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SANTA CRUZ

**IMPACTS OF DRY ATMOSPHERIC DEPOSITION ON AQUATIC
SYSTEMS – NUTRIENTS, TRACE METALS AND LEAD ISOTOPES**

A dissertation submitted in partial satisfaction
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

EARTH SCIENCES

by

Chia-Te Chien

March 2017

This dissertation of Chia-Te Chien
is approved:

Professor Patrick Y. Chuang, Chair

Dr. Adina Paytan

Professor A. Russell Flegal

Professor James Zachos

Tyrus Miller
Vice Provost and Dean of Graduate Studies

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ABSTRACT

Impacts of Dry Atmospheric Deposition on Aquatic Systems – Nutrients, Trace Metals and Lead Isotopes

Chia-Te Chien

Atmospheric deposition is a source of new N, P and trace metals to the ocean and water bodies on land. Nutrient and trace metal inputs from atmospheric deposition have been shown to induce phytoplankton growth and impact water chemistry. The three chapters presented in this thesis examine dry atmospheric deposition impacts on phytoplankton and water chemistry including: (1) How African dust impact phytoplankton growth at the low nutrient low chlorophyll (LNLC) ocean off Barbados; (2) Evaluate the contribution of Pb from Asian dust to the western Philippine Sea, and (3) Evaluate the contributions of nutrients and trace metals from aerosol to Lake Tahoe. In the first study, a bioassay incubation experiment conducted with nutrients and local atmospheric aerosol amendments indicates that phosphorus (P) availability limited phytoplankton growth in the low nutrient low chlorophyll (LNLC) ocean off Barbados. The results also suggest that atmospheric deposition induces P limitation in this LNLC region by adding more N and iron (Fe) relative to P. This favors the growths of *Prochlorococcus*, a genus characterized by low P requirements and highly efficient P acquisition mechanisms. In the second study, the

dissolved lead (Pb) concentrations and isotopic compositions in seawater of the western Philippine Sea (WPS) were determined to investigate sources and sinks of Pb. The results suggest sedimentary inputs are a major source of dissolved Pb in deep water and Asian aerosols in surface water. Differences in Pb concentrations and isotopic signatures between water samples collected from the Pacific Deep Water water-mass during this study and those collected a decade ago suggest that the anthropogenic input of Pb changes even in deep water on decadal scales. In the third study, the trace metal concentrations and Pb isotopic composition in aerosols and in lake water were determined. The results show a seasonal trend of trace metal concentrations and solubilities. Pb isotopes indicate atmospheric deposition is not a major source of Pb to the lake, or that the turn-over rate of lake water is faster than the Pb residence time.

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INTRODUCTION

Atmospheric aerosols are small colloids of fine particles, also referred to as dust, smoke and haze. Aerosols can be generated from natural or anthropogenic process. Natural sources include wind-blow dust, volcanic eruptions, wildfires and sea-salt spray. Human activities such as coal combustion and fossil fuel burning, various industrial processes such as mining and smelting or agriculture activities also produce aerosols. The broad variety of sources as well as the various transformation (gas phase and liquid phase reactions) occurring in the atmospheric during aerosol transport result in different chemical compositions of aerosols. Mineral dust contains mostly suspended soil materials and has a composition close to upper Earth crust. Volcanic emissions contribute materials from Earth interior, including gases (carbon dioxide and sulfur dioxide), and particles (ash). Sea-spray adds salts together with other elements and organic compounds from the ocean surface. Anthropogenic sources tend to emit particles enriched in heavy metals relative to crustal materials.

Atmospheric deposition is a source of new N, P and trace metals to the ocean (Duce et al., 2008; Duce et al., 1991; Jickells et al., 2005; Kanakidou et al., 2012; Prospero et al., 1996). Nutrient inputs from atmospheric deposition have been shown to induce phytoplankton growth (Boyd et al., 1998; Duarte et al., 2006; Erickson et al., 2003), enhance N fixation at some oceanic locations (Mills et al., 2004), impact phytoplankton species dynamics (Guo et al., 2012; Jordi et al., 2012; K.R. Mackey et al., 2012; Paytan et al., 2009) and intensify carbon sequestration via the biological

pump (Bressac et al., 2014; Guieu et al., 2014; Krishnamurthy et al., 2010; Parekh et al., 2006). I used bioassay incubation experiments with nutrients and local atmospheric aerosol amendments in order to understand how distinct phytoplankton species respond to nutrient loading from atmospheric deposition in Barbados. This can provide information on the impact of dust deposition on phytoplankton communities in other LNLC areas of the ocean. This is critical not only for our understanding of the current functioning of LNLC regions and the role these regions play in the carbon cycle, but also for the projection of future changes, since significant changes in the magnitude of dust distribution (Ginoux et al., 2012; Mahowald et al., 2007; Mahowald et al., 2010; Ward et al., 2014) and future expansion of LNLC regions are predicted (Henson et al., 2010; Steinacher et al., 2010). On the other hand, understanding variations in Pb concentrations and isotope composition in the ocean can provide information about anthropogenic and lithogenic sources, fluxes, and water mass mixing patterns that affect Pb distribution (Alleman et al., 1999; von Blanckenburg et al., 1996; Wu et al., 2010). However, there are relatively few studies reporting seawater Pb isotopes in the Pacific Ocean (Flegal and Patterson, 1983; Flegal et al., 1984; Gallon et al., 2011; Wu et al., 2010), particularly in the Northwestern Pacific Ocean, a region that might be impacted by the >20 fold increase in coal burning in China over the past three decades (Lee et al., 2014). Furthermore, trace metal composition along with other information (for example Pb isotopic composition) can be used to identify possible aerosol/dust sources. Specifically, the soluble fractions of nutrients and trace metals from aerosols are of

importance when considering the impacts of aerosol deposition on water chemistry and aquatic ecosystems.

In the first chapter, I carried out bioassay incubations with locally collected aerosols and native phytoplankton assemblages collected offshore of Barbados to investigate the impact of atmospheric nutrient and trace metal inputs on phytoplankton productivity and community structure. We additionally employed a numerical model to explore how species-specific differences in phytoplankton cellular elemental ratios and regional variation in atmospheric deposition together influence phytoplankton community structure. In the second study, I report Pb concentrations and isotopic compositions at 7 vertical profiles in the Western Philippine Sea (WPS), collected during the Taiwan GEOTRACES process study (March 2014). By comparing Pb concentrations and isotopic composition in the WPS to open ocean Pb signatures and to signatures of potential Pb sources, we are able to evaluate the impacts of atmospheric deposition and island arc inputs on seawater Pb in this region. In the third chapter, I present the first long term data set of aerosol nutrients, trace metals and Pb isotopes input in Tahoe basin. Five years of aerosol samples collected between Winter 2005 – Spring 2010 and water samples collected between Spring 2013 to Summer 2016 were analyzed. Our results indicate that aerosol concentrations in the air in the Tahoe basin are higher during Oct – April. Trace metal concentrations in aerosol samples are also higher in the cold period, however, trace metal solubilities of aerosol samples are higher during warm periods, likely due to differences in aerosol

sources or different chemical transformation occurring in different seasons. Based on the correlation between different elements and Al and calculated element enrichment factors we identify that V, Co and Fe are dominated by mineral dust sources, while Zn, Cu and Cd are contributed more by anthropogenic inputs. Among major nutrient concentrations in aerosols, $\text{NO}_3^- + \text{NO}_2^-$ levels are higher during cold periods while NH_4^+ and soluble phosphate are higher in the warm period. Typically trace metal concentrations and Pb isotopic ratios are similar throughout the water column, this implies that the water mixing time is shorter than residence time of trace metals include Pb. When considering river water and ground water in addition to aerosols as sources of Pb in a triple-isotopes plot ground water discharge and riverine input are more important Pb sources than aerosols, but aerosol still contributes some Pb to the lake.

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Chapter One

EFFECTS OF AFRICAN DUST DEPOSITION ON PHYTOPLANKTON IN THE WESTERN TROPICAL ATLANTIC OCEAN OFF BARBADOS

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Global Biogeochemical Cycles

RESEARCH ARTICLE

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Key Points:

- Phytoplankton in low-nutrient low-chlorophyll waters near Barbados are phosphate limited
- Atmospheric deposition with high nitrogen and iron relative to phosphorus drives this phosphate limitation
- *Prochlorococcus* thrives in this environment due to its low phosphorus requirements

Supporting Information:

- Supporting Information S1
- Table S2

Correspondence to:

A. Paytan,
apaytan@ucsc.edu

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Effects of African dust deposition on phytoplankton in the western tropical Atlantic Ocean off Barbados

Chia-Te Chien¹, Katherine R. M. Mackey², Stephanie Dutkiewicz³, Natalie M. Mahowald⁴, Joseph M. Prospero⁵, and Adina Paytan¹
¹Earth and Planetary Sciences Department, University of Santa Cruz, Santa Cruz, California, USA, ²Department of Earth System Science, University of California, Irvine, California, USA, ³Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, Massachusetts, USA, ⁴Department of Earth and Atmospheric Sciences, Cornell University, Ithaca, New York, USA, ⁵Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, Florida, USA

Abstract Bioassay incubation experiments conducted with nutrients and local atmospheric aerosol amendments indicate that phosphorus (P) availability limited phytoplankton growth in the low-nutrient low-chlorophyll (LNLC) ocean off Barbados. Atmospheric deposition provides a relatively large influx of new nutrients and trace metals to the surface ocean in this region in comparison to other nutrient sources. However, the impact on native phytoplankton is muted due to the high ratio of nitrogen (N) to P ($\text{NO}_3\text{:SRP} > 40$) and the low P solubility of these aerosols. Atmospheric deposition induces P limitation in this LNLC region by adding more N and iron (Fe) relative to P. This favors the growth of *Prochlorococcus*, a genus characterized by low P requirements and highly efficient P acquisition mechanisms. A global three-dimensional marine ecosystem model that includes species-specific phytoplankton elemental quotas/stoichiometry and the atmospheric deposition of N, P, and Fe supports this conclusion. Future increases in aerosol N loading may therefore influence phytoplankton community structure in other LNLC areas, thereby affecting the biological pump and associated carbon sequestration.

1. Introduction

Atmospheric deposition is a source of new N, P, and trace metals to the ocean [Duce *et al.*, 1991, 2008; Jickells *et al.*, 2005; Kanakidou *et al.*, 2012; Prospero *et al.*, 1996]. Nutrient inputs from atmospheric deposition have been shown to induce phytoplankton growth [Boyd *et al.*, 1998; Duarte *et al.*, 2006; Erickson *et al.*, 2003], enhance N fixation at some oceanic locations [Mills *et al.*, 2004], impact phytoplankton species dynamics [Guo *et al.*, 2012; Jordi *et al.*, 2012; Mackey *et al.*, 2012b; Paytan *et al.*, 2009], and intensify carbon sequestration via the biological pump [Bressac *et al.*, 2014; Guieu *et al.*, 2014b; Krishnamurthy *et al.*, 2010; Parekh *et al.*, 2006]. Atmospheric deposition of nutrients to the open oligotrophic ocean is particularly important in regions where there is little input from other new nutrient sources such as riverine input, ground water discharge, and sediment resuspension [Jickells *et al.*, 2005]. The bioavailability of nutrients and trace metals from aerosols is directly related to the solubility of these components. Solubility is controlled by aerosol mineral compositions and the physical and chemical characteristics of the aerosol, as well as chemical transformations in the atmosphere during transport [Anderson *et al.*, 2010; Baker *et al.*, 2006b; Hodge *et al.*, 1978; Krishnamurthy *et al.*, 2009; Mackey *et al.*, 2015a, 2012a; Sedwick *et al.*, 2007]. Arid regions of North Africa are the most important mineral dust source to the North Atlantic [Bristow *et al.*, 2010; Husar *et al.*, 1997; Schulz *et al.*, 2012]. The solubility of nutrients and trace metals from North African mineral dust is relatively low [Sholkovitz *et al.*, 2012], and it increases only slightly after long-distance transport [Baker *et al.*, 2006a].

Low availability of macronutrients (N, P) and metal micronutrients (Fe, Co) can limit or colimit phytoplankton growth in the ocean [Morel *et al.*, 1994; Saito *et al.*, 2008; Sunda and Huntsman, 1997] and drive genetic adaptation in different environments [Mackey *et al.*, 2015b; Morris *et al.*, 2012]. In contrast, high concentrations of some metals (e.g., Cu) can be toxic to phytoplankton [Jordi *et al.*, 2012; Mann *et al.*, 2002; Paytan *et al.*, 2009; Sunda and Huntsman, 1992]. The supply of new nutrients to the surface ocean from atmospheric deposition has been determined by direct measurements and through modeling [Baker *et al.*, 2003, 2010; Boyd *et al.*, 2010; Krishnamurthy *et al.*, 2010]. The impacts of atmospheric macro- and micronutrient deposition to the ocean have also been studied, particularly with respect to the impacts in iron-limited, high-nutrient

low-chlorophyll (HNLC) areas [Bishop *et al.*, 2002; Boyd *et al.*, 1998; Jickells *et al.*, 2005]. Less work has been done to assess the impacts of deposition in the vast low-nutrient low-chlorophyll (LNLC) regions, which cover ~60% of the global ocean [Giovagnetti *et al.*, 2013; Mackey *et al.*, 2012b; Paytan *et al.*, 2009; Guieu *et al.*, 2014b].

