_3^-$, SRP and $(\text{NH}_4^+ + \text{NO}_2^- + \text{NO}_3^-)/\text{SRP}$ ratio in TSP soluble fraction collected between 2006 and 2009.

Table 3

Calculated fluxes of TSP (kg), nutrients (kmol) and soluble trace metals (kg) in Summer/Fall, Winter/Spring and annual periods to Lake Tahoe, based on TSP annual deposition from Dolislager et al. (2012) and particle deposition rates of 0.2 and 2 cm s^{-1} based on TSP concentrations in this study.

	June to November			December to May			Annual		
	Dolislager et al., 2012	0.2 cm s^{-1}	2 cm s^{-1}	Dolislager et al., 2012	0.2 cm s^{-1}	2 cm s^{-1}	Dolislager et al., 2012	0.2 cm s^{-1}	2 cm s^{-1}
TSP	3.1×10^5	3.2×10^5	3.2×10^6	2.8×10^5	5.0×10^5	5.0×10^6	5.9×10^5	8.2×10^5	8.2×10^6
$\text{NO}_3^- + \text{NO}_2^-$	21	21	215	18	32	323	39	54	538
NH_4^+	71	74	736	16	28	281	87	102	1017
SRP	1.2	1.2	12.2	0.3	0.5	5.0	1.5	1.7	17.3
Al	77	79	791	20	35	352	96	114	1143
Fe	89	91	915	19	34	335	107	125	1250
Ca	1237	1277	12,766	667	1190	11,903	1903	2467	24,668
Na	923	953	9531	1361	2431	24,308	2285	3384	33,839
Mg	213	220	2202	91	163	1626	304	383	3828
Ti	2	2	16	0.5	0.8	8.4	2.0	2.4	24.3
P	56	57	574	11	20	201	67	77	775
Mn	29	29	295	10	18	184	39	48	479
Sr	7	7	74	4	7	65	11	14	140
Zn	41	42	419	21	37	369	61	79	787
Cu	10	11	105	3	5	47	13	15	152
V	1.3	1.4	13.6	0.2	0.4	3.5	2	2	17
Pb	2.4	2.5	24.8	0.7	1.2	11.7	3	4	37
Cr	0.5	0.5	4.7	0.3	0.6	5.7	0.8	1.0	10.4
Ni	0.4	0.4	4.3	0.1	0.2	2.2	0.5	0.7	6.5
Co	0.3	0.3	2.6	0.1	0.2	1.5	0.3	0.4	4.1
U	0.02	0.02	0.20	0.00	0.01	0.06	0.02	0.03	0.27
Cd	0.2	0.2	1.9	0.1	0.2	2.0	0.3	0.4	3.9