Barbados is a tropical island located at the eastern edge of the oligotrophic Caribbean Sea. The open water primary producers in this region are dominated by small cells, with about 50% of the pigmented biomass contributed by picophytoplankton [Dandonneau *et al.*, 2004]. *Prochlorococcus* is the most abundant photosynthetic organism in this environment, while picoeukaryotes and *Synechococcus* cell numbers are usually less than one tenth of *Prochlorococcus* [Dandonneau *et al.*, 2004]. Large amounts of African dust are deposited in the Caribbean Sea around Barbados throughout the year, with the lowest deposition rates in winter and peak rates in the summer [Trapp *et al.*, 2010]. Barbados receives relatively little anthropogenic air pollution from North America when compared to other subtropical islands such as Bermuda [Savoie *et al.*, 2002]. Accordingly, the open water around Barbados is an excellent location for studying how African dust impacts phytoplankton growth and community dynamics in an oligotrophic LNLC setting.

Understanding how distinct phytoplankton species respond to nutrient loading from atmospheric deposition in Barbados can provide information on the impact of dust deposition on phytoplankton communities in other LNLC areas of the ocean. This is critical not only for our understanding of the current functioning of LNLC regions and the role these regions play in the carbon cycle but also for the projection of future changes, since significant changes in the magnitude of dust distribution [Ginoux *et al.*, 2012; Mahowald *et al.*, 2007; Mahowald *et al.*, 2010; Ward *et al.*, 2014] and future expansion of LNLC regions are predicted [Henson *et al.*, 2010; Steinacher *et al.*, 2010]. In this study we carried out bioassay incubations with locally collected aerosols and native phytoplankton assemblages collected offshore of Barbados to investigate the impact of atmospheric nutrient and trace metal inputs on phytoplankton productivity and community structure. We additionally employed a numerical model to explore how species-specific differences in phytoplankton cellular elemental ratios and regional variation in atmospheric deposition together influence phytoplankton community structure.

2. Observational Material and Methods

2.1. Aerosol Sample Collection and Analysis

Daily high-volume total suspended particles (TSP) filter samples were collected at Ragged Point on the easternmost coast of Barbados [Trapp *et al.*, 2010; Zamora *et al.*, 2013]. The TSP sampler operated only when winds were from the ocean sector to minimize local sources. Several filters collected between November 2009 and August 2010 were selected for the bioassay incubation experiments. Specifically, three sample sets were used in this study representing three seasons; winter, spring, and summer (Table 1). For the winter and summer two filters were combined to supply sufficient material for the experiment. These seasons capture differences in aerosol loading, chemical composition, and source, as described in previous studies from this region [Yu *et al.*, 2015; Jung *et al.*, 2013; Prospero *et al.*, 2014]; however, the differences in the concentration of leachable nutrients and trace metals in the specific samples used were relatively small (see Table 1).

To determine the soluble nutrients and trace metal content of these samples, the filters were extracted by shaking for 1 h in Milli-Q water. The solution was then filtered (0.2 μ m polysulfone membrane) and the soluble nutrients and trace metals in the filtrate were measured as described in Chen *et al.* [2006, 2007] (see Table 1).

2.2. Incubation Setup

Nutrient and aerosol addition bioassay experiments were carried out over 3 days in February 2012, similar to previous work by Paytan *et al.* [2009] and Mackey *et al.* [2012a, 2012b]. Surface seawater was collected from offshore (bottom depth >700 m) outside the Bellairs Research Institute at West Barbados (13°11.309'N, 59°38.267'W). Surface water was pumped into acid-cleaned sample-rinsed carboys using a peristaltic pump with acid-washed Teflon tubing and prefiltered through a 20 μ m acid-washed Nitex[®] mesh to remove grazers. The seawater was stored in the dark during transport to the lab (<2 h). Seawater was dispensed into acid-washed and sample-rinsed polycarbonate bottles (500 mL each) and randomly assigned to different treatments (12–20 bottles per treatment). Treatments included single nutrient (N, P, or Fe) additions, as well

Table 1. Nutrients and Trace Metal Concentration in Aerosols Used for the Incubation Experiment and in the Bioassays at 10⁸

Aerosol	Collection Dates	Atmospheric Dust Load ($\mu\text{g m}^{-3}$)	Weight on Filter (mg cm^{-2})	NO ₂ + NO ₃	NH ₄ ^b	PO ₄	NO ₂ + NO ₃ :P	Mn	Fe	Co	Ni	Cu	Cd	Pb
Soluble Fraction (nmol mg^{-1})														
1	11/25/2009 to 11/27/2009	33.9	0.0796	164	182	2.6	64	4.1	1.08	0.032	0.09	0.14	0.0025	0.0003
2	3/31/2010 to 4/1/2010	91.6	0.1546	231	256	5.4	43	4.2	0.31	0.015	0.03	0.05	0.0008	0.0001
3	8/17/2009 to 8/19/2009	14.8	0.0902	357	395	2.7	132	2.5	0.28	0.013	0.05	0.09	0.0007	0.0001
Bulk Composition (nmol mg^{-1})														
1	11/25/2009 to 11/27/2009					27.8		10.1	619	0.228	0.24	0.68	0.003	0.12
2	3/31/2010 to 4/1/2010					37.0		17.0	913	0.350	0.96	0.58	0.006	0.16
3	8/17/2009 to 8/19/2009					34.6		12.5	899	0.342	0.66	0.79	0.004	0.19
% Solubility														
1	11/25/2009 to 11/27/2009					9.3		40.5	0.17	14.0	36.9	20.7	96	0.25
2	3/31/2010 to 4/1/2010					14.6		24.7	0.03	4.3	3.1	8.6	13	0.06
3	8/17/2009 to 8/19/2009					7.8		20.0	0.03	3.8	7.6	11.4	16	0.05
Concentrations in Amended Seawater at 10 (nmol kg^{-1})														
Amendments														
Control				330	305	BD	>27.5 ^c	2.87	1.02	0.01	2.00	2.19	0.06	0.04
NO ₃ + NH ₄				11107	805	17	647	2.81	0.91	0.004	1.88	2.14	0.06	0.04
PO ₄				288	305	490	0.59	2.32	1.42	0.009	2.04	2.26	0.07	0.05
NO ₃ + NH ₄ + PO ₄				11111	609	506	21.9	2.04	0.81	0.004	1.71	2.29	0.05	0.05
Fe + NO ₃ + NH ₄				9839	657	BD	>820 ^c	2.49	8.48	0.010	1.83	2.78	0.06	0.05
Spring dust low				251	241	BD	>21.0 ^c	3.41	0.89	0.010	1.94	2.23	0.06	0.05
Spring dust high				689	578	27	25.4	9.97	1.00	0.033	1.68	2.46	0.06	0.05
Summer dust low				407	274	BD	>33.9 ^c	2.98	0.47	0.013	1.67	2.15	0.05	0.05
Summer dust high				457	682	17	27.6	8.13	1.15	0.033	1.97	2.16	0.07	0.06
Winter dust high				442	425	19	23.7	8.89	1.54	0.052	1.98	2.24	0.06	0.04

^aBD, below detection limit. Aerosol 1 (winter) has slightly higher trace metals compared to 2 and 3. Aerosol 2 (spring) slightly higher P. Aerosol 3 (summer) lower Mn. Dates are formatted as month/day/year.

^bDust NH₄ were calculated by multiplying N + N by average NH₄ to N + N ratio in Barbados dust described in *Zamora et al.* [2011].

^cEstimated by using detection limit of PO₄ as the upper limit of PO₄ concentration.

as a combination of N and P and a combination of N and Fe, at concentrations representative of deep water in this area (see Table 2). The selected aerosol samples representing the three seasons (described above) were immersed in 50 mL of locally collected seawater (the same water used for the incubation experiment), shaken for 1 h and filtered through a 0.2 μm polysulfone membrane syringe filter. The seawater containing the

Table 2. Amendments to Incubation Bottles

Treatment	Concentration
Control	No addition
NO ₃ + NH ₄	Deep water (200 m) concentration, 10 μM NO ₃ and 0.5 μM NH ₄
PO ₄	Deep water (200 m) concentration, 0.5 μM PO ₄
NO ₃ + NH ₄ + PO ₄	As above
African dust, low	0.03 mg dust per 500 mL water
African dust, high	0.5 mg dust per 500 mL water
Fe + NO ₃ + NH ₄	Fe 10 nmol/kg (10 times the ambient seawater concentration of ~1 nmol/kg)
	10 μM NO ₃ and 0.5 μM NH ₄

soluble fraction of the aerosols was added to the incubation bottles in volumes that represent aerosol loads during “typical” and “high” deposition events in this region (Table 2 and see also supporting information). High and low deposition rates used for the additions were calculated based on atmospheric deposition estimates from Mahowald *et al.* [2005]; the “typical” deposition corresponds to annual average dust deposition rates in Barbados during summer, $\sim 10 \text{ g m}^{-2} \text{ yr}^{-1}$, and the high deposition represents extreme dust storms corresponding to a fifteenfold increase in deposition, $\sim 150 \text{ g m}^{-2} \text{ yr}^{-1}$ [Jung *et al.*, 2013]. The amount of dust added simulates the cumulative deposition flux over 20 days to the upper 10 m mixed layer. Details for the calculation of the amount of dust added are provided in the supporting information. Concentrations of nutrients and metals at the start of the incubations, immediately after the amendments were added, are reported in Table 1. A control (no addition, blank filter extract) treatment and procedural blanks (Milli-Q water) were also included. All bottles were incubated in a pool filled with circulating seawater to maintain the local surface ocean temperature. The pool was covered with a neutral density shading screen to reduce light intensity by 50% [Mackey *et al.*, 2012b]. Water samples used for the experiment (preadditions) were collected to characterize the baseline seawater chemistry (five replicates) and three replicate bottles for each treatment were collected immediately after the additions were administered (time zero, t0). The experiment took place over a total of 3 days. Each day at 4 pm, three bottles were randomly selected from each nutrient treatment, while five bottles were randomly selected from each aerosol treatment (e.g., time points t1–t3). Immediately upon collection, each bottle was sampled for chlorophyll *a* (Chl *a*), flow cytometry, nutrients, and trace metal concentrations (see below).

Statistical significance was tested with one-way analysis of variance (ANOVA) to check for differences between the mean values, and Dunnett’s test was then applied to compare control values with other treatments.

2.3. Nutrient Analyses

Soluble nutrients from the direct extraction of aerosol samples were analyzed on a flow injection autoanalyzer (FIA, Lachat Instruments model QuickChem 8000). Detection limits for soluble reactive phosphorus (SRP) and nitrate plus nitrite (N + N) were $0.1 \mu\text{M}$ and $0.29 \mu\text{M}$. Ammonium (NH_4^+) concentrations were calculated according to the average NH_4^+ to N + N ratio in dry deposition samples for the region as described in Zamora *et al.* [2011].

Seawater from each of the retrieved incubation bottles was filtered through a sample-rinsed $0.2 \mu\text{m}$ filter (Polyethersulfone, 150 ml Bottle Top Filter, CORNING), collected in acid-washed 50 mL falcon tubes and frozen until nutrients were analyzed. SRP and NH_4^+ were measured by a continuous flow autoanalyzer (TechniconAutoAnalyzer II[™]). SRP measurements followed a modification of the molybdenum blue procedure [Bernhardt and Wilhelms, 1967] and NH_4^+ analysis was done using a method modified from ALPKEM RFA methodology. N + N was analyzed by Alpkem RFA 300 following methods from Armstrong *et al.* [1967]. Detection limits for SRP, N + N, and NH_4^+ were $0.012 \mu\text{M}$, $0.03 \mu\text{M}$, and $0.05 \mu\text{M}$, respectively. Our estimates of the detection limits are based on 3 times the lowest resolvable signal from the instrument.

2.4. Trace Metals Analysis

For trace metal analyses 60 mL subsamples of $0.2 \mu\text{m}$ filtered water were collected in acid-washed, sample-rinsed LDPE bottles. Seawater samples were acidified to $\text{pH} < 2.0$ by adding $45 \mu\text{L}$ of concentrated trace metal grade HNO_3 at least 24 h prior to column chemistry. Nobias Chelate-PA1 resin (HITACHI, Japan) was used for seawater matrix removal and trace metal preconcentration [Biller and Bruland, 2012; Sohrin *et al.*, 2008]. Recovery yields are summarized in Table S1 of the supporting information. A 5 mL eluent from each sample was analyzed for a suite of trace metals (Mn, Fe, Co, Ni, Cu, Cd, and Pb) by HR-ICPMS (Thermo Element XR). Samples were introduced into the instrument with a peristaltic pump at a flow rate of $\sim 120 \mu\text{L min}^{-1}$ and passed through an ESI-PC3 Peltier cooled spray chamber before entering the torch. Sample and gas flow rates were optimized for each run; values were $0.75\text{--}0.80 \text{ ml min}^{-1}$ and $0.20\text{--}0.24 \text{ ml min}^{-1}$, respectively. In, Y, and Sc were added to each sample as internal standards for calibrating sensitivity shifts of the instrument. Method accuracy and precision were assessed relative to Certified Reference Material CASS5 and GEOTRACES SAFE reference seawater (Table S1).

2.5. Chlorophyll *a* Concentration and Flow Cytometry

From each bottle, 100 mL of seawater was filtered onto GFF filters, which were frozen in liquid nitrogen and then stored at -80°C until analyzed. Upon return from the field, samples were extracted for 24 h in the dark at

–20°C in 90% acetone. Fluorescence was measured on a TD-700 fluorometer (Turner Designs) calibrated with fresh Chl *a* standard from *Anacystis nidulans* (Sigma).

Water samples (1.5 mL) were collected from each incubation bottle for flow cytometry, preserved by adding 300 μ L of formalin, frozen in liquid nitrogen, and stored at –80°C until analysis. Approximately 10,000 beads 0.75 μ m in diameter (Fluoresbrite™ particles, YG, Polysciences, Inc.) were added to each sample, and samples were analyzed by flow cytometer (BD Influx cell sorter) triggering on forward angle light scatter (FSC). Total cell concentrations of *Prochlorococcus*, *Synechococcus*, and picoeukaryotic were enumerated. The groups were differentiated based on their characteristic autofluorescence and scattering properties (Figure S1 in the supporting information).

3. Numerical Modeling

The contribution of soluble nutrients from atmospheric deposition (based on a deposition model, see below) relative to other sources of nutrients to the surface mixed layer (based on an ocean-ecosystem model) was derived. The resulting impact on phytoplankton dynamics and species distribution was assessed in order to test if results from the incubation bioassays can be reproduced in silico at the location of the experiment. These new model simulations are unique, as we incorporate atmospheric deposition of multiple nutrients, internal cycling of nutrients in the ocean, and taxa-specific quotas for nutrient uptake.

3.1. Atmospheric Deposition Model

Simulations of N, P, and Fe deposition were conducted using the Community Atmospheric Model (CAM4), and online (climate model derived) winds with the slab ocean model [Neale *et al.*, 2013]. Simulations were conducted for 5 years, with the last year used for analysis. By using the prescribed aerosols for radiative transfer calculations, the meteorology in all the simulations was identical. The model simulates three-dimensional transport and wet and dry deposition for gases and aerosols [Lamarque *et al.*, 2011; Mahowald *et al.*, 2006; Rasch *et al.*, 2000]. For N, the CAM-chem model was used [Lamarque *et al.*, 2011], which simulates tropospheric chemistry, including ozone and organic compounds for current and preindustrial emissions using the emission data sets from Lamarque *et al.* [2010], except for fires. The baseline fire emissions used are the observation-based Global Fire Emission Database version 3 (GFED3) [Randerson *et al.*, 2013; van der Werf *et al.*, 2006]. We use the tuning methodology of Ward *et al.* [2012] in which, briefly, GFED fire emissions are scaled to ground and space-based observations of aerosol optical depth (AOD) for 14 regions by identifying high-fire emission and low-fire emission months for each region. The tuning factors are applied to all the species emitted by fire, including N, Fe, and P species. P was modeled following Mahowald *et al.* [2008] with some small differences (see supporting information). Fe is modeled following Luo *et al.* [2008]. Dust is assumed to contain 3.5% Fe, the same as average crustal abundance [Hans Wedepohl, 1995] and as previously measured on samples from this site [Trapp *et al.*, 2010]. Biomass burning is assumed to have a ratio of 0.2 gFe/g black carbon (BC) in the fine mode, and 1.4 gFe/gBC for the coarse mode [Luo *et al.*, 2008]. Industrial sources of Fe are emitted following Luo *et al.* [2008]. Source specific solubility was applied to the various P and Fe sources as discussed in the supporting information. The model output also produces the N:P ratio of the soluble fraction of atmospheric deposition to the ocean, which is as previously reported much higher than the Redfield Ratio (16N:1P) throughout the ocean [Okin *et al.*, 2011]. More detail on the deposition model is provided in the supporting information. Model-derived atmospheric deposition and associated nutrient and Fe input fluxes, along with dust, nutrient, and trace metal concentrations from the bioassay experiments are listed in Table 3.

3.2. Ocean Model

To investigate the implication of the high N:P ratio dust deposition on marine phytoplankton, and particularly to highlight the unique setting of our study region compared to the rest of the ocean, we employed a global three-dimensional model that includes physical, biogeochemical, ecosystem, and radiative transfer components, as well as an atmospheric deposition component [Dutkiewicz *et al.*, 2015]. The biogeochemical/ecosystem model resolves the cycling of C, P, N, silica (Si), Fe, and oxygen (O) through inorganic, living, dissolved, and particulate organic phases. The biogeochemical and biological tracers are transported and mixed using the MIT general circulation model (MITgcm) [Marshall *et al.*, 1997], which is constrained to be consistent with altimetric and hydrographic observations (the ECCO-GODAE state estimates, [Wunsch and Heimbach, 2007]). This configuration has a

Table 3. Model-Derived Atmospheric Deposition and Associated Nutrients and Iron Input Fluxes and Dust, Nutrients and Trace Metals Added in the Bioassay Experiments

	Dust Flux	Dust Addition	N	PO ₄	Fe
	(gm ⁻² yr ⁻¹)	(mg L ⁻¹)		(mmol m ⁻² yr ⁻¹)	
Mode annual average	8.7	NA	7.5	0.019 (nmol L ⁻¹)	0.044
Dust bioassay low	10	0.06	31.7	0.213	0.034
Dust bioassay high	150	1	528	3.55	0.56

1° × 1° horizontal resolution and 23 vertical levels ranging from 10 m in the surface ocean to 500 m at depth. We resolve two grazers and phytoplankton analogues of *Prochlorococcus*, *Synechococcus*, picoeukaryotes, coccolithophores, diatoms, and nitrogen fixing diazotrophs. The phytoplankton types differ in their growth parameters, nutrient requirements, as well as their pigment compositions. The biogeochemical and biological tracers interact through the formation, transformation, and remineralization of organic matter. Excretion and mortality transfer living organic material into sinking particulate and dissolved organic detritus, which are respired back to inorganic forms. Fe chemistry includes complexation and scavenging by particles [Parekh *et al.*, 2005], as well as sedimentary sources following Elrod *et al.* [2004]. Full equations and parameter values are provided in Dutkiewicz *et al.* [2015].

In the original model [Dutkiewicz *et al.*, 2015] the only element included in the atmospheric nutrient deposition was Fe. Here we incorporated additional deposition of PO₄³⁻, NO_y (NO₃⁻ and other oxidized N species) and NH₄⁺ along with Fe as provided by the deposition model described in section 3.2. We also introduced a crude representation of sedimentation as a constant rate of POM reaching the sea floor.

In the original model [Dutkiewicz *et al.*, 2015] all phytoplankton types, except diazotrophs, had the same C:N:P:Fe stoichiometric ratios. Because a central hypothesis of this study is that species-specific differences in elemental ratios are important for determining nutrient limitation status in this region (i.e., as observed in the incubation experiments), we also altered the model such that the stoichiometry of each phytoplankton functional group reflects literature values of C:N:P (Table S2). In particular, *Prochlorococcus* has a high N:P ratio (25:1), while *Synechococcus* has a lower N:P ratio (21:1), though still higher than picoeukaryotes (15:1).

Initial conditions use macronutrient fields (NO₃⁻, PO₄³⁻ and silicic acid) from the World Ocean Atlas climatology [Garcia *et al.*, 2006], and the Fe, NH₄⁺, nitrite, dissolved and particulate matter from previous simulations [Dutkiewicz *et al.*, 2015]. The plankton biomass is also initialized from previous model output, divided equally between groups. We ran the simulation forward for 10 years with a repeating generic “year” from the physical ECCO-GODAE products [Wunsch and Heimbach, 2007]. The phytoplankton establish a repeating pattern after about 3 years. A slow drift as deep water nutrient distributions adjust does not significantly change the results over the remaining time period. We show results from two simulations: (1) EXP1, where the elemental stoichiometry was the same between all phytoplankton (except diazotrophs) as in Dutkiewicz *et al.* [2015] and (2) EXP2, where the phytoplankton types had differing stoichiometry as discussed above (Table S2). We show the difference between the 10th year of each simulation.

In order to investigate the relative contribution of nutrients from different sources in the Atlantic Ocean, we used the model to calculate the relative contribution of N and P from atmospheric deposition to other nutrient inputs, including lateral advection, vertical advection and diffusion, and remineralization of dissolved organic matter (Figure 4).

4. Results

4.1. Aerosol Soluble Nutrient and Trace Metal Concentrations

Seawater soluble nutrients and select trace metal concentrations of the aerosol samples used in the bioassay incubation experiments are shown in Table 1. Aerosol 1 (winter) has slightly higher levels of soluble trace metals compared to aerosol samples 2 (spring) and 3 (summer). Aerosol sample 2 has slightly higher P concentration (5.4 nmol mg⁻¹) than aerosol samples 1 (2.6 nmol mg⁻¹) and 3 (2.7 nmol mg⁻¹). Aerosol 3 has higher N and lower Mn compared to aerosols 1 and 2. Overall the differences in the soluble fraction of nutrients and trace metals between these seasonally distinct aerosol samples were small (less than an order

Table 4. Nutrient and Trace Metal Concentrations in Baseline Incubation Seawater

Nutrients	Baseline Seawater (μM) (Mean $\pm$ SE ^d)	Caribbean/Tropical Atlantic Seawater
PO ₄	BD	0.04–0.14 ^a
N + N	0.241 $\pm$ 0.098	0–0.94 ^a
NH ₄	0.228 $\pm$ 0.093	
N + N:P	>20 ^e	0–19.2
NO ₃ + NH ₄ :P	>39 ^e	
Trace metals	(nmol/kg)	
Pb	0.066 $\pm$ 0.016	0.01 ^b
Cd	0.048 $\pm$ 0.026	0.0005 ^b
Mn	2.4 $\pm$ 0.115	3.19 ^b
Fe	1.09 $\pm$ 0.264	0.53 ^b , 1.31 ^c
Co	0.032 $\pm$ 0.012	
Ni	1.8 $\pm$ 0.078	2.16 ^b
Cu	2.3 $\pm$ 0.203	

^aData from World Ocean Database, nitrogen contains only nitrate value.

^bFrom GEOTRACES GAO2 cruise station 33 (same latitude).

^cFitzsimmons et al. [2013].

^dStandard error.

^eEstimated by using the detection limit of PO₄ as the upper limit of PO₄ concentration.

of magnitude). The bulk composition of dust samples was analyzed following a strong acid (HNO₃ and HF) digestion [Morton et al., 2013]. The solubility of P was higher in sample 2 (spring) and ranged from 7.8% to 14.6% among the samples. Overall, trace metal solubility was higher in Aerosol 1 (winter; Table 1).

4.2. Baseline Seawater Chemistry

The seawater used for the experiments had low baseline nutrient concentrations and relatively high Fe (1.09 $\pm$ 0.264 nmol kg⁻¹). Mean baseline nutrient concentrations were 0.241 $\pm$ 0.098 μM for N + N and 0.228 $\pm$ 0.093 μM for NH₄⁺, while SRP was below detection (<12 nM). Trace metal levels were in the same range as previously published data for this region [Fitzsimmons et al., 2013; Mawji et al., 2015; Rijkenberg et al., 2014]. Concentration levels and ratios between nutrients are shown in Table 4 along with previously reported surface seawater concentrations for this region.

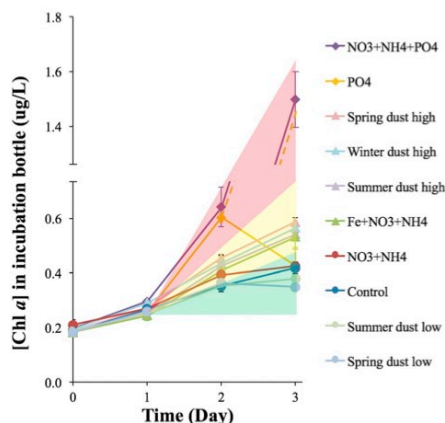


Figure 1. Growth response of phytoplankton under different nutrient addition during three consecutive days. Dashed line at phosphate represents expected response of phytoplankton growth without nitrogen limitation. Note break in scale for Chl *a*.

4.3. Chlorophyll *a*

Chlorophyll *a* (Chl *a*) concentration in the seawater sample collected for the experiment (baseline) was 0.19 $\pm$ 0.01 (average $\pm$ SE) mg m⁻³. After 3 days of incubation Chl *a* increased twofold to 0.42 $\pm$ 0.02 mg m⁻³ in the control bottles. Similar increases in Chl *a* were observed at day 3 for the addition of N alone and for all dust additions (Figure 1), though not significantly different than the control at $p < 0.05$. After 3 days of incubation, Chl *a* in the Fe + N and the high dust additions for all 3 seasons (Spring high, Summer high, and Winter high) were 0.53 $\pm$ 0.05, 0.59 $\pm$ 0.02, 0.54 $\pm$ 0.02, and 0.57 $\pm$ 0.02 mg m⁻³, respectively. This was an approximately threefold increase compared to t_0 and was higher than the control values at day 3. The increases compared to those of the control are statistically significant

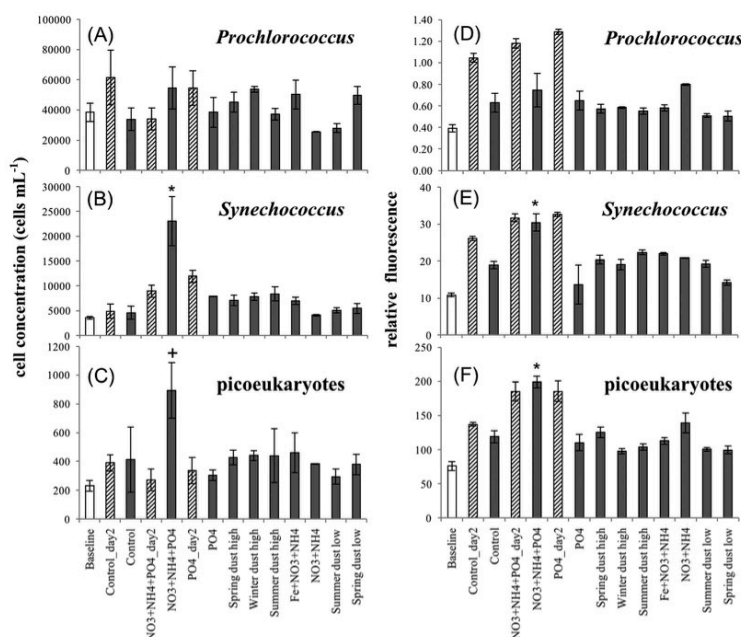


Figure 2. Growth response of phytoplankton on day 3, control, N + P and PO_4 are also reported for day 2. Cell concentrations of (a) *Prochlorococcus*, (b) *Synechococcus*, and (c) picocoeukaryotes on day 3 (cell ml^{-1}). Relative phytoplankton fluorescence of (d) *Prochlorococcus*, (e) *Synechococcus*, and (f) picocoeukaryotes were normalized with $0.75 \mu\text{m}$ beads' fluorescence. Note that significance was not determined for the P day 2 treatment as it is not comparable to the other data which use day 3 results; however, day 2 P is significantly different than day 2 control in fluorescence (day 2 data shown in striped bars). Growth condition that were statistically different from the control incubation water at day 3 are marked as "asterisk" for $P < 0.05$ and "cross" for $P = 0.104$.

for Spring high and Winter high ($p=0.011, 0.034$). Chl *a* in the N + P treatment showed the largest and most pronounced change, increasing eightfold compared to the baseline level from 0.19 to $1.50 \pm 0.10 \text{ mg m}^{-3}$. This increase is significantly different than the Chl *a* increase in the control after 3 days of incubation ($p=0.00001$). Chl *a* increased at the same rate in the P alone addition for the first 2 days of incubation (0.6 mg m^{-3} on day 2 increasing threefold compared to the baseline); however, in day 3 the levels decreased sharply and were similar to those of the control at the end of the experiment (Figure 1).