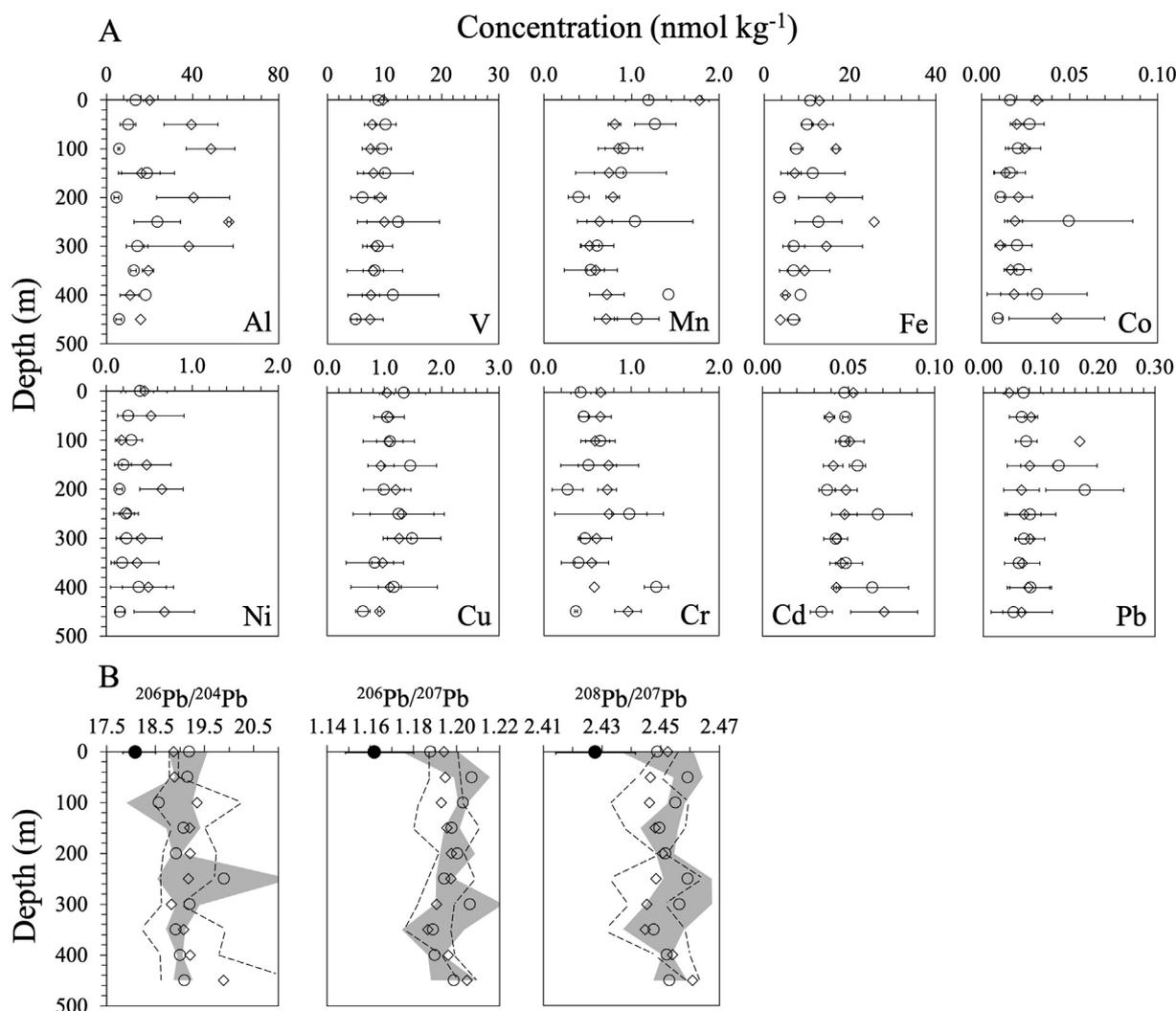


Fig. 6. (A) Trace metal concentration depth profiles. Samples were collected at MLTP at mid-lake. Three depth profiles were collected during June to November (open diamonds) and four during December to May (open circles) between Spring 2013 and Summer 2016. Error bars represent one standard error. (B) ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁷Pb lake water depth profiles (open diamonds and circles) and median values of 25 TSP samples (solid circles) collected during Jan 2006 to Sep 2009, note that the two sides of the bars for the TSP samples data represent maxima and minima isotope ratios, and the dash lines and shaded area represent 1SD for June to November (open diamonds) and December to May (open circles), respectively.