4.4. Phytoplankton Abundance

Cell abundances of *Prochlorococcus*, *Synechococcus*, and picoeukaryotes changed over time in the treatments (Figures 2a–2c). The most abundant species in the baseline water sample was *Prochlorococcus* with $38.4 \pm 6.1 \times 10^3$ cells mL^{-1} (91% of cells), followed by *Synechococcus* with an order of magnitude fewer cells ($3.6 \pm 0.3 \times 10^3$ cells mL^{-1} , 8.5% of cells) and picoeukaryotes comprising only $\sim 0.05\%$ of cells ($0.23 \pm 0.04 \times 10^3$ cells mL^{-1}). After 3 days of incubation, increases in *Synechococcus* and picoeukaryotes abundance were more pronounced compared to those of *Prochlorococcus* in all treatments that show a response in Chl *a* (e.g., high dust and N + P). In the N + P treatment, cell numbers of *Synechococcus* and picoeukaryotes increased fivefold to $23.1 \pm 5.0 \times 10^3$ cells mL^{-1} and $0.9 \pm 0.2 \times 10^3$ cells mL^{-1} , respectively. Although *Prochlorococcus* still comprised the largest fraction of the population (70%) they increased to a lesser extent (only 42% to $54.4 \pm 13.9 \times 10^3$ cells mL^{-1}). After 3 days of incubation the *Synechococcus* and picoeukaryotes cell number in the Fe and high dust additions also increased but only by a factor of 2 compared to the

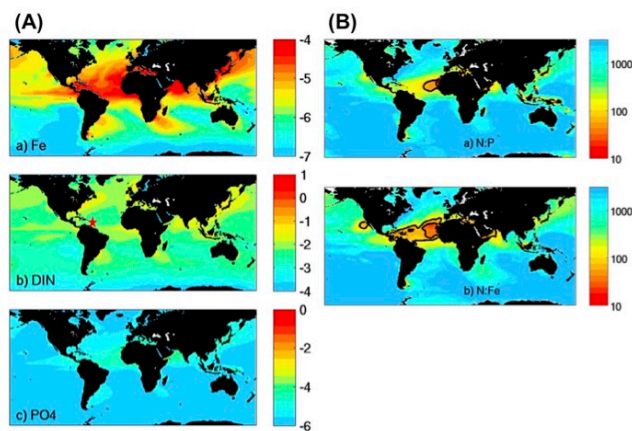


Figure 3. (A) Bio-available aeolian deposition of (a) Fe ($\text{mol Fe m}^{-2} \text{ y}^{-1}$), (b) $\text{NO}_3 + \text{NO}_2 + \text{NH}_4$ ($\text{mol N m}^{-2} \text{ y}^{-1}$), (c) PO_4 ($\text{mol P m}^{-2} \text{ y}^{-1}$), values are in log scale. Red star in Figure 3b represents for dust sampling site. (B) Ratio of aeolian deposition: (a) $(\text{NO}_3 + \text{NO}_2 + \text{NH}_4):\text{PO}_4$ (mol N/mol P), (b) $(\text{NO}_3 + \text{NO}_2 + \text{NH}_4):\text{Fe}$ (mol N/mol Fe). With contours [40, 80] for N:P and [20, 50, 100] for N:Fe.

baseline (7.1×10^3 to 8.4×10^3 cells mL^{-1} and 0.43×10^3 to 0.46×10^3 cells mL^{-1}). Unlike *Synechococcus* and picoeukaryotes, cell levels of *Prochlorococcus* on day 3 in these treatments did not show a significant difference when compared with the control, with numbers varying from 25.5×10^3 cells mL^{-1} to 54.4 cells mL^{-1} .

Fluorescence per cell values (normalized to $0.75 \mu\text{m}$ beads) in the control incubation at day 3 for *Prochlorococcus*, *Synechococcus*, and picoeukaryotes are 0.63, 18.92, and 119.05, respectively. In the N + P treatment, fluorescence per cell almost doubled in *Synechococcus* and picoeukaryotes (30.5 and 199), while the response was small in *Prochlorococcus* (0.75). Day 3 fluorescence values in the P treatment are close to those in the control (similar to Chl *a*), however, day 2 levels for *Synechococcus* and picoeukaryotes are 32.7 and 185.5, which are similar to those of the N + P treatment (31.7 and 185.2) (Figures 2d–2f).

Interestingly, the response observed in the dust amendments was limited to the high dust additions, and even that response was relatively small when compared to treatments where P was added. Specifically, addition of locally collected aerosols at rates similar to average deposition in this area did not trigger much growth of *Synechococcus*, picoeukaryotes, or *Prochlorococcus*, and even introduction at levels equivalent to those expected after 20 days of heavy dust storms resulted in a relatively small increase in Chl *a*, which is consistent with previous incubation experiments where high amounts of Saharan dust (2 mg L^{-1}) were added and the primary response measured was bacterial production [Maranon *et al.*, 2010]. This indicates that even extremely high levels of atmospheric deposition are not sufficient to completely alleviate the P limitation and induce substantial autotrophic growth in this region of the ocean.

4.5. Deposition Model

Annually averaged deposition maps of N, P, and Fe based on aerosol loads (dust and anthropogenic emissions) and specific solubility of each element, are shown in Figure 3A; a large spatial variability is simulated, consistent with observations e.g., Baker and Croot, 2010; Baker *et al.*, 2010; Dentener *et al.*, 2006; Mahowald *et al.*, 2008, 2009; Sholkovitz *et al.*, 2012]. The N:P and N:Fe ratio based on these deposition fields are calculated and shown in Figure 3b. The ratio of N:P in the soluble fraction of aerosols ($\sim 50:1$ to $>1000:1$; Figure 3b) is much higher than the ratio typically required by phytoplankton (16:1) [Okin *et al.*, 2011]. In particular, some of the highest N:P deposition ratios are found in the central North Atlantic subtropical gyre.

4.6. Ocean Model

Our ocean model shows that the N enrichment in dust and the high rates of deposition around the Caribbean, particularly around our sampling area, result in a relatively higher contribution of atmospheric N compared to

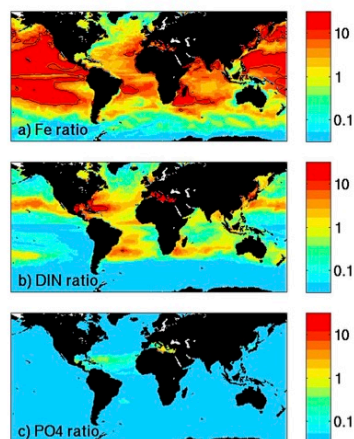


Figure 4. Relative contribution (%) of dust to the model-derived supply of nutrients to the top 100 m on the ocean for (a) Fe, (b) dissolved inorganic nitrogen (DIN), and (c) PO_4 . The “in water” supplies include vertical and horizontal advection and diffusion, as well as remineralization of organic matter. Contour is 10%. Color bars are in log scale.

other sources of nutrients (advection, diffusion, and remineralization of organic matter) (Figure 4). This tends to shift the total nutrient input ratio to the surface waters in this region toward higher N:P ratio, and toward P limitation. This regional increase in the relative contribution of aerosol nutrients to the combined nutrient inputs in the surface layer is also consistent with calculations using upwelling found by *Oschlies and Garçon* [1998] (Table 5).

The phytoplankton community in the North Atlantic subtropical gyre is dominated by picophytoplankton (Figures 5a–5c) in both model experiments (and the original model [Dutkiewicz et al., 2015]). However, there is a substantial difference (Figures 5d–5f) in the relative abundance of the three picophytoplankton groups between EXP1 (where species-specific elemental ratios were all the same except for *Trichodesmium*) and EXP2 (where species-specific elemental ratios were used). In particular, there is a significant difference in the region where the influence of atmospheric deposition with high N:P ratio is highest compared to other nutrient sources (upwelling, advection) (Figure 4). In this P-limited LNLC region, *Prochlorococcus* becomes more abundant when the model accounts for its low P requirements in EXP2 compared to EXP1. Specifically,

with their lower P requirements as simulated in EXP2 relative to EXP1, *Prochlorococcus* biomass increases (see red box in Figure 5) in the region with the highest aerosol N:P ratios. On the other hand, neither *Synechococcus* nor picoeukaryotes, with their lower N:P requirements, have any benefit in this mostly oligotrophic and P-limited region. However, on the edge of the gyre, we find the opposite response. Here where N is limiting, the high N:P quota of *Prochlorococcus* is not beneficial and *Synechococcus* increases in biomass at the expense of *Prochlorococcus*.

The main result from the difference between the two simulations is that the combination of including N and P in addition to Fe for the atmospheric deposition and using taxa-specific nutrient elemental ratios results in significant changes in phytoplankton species distribution. Specifically, *Prochlorococcus*, with its low P

Table 5. Relative Contribution of Nutrient Sources in Each Region of Atlantic Ocean

	Upwelling Fluxes ($\text{mmol m}^{-2} \text{yr}^{-1}$)			Dust Fluxes ($\text{mmol m}^{-2} \text{yr}^{-1}$) ^d		Dust flux to upwelling	
	NO_3^b	$\text{NO}_3:\text{PO}_4^c$	PO_4	N	PO_4	N	P
Subpolar 50 N–65 N	410	15.2	27.0	14.2	0.003	3.5%	0.01%
Midlatitude 30 N–50 N	580	20.0	29.0	17.7	0.006	3.5%	0.02%
Subtropical gyre 12 N–30 N, 70 W–22 W	47	25.4	1.85	6.2	0.017	13.1%	0.9%
Tropical 8 S–8 N	370	14.9	24.9	17.4	0.022	4.7%	0.09%
Barbados (13.1 N, 59.5 W) ^a	47	25.4	1.85	7.5	0.019	15.9%	1.04%

^aN and P fluxes are from *Zamora et al.* [2013].

^b NO_3 upwelling fluxes are from *Oschlies and Garçon* [1998, Table 1].

^cN to P ratios are median value of N:P at depth 150 m from GEOTRACES cruise GA02.

^dDust fluxes are from model results described in this paper, values are average fluxes of different regions defined in *Oschlies and Garçon* [1998].

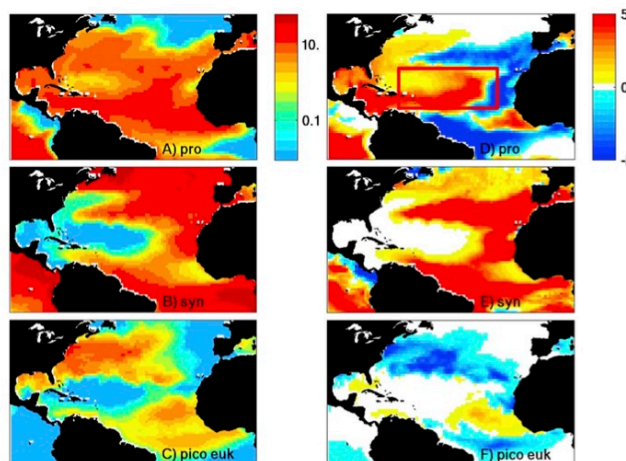


Figure 5. Biomass of phytoplankton in the top 10 m (mg C m^{-3}) in our model where phytoplankton have differing stoichiometry (EXP2): (a) *Prochlorococcus*, (b) *Synechococcus*, and (c) picoeukaryotes. Difference (mg C m^{-3}) between simulations where all phytoplankton have same stoichiometry (EXP1) and (EXP2): (d) *Prochlorococcus*, (e) *Synechococcus*, and (f) picoeukaryotes. Positive values indicate higher biomass in EXP2 when different phytoplankton stoichiometry is considered. *Prochlorococcus* biomass that was 5 mg C m^{-3} higher in EXP2 than EXP1 was observed at our study site. (Note that our study site is located at the southwest part of the north Atlantic subtropical gyre, which is defined as the region between 12°N – 30°N and 70°W – 22°W .)

requirement relative to N (Table S2), thrive and become more prolific in the high N:P ratio regions, particularly in our study area.

5. Discussion

5.1. Nutrient Limitation in the Caribbean Sea

The Caribbean Sea comprises a significant fraction of the western North Atlantic Ocean and generally fluctuates little in its hydrographic conditions [Muller-karger *et al.*, 1988]. The area is characterized by relatively low productivity, low nutrients, and low chlorophyll levels [Garcia *et al.*, 2010]. Previous studies, primarily from HNLC areas of the ocean, show that low atmospheric deposition rates and low Fe availability limit ocean productivity [Bishop *et al.*, 2002; Boyd *et al.*, 1998; Erickson *et al.*, 2003; Jickells *et al.*, 2005]. However, the role atmospheric deposition plays in influencing phytoplankton dynamics in LNLC regions has only recently begun to receive more attention [Giovagnetti *et al.*, 2013; Guieu *et al.*, 2014a; Mackey *et al.*, 2012b; Paytan *et al.*, 2009; Wuttig *et al.*, 2013]. Specifically, deposition rates are high in the Barbados region, yet LNLC conditions persist. High deposition rates are expected to supply new nutrients and sustain relatively high levels of productivity downwind of high deposition areas, yet productivity and Chl *a* concentrations in the euphotic zone of the LNLC-high dust deposition areas in general, and at our study site off Barbados in particular, are relatively low (Figure 5) [Volpe *et al.*, 2009].

To understand this observation, it is important to determine what limits productivity in the surface waters of the Caribbean Sea, as well as the role nutrients supplied from aerosol deposition play in such systems. In our incubation experiments, N addition (as a mixture of NO_3^- and NH_4^+) induced minimal response in Chl *a* or species abundance relative to the control, suggesting that N was not the limiting nutrient in the water at the time our samples were collected. The largest Chl *a* increase was obtained with treatments that received P addition as N + P or P alone (during the first 2 days), indicating that P was limiting growth in this region during our experiment (Figure 1). Indeed, measurable net P drawdown, calculated by the difference in SRP concentrations between t_0 and t_3 , was only seen in the treatments that received P additions (Figure S2); N

drawdown was also seen in these treatments, consistent with growth. The sharp decline in Chl *a* after day 2 and the associated decline in phytoplankton abundance in the P alone treatment indicates that N was also in relatively short supply; as soon as the P was utilized, colimitation with respect to N and P developed. While our experiment does not provide direct evidence for the change toward N limitation following the drawdown of P in the P alone treatment, this explanation is consistent with the negligible N drawdown in the P addition experiment between days 2 and 3, and with the findings of other studies in this region [C. M. Moore *et al.*, 2013]. Indeed, P limitation has been suggested for the western North Atlantic based on enzyme activities [Ammerman *et al.*, 2003; Lomas *et al.*, 2004], low SRP concentrations [Wu *et al.*, 2000], high thermocline N:P ratios [Fanning, 1992], short P turnover times [Sohm and Capone, 2010], fast uptake rates [Sohm and Capone, 2006], extensive utilization of dissolved organic P [Lomas *et al.*, 2010; McLaughlin *et al.*, 2013], low abundance of phospholipids in resident phytoplankton [Van Mooy *et al.*, 2009], efficient physiological P acquisition mechanisms [Martiny *et al.*, 2006; Scanlan and Wilson, 1999] and the presence of intracellular polyphosphate [Martin *et al.*, 2014]. Phosphorus limitation in this region is also consistent with previous model results [Krishnamurthy *et al.*, 2007]. For example, both the Marine Ecosystem Dynamics and Biogeochemical Cycling Community Earth System Model (CESM1(BGC) [J. K. Moore *et al.*, 2013] and the MITgcm Darwin Project model (this study, as well as Dutkiewicz *et al.* [2014]) identify this region as one of the few areas of P limitation in the open ocean, particularly for diazotrophs but also for other phytoplankton. The decline in Chl *a* observed in the P addition experiments once N was depleted suggests that N is also in low abundance and may explain why other studies have identified this area as N and P limited [C. M. Moore *et al.*, 2013]. The timing of the Chl *a* decline in the P alone addition (low N:P ratio) is also consistent with previous work which demonstrates that the length of time some *Prochlorococcus* strains (the most abundant photosynthetic organism in the incubation water) stay in stationary phase (i.e., how quickly they crash) is a function of the N:P ratio. Specifically, Moore *et al.* [2002] show that some strains (NATL1, NATL2, MIT9211, and MIT9215) crashed within 2 days when N was limited.

Bacterial growth and respiration have also been shown to be stimulated by Saharan dust [Pulido-Villena *et al.*, 2014] and SRP additions [Cotner *et al.*, 1997; Obernosterer *et al.*, 2003] and could have contributed to P drawdown in the P addition experiments, although we did not measure changes in bacterial productivity or abundance. The diazotrophic cyanobacterium *Trichodesmium* spp. also appears to be P limited in this basin [Sañudo-Wilhelmy *et al.*, 2001; Sohm *et al.*, 2008] but was not detected in our samples. Note that the experimental design is different from the experiment carried out by Thingstad *et al.* [2005] in which grazing was implicated as the cause for Chl *a* decline, as we filtered out grazers larger than 20 μ m before incubation. While smaller grazers could pass through the mesh in this experiment, it seems unlikely that they would cause a decline in Chl *a* only in the P alone treatment, but not in the N + P treatment (Figure 1). Thus our incubation experiments are consistent with the currently available body of research that indicates that biomass growth in this region is limited by P and that different organisms within the community could be colimited by N and P.

5.2. Taxa-Specific Responses to Nutrient Additions

In our study, Chl *a* concentrations by day 2 show a substantial increase in treatments to which P was added (and not with other additions); however, flow cytometry data suggest that not all phytoplankton taxa responded similarly. *Synechococcus* and picoeukaryote populations both increased in cell number and fluorescence (Figures 2a and 2b). *Synechococcus* showed the fastest response, increasing in the P alone treatment after only 2 days of incubation (Figure 2a). Similar increases in *Synechococcus* have been recorded in incubations from this region before [Moore *et al.*, 2008]. *Prochlorococcus*, however, shows a much smaller increase in both cell numbers and fluorescence relative to the control. *Prochlorococcus* was the most abundant photosynthetic organism in the water at the time of our sampling, and they did not respond strongly to any of the amendments in the bioassay incubation. This suggests that *Prochlorococcus* is more adapted to survive in the low nutrient, P-deficient waters of the western Tropical Atlantic Ocean and that they have acclimatized for coping with low P concentrations and high N:P ratio conditions. Higher surface area to volume ratio, increased nutrient uptake efficiency [C. M. Moore *et al.*, 2013], lower P requirements [Morris *et al.*, 2012; Van Mooy *et al.*, 2006], and efficient P acquisition, regulation, and utilization pathways [Martiny *et al.*, 2009] all give *Prochlorococcus* an advantage in low P waters. These mechanisms include using less P in cellular building blocks, storing P intracellularly as storage compounds to be reused later (e.g., polyphosphate)

[Martin et al., 2014], using organic P compounds, and having efficient P acquisition abilities (transporters). When P or N + P were added in our experiments, *Synechococcus* and picoeukaryotes, which did not bloom under the natural P-limited conditions, were able to grow faster because the added P shifted the nutrient regime away from P limitation, thereby opening a new niche. This suggests that addition of P in the incubation increased biomass by enhancing the growth rates of *Synechococcus* and picoeukaryotes while providing little immediate benefit for *Prochlorococcus* (Figure 2). Rather, *Prochlorococcus* initially dominated the community because it is adapted to the naturally P-limited conditions, and the cells were likely already operating at their maximum growth rate. Moreover, the higher proportion of NH_4^+ relative to NO_3^- in aerosols in this region may benefit *Prochlorococcus*, due to its high affinity NH_4^+ transporters and preference for NH_4^+ [García-Fernández et al., 2004].

In this area, despite high atmospheric input of nutrients, P requirements for the other taxa are not met. To test if our conclusion (e.g., that relative nutrient availabilities dictate taxa distribution favoring *Prochlorococcus* in regions of low P and high N:P ratio) is consistent with global coupled atmosphere–ocean–ecosystem models, we used the MITgcm Darwin Project model as described above, specifically testing the effect of taxon-specific nutrient ratios and quotas. The model results were consistent with the bioassay results where *Synechococcus* and picoeukaryotes were P limited (Figure 2), and where *Prochlorococcus* dominates due to low P requirements and low P availability that is driven by atmospheric deposition in our study region (red box in Figure 5). The Mediterranean Sea, another LNLC area with high dust deposition and low P availability, showed a similar response to our study area, but other ocean regions did not. This was also true in a further experiment (see Figure S3) where we removed the dust supply of N and P; *Prochlorococcus* was the only species affected.

5.3. Atmospheric Deposition Control of Nutrient Ratios and Species Abundance

The ratio of N + N to SRP in aerosol samples used in our experiment ranged from 43:1 in the spring to 132:1 in summer, much higher than Redfield ratio (16:1). The ratios in aerosols are even higher when considering NO_3^- and NH_4^+ together: both are typically present at similar concentrations in aerosols [Zamora et al., 2011]. Both N species are bio-available and utilized by phytoplankton. These ratios are consistent with the high ratios previously reported for aerosols collected in this region over the past two decades [Baker et al., 2010; Zamora et al., 2013] and with the relatively low phosphate solubility of African dust over this region (~8%) [Zamora et al., 2013]. This high N:P ratio in the soluble fraction of atmospheric deposition throughout the world's ocean is simulated in the atmospheric deposition models we used (Figure 3b) and fits other model predictions [Okin et al., 2011] and many observations of aerosol chemistry throughout the world [Baker et al., 2003; Baker et al., 2007; Chen et al., 2007; Mackey et al., 2013; Markaki et al., 2003; Paytan et al., 2009; Srinivas and Sarin, 2013]. Although we used only dry deposition in our incubation experiment, similarly high N:P values have been reported for wet deposition in this region [Zamora et al., 2013] and elsewhere [Altieri et al., 2009; Markaki et al., 2003; Özsoy, 2003; Williams et al., 1997; Zhang et al., 2008].

We argue that in this specific region the high N:P ratio in atmospheric deposition sustains the observed P limitation. This is because the N supplied by atmospheric deposition, in this region of relatively high atmospheric deposition and limited nutrient supply from other sources, constitutes a relatively large fraction of the total new N input to the euphotic zone (Table 5 and Figure 4), thereby maintaining a high N:P ratio in the surface ocean. Other external input sources (e.g., upwelling, river plumes) have much lower N:P ratios. *Prochlorococcus*, with its low P requirement and efficient P utilization has an advantage in areas of low P and high N:P ratios. Diazotrophs may be P limited and are less competitive in high N:P regions [C. M. Moore et al., 2013], as seen in the modeling study of Dutkiewicz et al. [2014]. Indeed, the occasional influx of nutrient rich water from the Orinoco and Amazon Rivers [Mullerkarger et al., 1989], which have higher P levels and lower N:P ratios, have been linked to increases in both *Trichodesmium* and diatom abundance in this region [Borstad, 1982a, 1982b; Mullerkarger et al., 1989; Steven and Glombitz, 1972; Subramaniam et al., 2008]. The stable stratification and shallow mixing depth limit the input of deeper water with N:P ratios closer to Redfield when compared to other oceanic settings [Blain et al., 2015; Flohr et al., 2014], and this enhances the effect that atmospheric deposition has in controlling surface N:P ratios. High N:P ratios in the euphotic zone and in sinking particulate matter, along with a positive N^* ($\text{N}^* = (\text{N} - 16\text{P} + 2.90 \mu\text{mol kg}^{-1})/0.87$), see Gruber and Sarmiento [1997]) for subsurface water in this region (and throughout the North Atlantic subtropical thermocline) have also been observed [Hansell and Follows, 2008; Hansell et al., 2004, 2007] and are consistent with addition of more N relative to P. The idea that atmospheric deposition contributes to high

N:P ratios in this region is also consistent with the observed relationship between excess N in the water column of the Sargasso Sea and the North Atlantic Oscillation (NAO) [Bates and Hansell, 2004], because the magnitude and timing of atmospheric transport to the region is affected by NAO-related changes in atmospheric circulation. The high excess N in the eastern tropical South Atlantic [Hansell et al., 2004] could also be explained by high atmospheric deposition rates off the west coast of Africa.

The potential role of atmospheric deposition as a new N source has been previously recognized [Duce et al., 2008]; however, it was suggested that due to low atmospheric deposition fluxes relative to other nutrient sources, atmospheric deposition would have relatively little direct impact on open ocean biota [Knap et al., 1986; Krishnamurthy et al., 2009; Michaels et al., 1993]. Moreover, most previous studies have attributed the excess N, high N:P, and low $\delta^{15}\text{N}$ signatures in NO_3^- seen in this region to nitrogen fixation [Hansell et al., 2004; Knapp et al., 2008; Wu et al., 2000]. The contributions from atmospheric N deposition and N_2 fixation have similar biogeochemical signatures (low N isotope and high N:P ratios) and thus are difficult to differentiate [Hansell et al., 2007; Knapp et al., 2010]. Our incubation results, however, suggest that N from atmospheric deposition, or more specifically the high N:P ratio in atmospheric deposition, could enable *Prochlorococcus* to outcompete diazotrophs. In fact, the high N:P ratios (and low P concentrations) could in themselves limit the activity of diazotrophs [Mills et al., 2004; Sañudo-Wilhelmy et al., 2001; Voss et al., 2004]; hence, it is likely that at least part of the observed excess N in the subsurface and low $\delta^{15}\text{N}$ of NO_3^- in this region is a result of direct input of N from atmospheric deposition sources.