each year. Trace metal concentrations in the lake water, however, did not show apparent seasonal or depth variations except for Mn which shows a surface maximum in concentration (Fig. 6A and Table S4). Average lake water concentration of Al, Fe, Co, V, Mn, Ni, Pb, Cr, Cu, and Cd at 50 m is 22.6, 11.2, 0.02, 9.2, 1.1, 0.37, 0.07, 0.54, 1.1 and 0.04 nmol kg⁻¹, respectively (Table S5). The concentrations for Al, Mn and Cd are well below the threshold concentrations that could be toxic to aquatic organisms. In general, the trace metal concentrations in Lake Tahoe are similar to those reported for Lakes Erie, Ontario and Superior (Nriagu et al., 1996). Compared to other lakes of similar size in California, trace metal concentrations in Lake Tahoe are lower. This could be due to higher inputs in lakes where agriculture activities are typical in the watershed (e.g. Clear Lake) or in arid environments where higher lithogenic inputs are expected (Walker Lake) (Romero et al., 2013). Alternatively, since the volume of Lake Tahoe is larger than that of these other California lakes it is possible that the low concentrations in Tahoe are resulting from a more significant dilution effect in the Lake Tahoe. Water volumes of Clear Lake and Walker Lake are about 1% of the volume of Lake Tahoe (150 km³), while water volumes are much larger in Lakes Erie, Ontario and Superior (480, 1640 and 12,000 km³, respectively). Previously reported metal concentrations in north and south Lake Tahoe water, collected in 2009 and 2010 (Romero et al.,

2013), are higher than those measured in this study, the concentrations in the middle of the lake reported in Romero et al. (2013), however, are similar to those measured in our study (Table S5).

The lack of seasonal or depth variation in trace metal concentrations in Lake Tahoe's water column is likely because of the relatively low input fluxes and the great depth, hence volume of the lake. Typically, the lake mixes thoroughly to 500 m every 4 to 5 years, and in other years, the mixing depth is between 80 and 300 m (TERC, 2016). This vertical mixing redistributes the trace metals with depth and the net input of these metals over the stratified season is not sufficient to change the distribution to observe seasonal variation in surface water. For example, a 10 nmol kg⁻¹ increase in Al above the 20 nmol kg⁻¹ background deep water concentration (a 50% increase) during the stratified months, assuming a 20 m mixed layer based on the thermocline for the stratified season (Coats et al., 2006), would require an extra 2700 kg of Al to be deposited onto the lake surface over that time interval. This flux is 35 times the typical warm periods (May–September) Al flux (based on the Al concentrations in TSP, Al solubility and the deposition velocities from Dolislager et al. (2012)). For elements with a lower atmospheric flux such as V, a > 1600-fold increase in deposition is required to increase the concentration by 50%. For elements like Pb, with very low concentrations in lake water, a > 30-

Table 4
Trace metal inventories in the 0–20 m water column, annual TSP soluble trace metal fluxes and flux to inventory ratios.

	Metal inventory 0–20 m (kg)	TSP metal flux (kg yr ⁻¹)	Annual flux to inventory ratio
Cd	53	0.3	0.56%
Pb	139	3.1	2.13%
Al	5134	96	1.93%
V	4647	1.5	0.03%
Cr	276	0.8	0.28%
Mn	679	39	5.73%
Fe	6343	107	1.70%
Co	19	0.3	2.52%
Ni	203	0.5	0.27%
Cu	725	13	1.77%

fold increase of the average atmospheric flux is needed to observe a measurable increase in concentration in the surface water. To estimate the contribution of atmospheric deposition of trace metals to the lake, we divided the TSP annual deposition of each dissolved trace metal calculated based on TSP deposition from Dolislagar et al. (2012) by the respective dissolved trace metal inventories in the upper 20 m of Lake Tahoe (Table 4) calculated based on average metal concentrations at 0 to 20 m water depth. The calculated atmospheric contributions typically are low, ranging from 0.03% for V to 5.7% for Mn and are consistent with the lack of surface maxima for most of the metals at this site.

In contrast to the trace metals, the atmospheric deposition is much higher for major nutrients (particularly when including gas phase contribution) with 20% for P and 57% for N attributed to atmospheric deposition (Sahoo et al., 2013). The input of fine particles to the total fine particle inventory in the surface layer of the lake is also relatively high at 16% (Sahoo et al., 2013). Overall, while trace metal fluxes from atmospheric deposition have been shown to contribute to lake budgets, biogeochemistry, and ecology at other sites worldwide (Bacardit and Camarero, 2009; Sweet et al., 1998), in Lake Tahoe atmospheric deposition of trace metals is low, but it is important for nutrients and fine particle loads which can affect lake clarity directly by fine particle addition or indirectly by increasing chlorophyll through an external input of limiting nutrients.