Atmospheric deposition of N, P, and Fe (Figure 3a), as well as the associated N:P and N:Fe ratios (Figure 3b), vary considerably in space. This is due to the different sources of these elements in aerosols. The relatively high contribution of aeolian (mineral dust) deposition in the North Atlantic, and specifically in our study site (where other new N sources are small), results in both a high N:P ratio and a high excess N input (relative to P) to the euphotic zone (Table 5). Our model results, which take into account variability in the stoichiometry of nutrient supply as well as phytoplankton group specific demand, indicate that aerosol deposition not only impacts but plays a major role in phytoplankton community structure in the LNLC regions of the west tropical North Atlantic Ocean by controlling nutrient distribution in surface seawater, particularly by maintaining high N:P ratios and high Fe. Specifically, including phytoplankton taxon-specific C:N:P in conjunction with N, P, and Fe in atmospheric deposition had a large impact on the distributions of phytoplankton taxa, as shown by comparing these results to model outputs that do not include variable nutrient stoichiometry demand (Figure 5). The largest impact in our region is an increase in *Prochlorococcus* relative to higher-latitude waters. Previous model studies [e.g., Krishnamurthy et al., 2010] have shown that the addition of aeolian N and P sources does not produce a large change in global productivity or phytoplankton distributions (see supporting information Figure S3). However, here we show that there is a change in phytoplankton community structure in the North Atlantic subtropical gyre, specifically in the region where the contribution of atmospheric nutrients is greatest relative to other sources. Here *Prochlorococcus* benefits because of its low P requirement relative to N, and as a result their abundance is higher, particularly in the central portion of the region (Figure 5d).

6. Summary and Implications

Direct observations and modeling results suggest that high atmospheric deposition rates and N:P ratios in the Caribbean Sea create conditions that favor phytoplankton with low P requirements and efficient P acquisition strategies, such as *Prochlorococcus*. This work provides insight into the observation that the southwestern North Atlantic is characterized by relatively low productivity and high abundance of *Prochlorococcus* and demonstrates the impact of atmospheric nutrients in this LNLC area. Similar conditions prevail in the Mediterranean Sea and the Gulf of Aqaba, Red Sea, where *Prochlorococcus* is also prevalent. Models predict that future climate will enhance ocean stratification [Sarmiento et al., 2004; Steinacher et al., 2010], and N loading in aerosols is also expected to increase [Duce et al., 2008; Gruber and Galloway, 2008; Krishnamurthy et al., 2009]. Based on our observations, this may impact phytoplankton community structure and productivity in some regions of the ocean, most notably regions that are close to being P limited. Indeed a recent study has already detected changes that are consistent with higher anthropogenic N deposition and expansion of P limitation [Kim et al., 2014]. This may also have cascading impacts on other processes such as carbon export to depth because particle sinking rates in systems characterized by small cells are slow [Bach et al., 2012].

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Chapter Two
THE DISTRIBUTION OF LEAD CONCENTRATIONS AND ISOTOPIC
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Lead concentrations and isotopic compositions in the Western Philippine Sea

Chia-Te Chien^a, Tung-Yuan Ho^b, Matthew E. Sanborn^c, Qing-Zhu Yin^c, Adina Paytan^{a,*}^a Earth & Planetary Sciences Department, University of Santa Cruz, Santa Cruz, CA, USA^b Research Center for Environmental Changes, Academia Sinica, Taipei, Taiwan^c Department of Earth and Planetary Sciences, University of California at Davis, Davis, CA 95616, USA

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ABSTRACT

Dissolved lead (Pb) concentrations and isotope ratios in seawater of the Western Philippine Sea (WPS) were determined to investigate sources of Pb in the region. Surface seawater concentrations at seven sampling stations ranged from 36.2 to 68.1 pmol kg⁻¹. Isotopic composition of surface water, with ²⁰⁶Pb/²⁰⁷Pb ranging from 1.162 to 1.170, ²⁰⁸Pb/²⁰⁷Pb ranging from 2.445 to 2.451, and ²⁰⁶Pb/²⁰⁴Pb ranging from 18.14 to 18.27, reflects Asian anthropogenic aerosols input to the WPS. Shallow water Pb concentrations within the Kuroshio Current domain are about 15 pmol kg⁻¹ lower than at other sites and, together with a distinct isotopic signature (²⁰⁶Pb/²⁰⁷Pb = 1.167–1.170, ²⁰⁸Pb/²⁰⁷Pb = 2.447–2.451 and ²⁰⁶Pb/²⁰⁴Pb = 18.22–18.27), reflect water originating from the Equatorial Pacific that is relatively less impacted by contamination from anthropogenic inputs. An isotopically distinct sub-surface Pb maximum at about 100 to 250 m, representing water originating from the Western North Pacific where anthropogenic Pb deposition is high, was seen at all seven sites. Lead concentrations in deep water in the stations further from shore are typically lower than in the surface layer and ranged from 11.2 to 51.6 pmol kg⁻¹. Lead isotopic signatures in deep water at these sites (²⁰⁶Pb/²⁰⁷Pb = 1.162–1.184; ²⁰⁸Pb/²⁰⁷Pb = 2.448–2.471; ²⁰⁶Pb/²⁰⁴Pb = 18.13–18.51) are offset from pre-anthropogenic values and suggest that anthropogenic sources have penetrated the deep water column. Elevated concentrations and isotopic signatures observed in the deep water at stations closer to shore, where sediment transport is prevalent, indicate that sedimentary input is a major source of dissolved Pb at these sites. Differences in Pb concentrations and isotopic signatures between samples collected from the Pacific Deep Water (PDW) water-mass during this study and those collected a decade ago suggest that Pb inputs even in deep water change on decadal scales.

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1. Introduction

Human activities have introduced high amounts of anthropogenic Pb into the environment through the use of leaded gasoline and other activities (Nriagu, 1979). The imprint of anthropogenic Pb in the ocean and its temporal evolution over time however are unevenly distributed in different major oceanic basins (Boyle et al., 2014; Echegoyen et al., 2014; Gallon et al., 2011). For example, the elevated Pb concentrations in the North Atlantic ocean have decreased since the phasing out of leaded gasoline, with Pb concentrations in surface water dropping from ~170 pmol kg⁻¹ in 1970s to ~20 pmol kg⁻¹ in 2010s (Boyle et al., 2014), but, surface water Pb concentrations in the North Pacific Ocean remained relatively high (up to 104 pmol kg⁻¹). The North Indian Ocean also has high Pb concentrations (82 pmol kg⁻¹) (Echegoyen et al., 2014) relative to the North Atlantic. This is likely a result of the late phase-out of leaded gasoline in Southeast Asia and the

rapid growth of coal burning and high temperature industries in Asian countries (Q. Li et al., 2012).

Understanding variations in Pb concentrations and isotope compositions in the ocean can provide information about anthropogenic and lithogenic sources, fluxes, and water mass mixing patterns of Pb (Alleman et al., 1999; von Blanckenburg et al., 1996; Wu et al., 2010). However, there are relatively few studies reporting seawater Pb concentrations and isotopes in the Pacific Ocean (Flegal and Patterson, 1983; Flegal et al., 1984; Gallon et al., 2011; Wu et al., 2010), particularly in the Northwestern Pacific Ocean, a region that might be impacted by the >20 fold increase in coal burning in China over the past three decades (Lee et al., 2014). A vertical advection/diffusion model presented by Wu et al. (2010) demonstrated how Pb concentration and isotopic composition in the central Pacific Ocean may have changed over the past few centuries following changes in the input of anthropogenic Pb. In marginal seas, however, lateral transport from sediments and the contribution of Pb from local sources, together with the unique hydrography of these basins, may lead to Pb concentrations and isotopic signatures that differ from those of the open ocean. In this work, we report Pb

* Corresponding author.

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

concentrations and isotopic compositions at 7 vertical profiles in the Western Philippine Sea (WPS), collected during the Taiwan GEOTRACES process study (March 2014). By comparing Pb concentrations and isotopic composition in the WPS to open ocean Pb signatures and to signatures of potential Pb sources, we are able to evaluate the impacts of atmospheric deposition and sedimentary inputs on seawater Pb in this region.

2. Materials and methods

2.1. Study site

The Philippine Sea is a marginal sea located in the Western Pacific Ocean, bordering the Philippines, Taiwan, and Japan from south to north. It is adjacent to the South China Sea on the southwest, the East China Sea to the northwest and the Pacific Ocean to the east. The Kuroshio Current is a strong western boundary surface current that transects the West Philippine Sea (WPS) flowing from south to north transporting water from the tropical Pacific Ocean to the Philippine Sea (Fig. 1). Water samples were collected at 7 vertical profile stations along an off shore transect in March 2014 (Fig. 1). Samples collected represent several oceanic water masses including the Western North Pacific Central Water (WNPCW) between 100 and 250 m, the North Pacific Intermediate Water (NPIW) between 400 and 900 m and the Pacific Deep Water (PDW) mass below 2000 m depth.

2.2. Water sampling and analysis

Seawater samples were collected using Teflon-lined GO-FLO bottles (General Oceanics) on a trace metal clean sampling rosette. The GO-FLO bottles were moved into a trace metal clean van after seawater collection and each sample was filtered through an acid cleaned 0.2 μm capsule filter (PolycapTC, Whatman) into an acid washed, sample rinsed, 1 L low density polyethylene (LDPE) bottle and acidified with 4 mL of 6 M ultrapure HCl (final concentration 0.024 M). After collection, samples were shipped to University of California at Santa Cruz (UCSC) and stored at room temperature until they were analyzed. Typically 500 to 1000 g of each seawater sample was extracted by Nobias Chelate-PA1 resin (HITACHI, Japan) for seawater matrix removal and Pb pre-concentration (Billir and Bruland, 2012; Sohrin et al., 2008). The Pb in the seawater was then recovered by eluting the column with 3 mL 1 M HNO_3 and measured using a Thermo Element XR high-resolution inductively coupled plasma mass spectrometer (HR-ICP-MS) at UCSC for concentration determination. To estimate recovery yield, Pb free seawater (pretreated with the Nobias Chelate-PA1 resin) was spiked with varying

amounts of a Pb standard and processed with every sample batch. The Pb concentrations of these standard spiked seawater samples were compared to standards of similar concentration prepared in 2% HNO_3 . The Pb blank for the full procedure was $0.33 \pm 0.16 \text{ pmol kg}^{-1}$. Method accuracy and precision were assessed relative to GEOTRACES SAFE, S and D1 reference seawater samples (see Supplementary material Table S1). After Pb concentration measurements were made, samples were dried on a hot plate in preparation for Pb isotope ratio determination. All work was performed in a class 1000 clean lab inside class 100 laminar flow hoods. Inter-lab comparison of Pb concentration profiles at station 7 between the UCSC Marine Analytical lab and the Marine Biogeochemistry Laboratory in the Research Center for Environmental Changes, Academia Sinica in Taiwan, is shown in Supplementary material Fig. S1. Results show good agreement between data obtained using different methods; our method described above and an automated trace metal extraction system used in Taiwan (Wang et al., 2014a).

Lead isotope ratios in seawater samples were measured using a Thermo Neptune Plus multi-collector ICP-MS the University of California, Davis. Detailed information about measurement conditions and instrument settings are described by (Erhardt, 2013). Sample were dried down and then brought up in 2% HNO_3 to a concentration of at least 3 ppb, NBS SRM 997 Tl solution was added to obtain a Tl/Pb ratio of 0.2 to correct for the mass fractionation using an exponential law correction. The diluted samples were self-aspirated using a 50 $\mu\text{L min}^{-1}$ PFA nebulizer. An ESI APEX-IR desolvating system was used to increase sensitivity with the Neptune Plus configured with a jet sample cone and X-style skimmer cone. Samples (in sets of 5) were bracketed with a 5 ppb solution of the NBS SRM 981 Pb standard. The bracketing standard was used to correct for instrumental mass bias and the mass bias correction was applied to the measured samples. A 2% HNO_3 blank was analyzed after each sample with the analyzed blank subtracted from each sample to ensure no sample crossover contamination. The ^{204}Pb signal in the 2% HNO_3 blank relative to the ^{204}Pb signal of the samples was $<10^{-4}$ for most samples, hence blank correction was negligible. The instrumental running conditions resulted in 0.5 V for ^{208}Pb and had internal one standard deviations of 0.014 for $^{206}\text{Pb}/^{204}\text{Pb}$, 0.013 for $^{207}\text{Pb}/^{204}\text{Pb}$ and 0.036 for $^{208}\text{Pb}/^{204}\text{Pb}$.

To evaluate the influence of the pre-concentration procedure on Pb isotope ratios, NIST SRM 981 was added to Pb free seawater (processed using the Nobias Chelate-PA1 resin twice) and analyzed. The Pb concentrations used covered almost the whole range of seawater concentration observed in this study (15 to 150 pmol kg^{-1}). The samples with the NIST SRM 981 Pb addition were treated exactly as all other samples. Fig. S2A–C in the supplementary materials show that our sample processing did not result in fractionation of the $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios.

3. Results

Lead concentrations in the upper 400 m of the water column in the WPS range from 36.2 to 68.1 pmol kg^{-1} and show a distinct sub-surface maximum at about 100 to 250 m associated with the Western North Pacific Central Water (WNPCW) water mass. Surface water concentrations are lower at stations 1 and 3 within the Kuroshio Current than in off-shore stations and are also lower at station 8 the furthest station from shore. Lead in deep water (2000 m and deeper, corresponding to Pacific Deep Water (PDW) water mass) are typically lower than in the upper 400 m and range from 11.2 to 19.1 pmol kg^{-1} with higher values close to the bottom at sites where sediments are re-suspended. Specifically Pb concentrations decrease with depth below the sub-surface maxima at sampling sites 4–8 which were farther from shore while at stations closer to shore (Stn. 1 and 3) Pb concentrations increase below 2000 m following the mid depth decrease (Fig. 2A–D).

Isotopic ratios show strong correspondence to the concentrations. In the upper layer (0–400 m) where concentrations are relatively high the isotope ratios are: $^{206}\text{Pb}/^{207}\text{Pb} = 1.162\text{--}1.170$; $^{208}\text{Pb}/^{207}\text{Pb} = 2.445\text{--}$

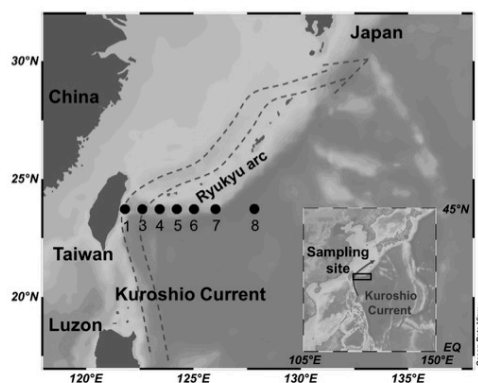


Fig. 1. Location of sampling stations in Western Philippine Sea.

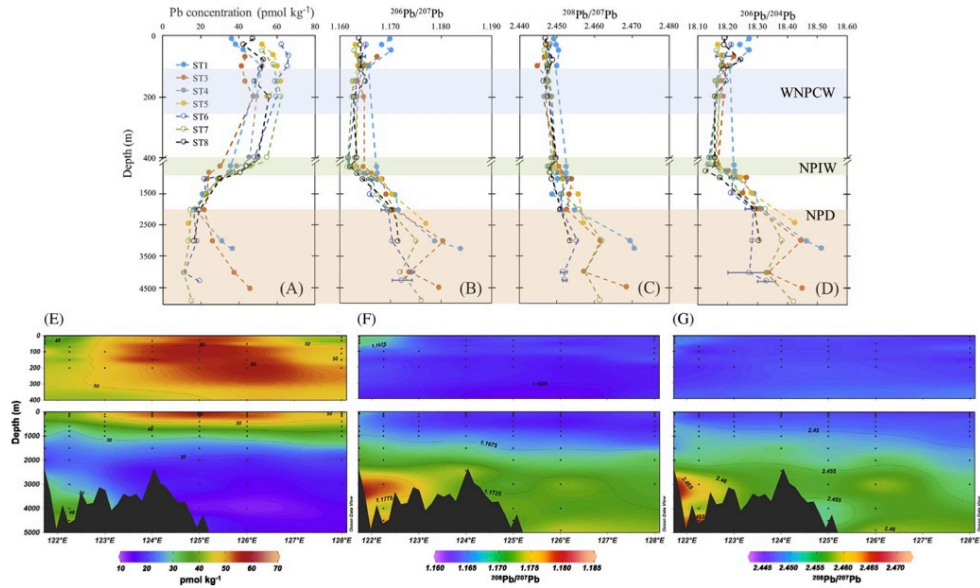


Fig. 2. Pb concentration and isotopic composition. (A) Pb concentration profile, (B) ²⁰⁶Pb/²⁰⁷Pb ratio, (C) ²⁰⁸Pb/²⁰⁷Pb ratio and (D) ²⁰⁶Pb/²⁰⁴Pb ratio. The error bar at station 6 represented analyses error (2 S.E.). (E–G) Full water column and zoomed in 0–400 m Pb concentration, ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁷Pb profile in ocean data view, respectively.

2.451; ²⁰⁶Pb/²⁰⁴Pb = 18.14–18.27 and the ratios increase with depth as Pb concentrations decrease (²⁰⁶Pb/²⁰⁷Pb = 1.162–1.184; ²⁰⁸Pb/²⁰⁷Pb = 2.448–2.471; ²⁰⁶Pb/²⁰⁴Pb = 18.13–18.51). Similar to the concentration profiles, isotopic signatures at stations 1 and 3 are distinct. In the surface

layer ²⁰⁶Pb/²⁰⁷Pb ratios are higher compared to the other sites and below 2000 m the ratios at some depths at these sites are higher reaching ²⁰⁶Pb/²⁰⁷Pb = 1.184; ²⁰⁸Pb/²⁰⁷Pb = 2.471; ²⁰⁶Pb/²⁰⁴Pb = 18.51) (Fig. 2A–D). Two dimensional section profile plots for the

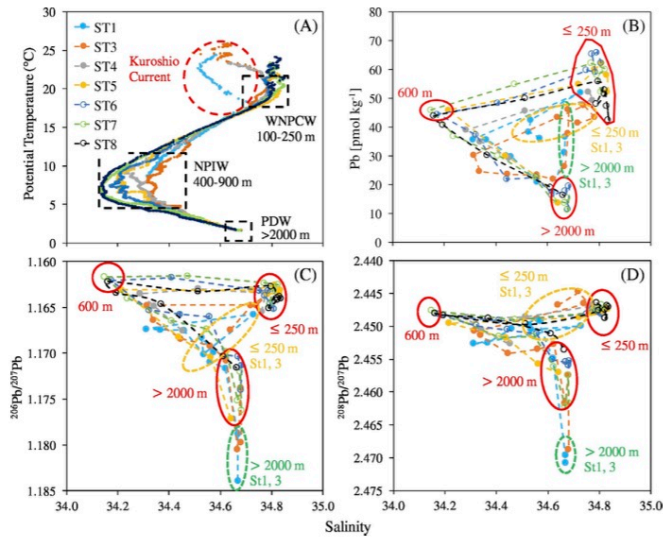


Fig. 3. Salinity vs (A) Potential temperature, (B) Pb concentration, (C) ²⁰⁶Pb/²⁰⁷Pb and (D) ²⁰⁸Pb/²⁰⁷Pb in the Western Philippine Sea. Note that yellow and green circles represent Pb concentrations and isotopic ratios at stations 1 and 3 in water shallower than 250 m and deeper than 2000 m, respectively.

whole water column depth and for the upper 400 m are shown in Fig. 2E–G), and all data are listed in Table S2.

4. Discussion

4.1. Pb concentrations and isotope ratios in the WPS

In the WPS Pb concentrations and isotope ratios as well as their trends with depth (Fig. 2) are related to water masses distribution in the area. A distinct surface water mass and three deeper water masses can be identified in the region based on their Temperature–Salinity (S–T) characteristics (Fig. 3A). The Kuroshio Current, a strong western boundary current, is a branch of the North Equatorial Current (NEC) that moves northward after the NEC encounters the Philippine coast. The Kuroshio Current occupies the surface water at the near shore stations in the study area. Stations 1 and 3 are within the Kuroshio Current and Pb concentrations in the surface water at these sites are lower compared to the other stations. The sub-surface layer throughout the sampling stations represents the WNPCW. The WNPCW is formed near the centre of the Western North Pacific (Emery and Meincke, 1986) and is then transported through subduction and advection to the Philippine Sea (PS) as a sub-surface salinity maximum typically between 100 m and 250 m depth. At intermediate depth the North Pacific Intermediate Water (NPIW) is present. This water mass originates at the west Pacific subpolar gyre and moves towards the south while sinking to water depths between 400 and 900 m in the Western Pacific including the WPS (You et al., 2000). The deep water mass in the region is the Pacific Deep Water (PDW) which is derived from the shallower Circumpolar Water in the Southern Ocean and can be found below 2000 m at our sites (Mantyla and Reid, 1983).

4.1.1. Near surface water Pb in the WPS

The Pb concentrations and isotope ratios in the WPS near surface water at the 7 stations sampled show some small differences. Specifically, the two sites closest to shore (stations 1 and 3) have lower Pb concentrations and Pb isotope ratios that are distinct from the offshore sites (stations 5 to 8), which are more similar to each other (Fig. 2). Near surface water at stations 1 and 3 are expected to have a higher influence of atmospheric Pb deposition as they are closest to land (Taiwan) a potential source of high Pb atmospheric aerosols. However, they have lower Pb concentrations than the offshore samples (15 pmol kg^{-1} lower than at station 8). Near surface water isotopic signatures of the Pb at these stations are also distinct ($^{206}\text{Pb}/^{207}\text{Pb} = 1.167\text{--}1.170$, $^{208}\text{Pb}/^{207}\text{Pb} = 2.447\text{--}2.451$ and $^{206}\text{Pb}/^{204}\text{Pb} = 18.22\text{--}18.27$). This suggests that sites 1 and 3 are within a different water mass influenced by different Pb sources than the open ocean surface water. This grouping is likely because the

offshore stations are less impacted by the influence of the Kuroshio Current (see Fig. 3A T–S diagram). Specifically, the Kuroshio Current dominates near surface water at station 1 and is also present at station 3 and to some degree at station 4, as can be seen in the salinity of these waters (Kuroshio Current ranged from 34.49 to 34.70 while offshore sites salinity ranges from 34.76 to 34.85; Fig. 3A). The Kuroshio Current is coming from the Equatorial Pacific Ocean (southeast of the WPS), an area with less anthropogenic impact and lower atmospheric deposition. The lower concentrations close to shore also suggest that Taiwan is not the main source of aerosols to the region. The high speed of the Kuroshio Current also leads to a short residence time of the near surface water in the region allowing for less aerosol deposition to accumulate. Consequently, the overall Pb concentrations are lower and isotopes are slightly different from offshore sites although the Pb isotopic composition still carries the dominant signature of anthropogenic Pb.

A recent study reports that in a coral from around Vietnam the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio has decreased from 1.191 to 1.195 before the mid-1950s to ~ 1.165 in 2004 (Chen et al., 2016a). This change indicates that Pb from Asian emissions may be impacting the whole region. In order to better understand Pb sources to the WPS, we applied a triple-isotope plot ($^{208}\text{Pb}/^{207}\text{Pb}$ vs. $^{206}\text{Pb}/^{207}\text{Pb}$, Fig. 4) to distinguish between aerosol particles collected from Taipei, Taiwan and regional Asian aerosol signatures. Based on the plot, the Pb signature in seawater <400 m in the WPS is likely due to the input of aerosols from Asian countries throughout the region and not specifically from Taiwan. This Pb signature is similar to that reported for the anthropogenic sources to the North Pacific by Gallon et al. (2011) and consistent with the observation of lower Pb concentrations in near surface water at stations 1 and 3 despite the proximity to Taiwan.

Among the offshore stations, near surface Pb concentration at station 8, the station furthest from shore and the most representative of open ocean conditions are somewhat lower than at stations 5–7 (Fig. 2). This is likely due to a combination of lower input from atmospheric Pb due to distance from land and less influence of water from the South China Sea, which has higher surface Pb concentration and could be a source of Pb in this area. Indeed seawater Pb concentrations in South China Sea (Ho et al., 2010) are higher than those of the WPS (up to 126 pM) and any mixing with this water mass will increase Pb concentrations in the WPS. The Pb isotope ratios at station 8, however, didn't show distinguishable difference from stations 5 to 7 (Fig. 2B, C and D). It is possible that the Pb in the near surface waters throughout this region (East and South China Seas and the WPS offshore stations) is dominated by similar sources; hence the isotope signatures are indistinguishable, despite differences in concentrations.

Collectively, the near surface water Pb data indicate that near surface waters at the WPS are all receiving anthropogenic Pb (with a

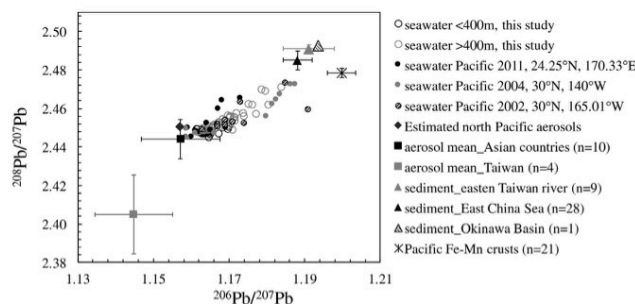


Fig. 4. Triple-isotope plot of Pb in WPS seawater in this study and Pacific Ocean seawater (Zurbrick, 2014; Wu et al., 2010), estimated north Pacific aerosols (Gallon et al., 2011), average Asian countries aerosols from Korea, Japan, China and Vietnam (Bollhöfer and Rosman, 2001), average Taiwan aerosols (Hsu et al., 2006), sediments (Dou et al., 2016; Wang et al., 2014a, 2014b; Benthaila et al., 2008) and Pacific Fe–Mn crusts (von Blanckenburg et al., 1996). The error bars represent 1 S.D.

$^{206}\text{Pb}/^{207}\text{Pb} = 1.157$; Gallon et al., 2011) which is mixed to varying degrees by different water masses, the Kuroshio Current with low Pb concentrations (with weaker anthropogenic signature) close to shore and waters from the East and South China sea (with higher Pb concentration and a strong anthropogenic signature) offshore. The near surface water Pb concentrations in this region are lower than those seen in the East China Sea and the Indian Ocean suggesting that this area does not get as much atmospheric deposition as surface waters in the East China Sea (Mahowald et al., 2005) and the Indian Ocean (Echegoyen et al., 2014) because it is located outside the main path of the Asian monsoon.

4.1.2. Sub-surface and deep water Pb in the WPS

In all profiles from the WPS, a clear sub-surface maximum (between ~100–250 m depth) in Pb concentration is observed, as also seen in all North Pacific profiles measured thus far (Flegal and Patterson, 1983; Schaule and Patterson, 1981; Wu et al., 2010; Zurbrick, 2014). The sub-surface concentration maximum has been attributed to a water mass carrying anthropogenic Pb that originates from subduction and advection of North Pacific surface water (Wu et al., 2010). From the T-S diagram and a plot of Pb concentration vs. salinity (Fig. 3A and B), we can identify that this concentration maximum is associated with the WNPCW which originates near the centre of the Western North Pacific (Emery and Meincke, 1986); indeed atmospheric deposition of Pb is currently, and has been for decades, high in the zone where the WNPCW originates at the Western North Pacific Ocean around 40°N resulting in the distinct sub-surface signatures (higher Pb concentration and slightly lower $^{206}\text{Pb}/^{207}\text{Pb}$).