3.5. Pb isotopic composition and the contribution of TSP deposition to Pb in lake water

To better determine possible sources of trace metals to Lake Tahoe, we analyzed the Pb isotopic composition in TSP, lake water, river water and groundwater samples. ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁷Pb of 25 representative TSP samples were measured (Table S6). Fig. 6B shows the three Pb isotope ratios for samples representing the warm and cold periods. No seasonal trends in Pb isotope ratios are seen, suggesting that the sources of Pb do not vary seasonally or that different sources have similar isotope ratios. The average and standard deviation of ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁷Pb are 18.11 ± 0.14, 1.162 ± 0.006 and 2.428 ± 0.007, respectively. There is also no seasonal variation in the depth distribution of Pb isotopes in lake water, consistent with the homogenous distribution of dissolved metals (Fig. 6A). The average and standard deviation of ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁷Pb in lake water are 19.09 ± 0.52, 1.197 ± 0.008 and 2.451 ± 0.010, respectively. Annual atmospheric Pb input contributes only 2.1% to the upper 20 m Pb inventory (Table 4). Both lake water isotope profiles and atmospheric Pb contribution to the surface layer show that Pb from TSP deposition has a relatively weak effect on the Pb isotopic composition in the upper water layer of the lake.

To assess the relative contribution of different Pb sources to the lake we measured the concentration and isotope ratios of several potential

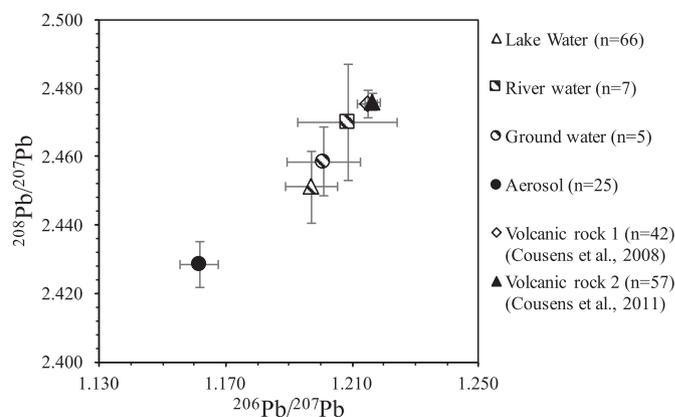


Fig. 7. Triple-isotope plot of Pb in lake water, river water, ground water, TSP and volcanic rocks (1 and 2 are mean values of Pb isotopes from (Cousens et al., 2008) and (Cousens et al., 2011), respectively). Numbers in parentheses are number of samples used. Note the river water ratio is an average of weighted ratios based on their individual annual discharges.

sources. Weighted average of ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁷Pb in seven of the major rivers in the Tahoe Basin, based on their annual discharge, are 19.00 ± 0.27, 1.215 ± 0.016 and 2.474 ± 0.017, respectively, and groundwater samples ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁷Pb ratios are 18.87 ± 0.27, 1.201 ± 0.012 and 2.459 ± 0.010, respectively. We also report published Pb isotope ratios for additional potential sources in the region (Cousens et al., 2011; Cousens et al., 2008). We plotted all Pb isotope data in a ²⁰⁶Pb/²⁰⁷Pb vs. ²⁰⁸Pb/²⁰⁷Pb tri-isotope diagram (Fig. 7). The Pb isotope ratios in lake water are similar to those of groundwater and some of the river water samples, suggesting that river water and possibly groundwater are likely the major Pb sources to the lake. To estimate the relative contribution of soluble Pb from groundwater, river water and atmospheric deposition, we used the average groundwater and flow-weighted average river water Pb concentrations (3.43 and 0.143 nmol kg⁻¹, respectively), a groundwater annual discharge that ranges from 3.7 to 6.4 × 10⁷ m³ year⁻¹ (Fogg, 2002; Thodal, 1997; USACE, 2003) and an annual streamflow of 4.05–4.32 × 10⁸ m³ year⁻¹ (Lahontan and NDEP, 2010; Thodal, 1997) to estimate contributions from these different sources. The annual Pb loads from rivers and groundwater were estimated to be 26.3 to 45.4, and 12.0 to 12.8 kg year⁻¹, respectively, while Pb loads from TSP deposition were 3.1 kg year⁻¹. Based on this calculation, atmospheric deposition contributes only about 5–8% of the Pb in the lake. The concentrations of Pb in groundwater are > 10-fold higher than in river water and thus its proportional contribution to the lake is larger despite the lower water flux. Our groundwater Rn tracer surveys during August 2013 revealed extremely large spatial variability in groundwater fluxes to the west shore of Lake Tahoe (Fig. S1). Because currently there is no detailed comprehensive study assessing groundwater fluxes to Lake Tahoe, fluxes reported here and in previous studies are associated with high uncertainty when used to calculate metal (or other solute) fluxes. Nevertheless, based on our mass balance radon-based tracer method (Dimova and Burnett, 2011), we found that groundwater fluxes to Lake Tahoe specifically on the west shore, where we performed our Rn survey, can range from 0.02 to 7.5 cm day⁻¹. Considering only the seepage areas of the two identified “hot spots” during the Rn survey (see Rn survey map, Fig. S1) at the Tahoe Pier (north-west Tahoe, area = 2.0 × 10⁶ m², ArcGIS) and Emerald Bay (seepage area = 1.8 × 10⁶ m², ArcGIS), water discharge in the area ranges from 7.6 × 10² m³ day⁻¹ to 2.9 m³ day⁻¹, or between 2.8 × 10⁵ and 1.0 × 10⁸ m³ annually. When we apply this discharge rate to the groundwater Pb flux, contribution from atmospheric deposition are 4–20% of the total flux. This agrees with the calculation based on Pb concentrations and isotope ratios results from the lake

water column.

4. Conclusions

Our results indicate that TSP concentrations in the air in the Tahoe Basin are higher during October to April than during May to September, likely due to seasonal differences in atmospheric mixing layer thickness that result from different sensible heat conditions. Consistent with the TSP higher concentration, bulk trace metal concentrations (total concentrations) in the atmosphere are also higher during October to April. The solubilities of trace metals in TSP are, however, higher during May to September. We attribute this to seasonal differences in atmospheric processes rather than the changes in sources, specifically acids of sulfate and nitrate which increase the solubility of metals and are also high between May and September. Based on the correlation between various elements and Al, the enrichment factors for these elements, and PCA analyses, we conclude that most of the elements are sourced primarily from mineral dust, while Zn, Cu and Cd are contributed also by anthropogenic inputs (transportation and biomass combustion). Among major nutrients, the soluble concentrations of $\text{NO}_3^- + \text{NO}_2^-$ in TSP are slightly higher between October and April while NH_4^+ and SRP concentrations are higher between May and September. Typically trace metal concentrations and Pb isotopic ratios do not show much variability throughout the lake water column and lack surface maxima even during the stratified season, indicating that TSP is not a significant source of soluble metals to the lake. Based on calculations using Pb isotope ratios in TSP, rivers, and groundwater, TSP deposition only contributes about 4–20% of soluble Pb, assuming rivers and groundwater are the only other sources.

Acknowledgment

We thank the staffs in Tahoe Environmental Research Center for providing accommodation and assistance on TSP and water sampling. This work was supported by NSF-OCE grant 0850467 to Adina Paytan.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemgeo.2019.02.005>.

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