Despite the clear concentration maximum in the sub-surface (and change in salinity), at the offshore stations the Pb isotope ratios associated with the sub-surface maximum show only a small difference from the surface waters above (Pb ratios between 100 and 250 m $^{206}\text{Pb}/^{207}\text{Pb} = 1.1623$ – 1.1651 and $^{208}\text{Pb}/^{207}\text{Pb} = 2.4465$ – 2.4487) or the water below (400–900 m). From the T-S diagram (Fig. 3A) the NPIW occupies the depth around 400–900 m. The west part of NPIW is dominated by Okhotsk Intermediate Water (OIW) which originates at the west Pacific subpolar gyre (You et al., 2000). Indeed, these isotope ratios are consistent with those reported for the western Pacific subpolar surface water (Zurbrick, 2014). Overall, while a small difference is observed particularly in station 1 the differences in Pb isotope ratios of surface water, the WNPCW and the NPIW are relatively small and may suggest similarity in Pb sources (e.g. anthropogenic emissions possibly from China) or different sources with similar isotopic signatures.

Deep water Pb concentrations in our samples are higher than those reported for the north eastern and south Pacific Ocean (Wu et al., 2010). Specifically, at station 8 at 3000 m, the Pb concentration is 16.3 pM while in the south Pacific, the source of this deep water, it is only about 1.5 pM. This suggests that >85% of Pb observed in the WPS deep water was contributed by atmospheric Pb input via vertical transportation during water mass propagation from the south Pacific to the WPS. Alternatively, there could be a local lateral source of Pb contributing to the deep water Pb inventory in this region. Isotope ratios in the deep water below 2000 m at stations 5 to 8 ranged from 1.1695 to 1.1772 for $^{206}\text{Pb}/^{207}\text{Pb}$ and 2.4512–2.4623 for $^{208}\text{Pb}/^{207}\text{Pb}$, these values are different from the isotopic signatures of surface sediments in the WPS with $^{206}\text{Pb}/^{207}\text{Pb} = 1.1805$ and $^{208}\text{Pb}/^{207}\text{Pb} = 2.4782$ (Bentahila et al., 2008) or those from the southern Okinawa Trough ($^{206}\text{Pb}/^{207}\text{Pb} = 1.1958$; $^{208}\text{Pb}/^{207}\text{Pb} = 2.4954$; (Dou et al., 2016)), and are closer to surface water signatures of the eastern Pacific Ocean (Wu et al., 2010; Zurbrick, 2014) and western/central Pacific Ocean sampled in 2002 (Zurbrick, 2014). This deep water Pb isotopic signature in the WPS agrees with deep water values reported in Zurbrick (2014) for the western/central Pacific Ocean sampled in 2011. Zurbrick (2014) proposed that higher Asian anthropogenic Pb input to the west Pacific Ocean resulted in a change in the Pb isotope ratios in the deep water of the Pacific Ocean between 2002 and 2011. It is likely that the deep water in the WPS also shows this shift in Pb isotope ratios towards

increased anthropogenic influence and may indicate similar anthropogenic Pb sources impacting deep water throughout most of the western Pacific Ocean. A recent laboratory study indicates a rapid (days-months) Pb isotope exchange between seawater and suspended particulate materials (Chen et al., 2016b), which is consistent with fast changes in deep water Pb signature in the western Pacific Ocean resulting from high anthropogenic Pb inputs and rapid Pb isotope exchange between seawater and particles.

It is possible that since the WPS is geologically closer to the continent, it receives higher anthropogenic Pb from atmospheric deposition. Indeed, two years of marine aerosol collection in the East China Sea show that overall Pb solubility is over 30% (Hsu et al., 2010) and Mackey et al. (2015) emphasize the rapid dissolution of atmospheric Pb in seawater. However, if that were the case one would expect that the surface Pb concentration in WPS would also be elevated. In this study, surface Pb concentrations are not higher than at other locations in the centre and eastern Pacific (Fig. 5), hence local atmospheric deposition is likely not higher in the WPS when compared to other Pacific sites. Regardless we do see high Pb concentration in the deep water specifically at stations 1 and 3 therefore there must be other sources of lead to the deep water at this location.

One potential source of Pb to the deep waters in the WPS, which are distinct from the open Pacific Ocean deep water, can be gleaned from the Pb concentration trend below 2000 m at stations 1 and 3. From 2000 m to the bottom, Pb concentration increases from 17.7 to 36.7 pmol kg⁻¹ at station 1 and from 21.9 to 46.1 pmol kg⁻¹ at station 3 (Figs. 2A and 6A). Although terrestrial inputs seem unlikely at this depth, a previous study reveals the possibility that sediments could be transported to the deep ocean basin during tropical cyclone events around Taiwan (Kao et al., 2010). Furthermore, another study showed that sediment transport to depth can result from flood runoff from Taiwan rivers, as well as following large earthquakes (Hsu et al., 2004). The deep water mass at stations 1 and 3 is not distinguishable from deep water at other stations sampled based on the T-S diagram (Fig. 3A). However, Pb concentrations are much higher below 2000 m at these two stations (Fig. 3B). Further more, beam transmittance data show that below depths of 2000 m, suspended particle levels are higher at stations 1 and 3 than at stations 5, 6, 7 and 8 (Fig. 6B). In order to quantify the contributions of sediment inputs to the WPS deep water at stations 1 and 3, we use the average concentration from stations 6, 7 and 8 at the depth of 3000 m as representative of regional deep water signatures, the contributions of sediment input of Pb at stations 1 and 3 at 3000 m can then be calculated by mass balance to contribute as much as 49% and 40%, respectively.

The $^{206}\text{Pb}/^{207}\text{Pb}$ ratios associated with the high concentrations in the deep water at stations 1 and 3 are higher than those seen at similar depths in off shore stations (Figs. 3C–D and 6C), and are closer to Pb signatures of sediment seen in the East China Sea (Wang et al., 2014b), the WPS (Bentahila et al., 2008), eastern Taiwan rivers and the Okinawa Trough (Dou et al., 2016). This similarity in isotope signatures of these potential sources and deep water in stations 1 and 3 indicates that sediments could be an important source of Pb to the deep water at stations close to shore in the WPS. This is seen also in Fig. 4 where the seawater Pb isotopes in the WPS (particularly for samples below 400 m depth) lay on the trend between anthropogenic aerosols and sediments of the Okinawa Basin, East China Sea and rivers in Taiwan (Fig. 4), further supporting sediment transport as a local source of Pb to deep water in the WPS. Notably none of the isotope ratios we measured seem to be similar to pre anthropogenic Pb signatures as recorded in Pacific Fe–Mn crusts that represent pre-anthropogenic Pb.

4.2. Comparison between the WPS and other North Pacific Ocean Pb profiles

While surface Pb concentrations in the North Atlantic Ocean have decreased >8-folds over the last four decades as a result from phasing out of leaded gasoline, the Pb concentrations in the upper water in the

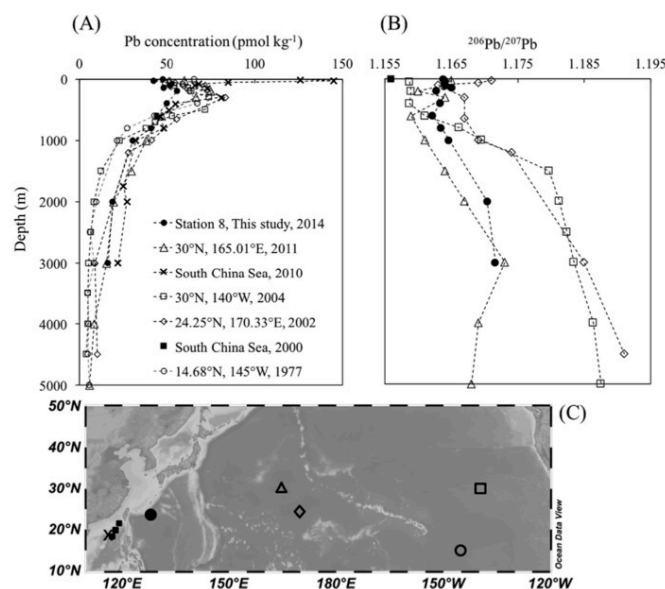


Fig. 5. Comparison of Pb concentration and $^{206}\text{Pb}/^{207}\text{Pb}$ of North Pacific seawater. Include seawater collected in 1977 (concentration only) (Schaule and Patterson, 1981), 2000 ($^{206}\text{Pb}/^{207}\text{Pb}$ only, mean value from three surface water samples at South China Sea) (Lee et al., 2014), 2004 (Wu et al., 2010), 2002 and 2011 (Zurbrick, 2014), 2010 (concentration only, South China Sea) (Ho et al., 2010) and station 8 in this study.

North Pacific Ocean remain relatively high due to the rapid growth of coal burning in China and other Asian countries in the last decades. The typical Pb concentration trends with depth observed in the off shore stations of the WPS are similar to those seen in previous studies from the North Pacific open ocean, with low concentrations in the surface, a sub-surface maximum and a decrease with depth below the maximum (Flegal and Patterson, 1983; Schaule and Patterson, 1981; Wu et al., 2010; Zurbrick, 2014; Zurbrick et al., 2012). The similarity is indicative of the basin-wide anthropogenic impact on Pb in the Pacific Ocean. Comparing these data to the model prediction of natural Pb distribution in the ocean reported by Henderson and Maier-Reimer (2002), the anthropogenic contribution of Pb in this region is >8-folds larger than Pb from natural sources.

Isotope signatures of Pb in surface and sub-surface water are also comparable to those seen in previous studies (Gallon et al., 2011; Wu et al., 2010; Zurbrick, 2014). $^{206}\text{Pb}/^{207}\text{Pb} = 1.162\text{--}1.170$ and $^{208}\text{Pb}/^{207}\text{Pb} = 2.445\text{--}2.451$ are close to the values which Gallon et al. (2011) estimated for anthropogenically sourced Pb in the North Pacific Ocean ($^{206}\text{Pb}/^{207}\text{Pb} = 1.157$ and $^{208}\text{Pb}/^{207}\text{Pb} = 2.451$). A comparison of

Pb concentrations and isotope ratio in the water column at station 8 in the WPS (the station furthest away from shore) to two sites from the North Pacific Subtropical Gyre (NPSG) collected in 2002 and 2011 (Zurbrick, 2014), two sites from eastern Pacific Ocean collected in 1977 and 2004 (Schaule and Patterson, 1981; Wu et al., 2010) and results from the South China Sea (SCS) collected in 2000 (Lee et al., 2014) and 2010 (Ho et al., 2010) reflects the similarity in trends as well as the differences (Fig. 5). Lead concentrations and isotope ratios in the near surface and sub-surface water at station 8 are comparable to those at the other locations. In deep water, station 8 concentrations are close to those in the NPSG and SCS collected after 2010 but are higher than those in the NPSG and eastern Pacific Ocean collected in 2002 and 2004, respectively. Specifically the isotopic signatures of Pb in the deep water below 2000 m at station 8 in the WPS are comparable to those seen in the western Pacific Ocean at 30°N in 2011 (Zurbrick, 2014) ($^{206}\text{Pb}/^{207}\text{Pb} = 1.167\text{--}1.173$ and $^{208}\text{Pb}/^{207}\text{Pb} = 2.450\text{--}2.466$), the concentration in the WPS deep water is also comparable to this western Pacific Ocean deep water (16.3 and 15.3 pmol kg⁻¹ at 3000 m, respectively). These concentrations are higher than those in

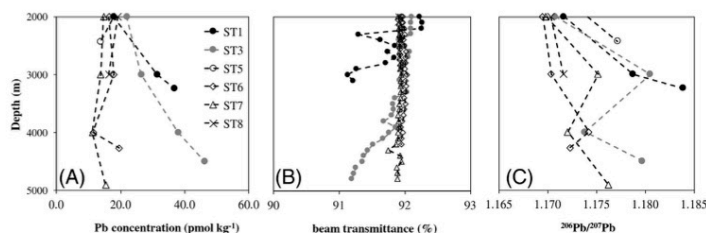


Fig. 6. Deep water profiles at stations 1, 3, 5, 6, 7 and 8 (A) Pb concentration (B) beam transmittance and (C) $^{206}\text{Pb}/^{207}\text{Pb}$.

water sampled in western Pacific Ocean in 2002 (8.9 pmol kg^{-1} at 3000 m) (Zurbrick, 2014) and eastern Pacific Ocean in 2004 (5.1 pmol kg^{-1} at 3000 m) (Wu et al., 2010) (Figs. 2A and Fig. 5A). The concentrations and $^{206}\text{Pb}/^{207}\text{Pb}$ differences in deep water among sites seem to be related to the years of collection, with samples collected in 2002 and 2004 (Wu et al., 2010; Zurbrick, 2014) being similar to each other, while samples collected in 2011 (Zurbrick, 2014) and 2014 (this study) both show considerably lower values and are similar to each other. We note that while these stations are far from each other the deep water at all sites represent a single water mass the PDW. Lead concentration and isotope signatures are influenced by regional water mass, as well as terrestrial and anthropogenic inputs. The observed variability among sites within the PDW mass collectively suggest that Pb in seawater is very dynamic spatially and temporally showing distinct differences for profiles collected at NPSG from the same water mass (PDW) less than a decade apart (Fig. 5), while profiles collected at the same time only 180 km apart (e.g., stations 1 and 3 relative to the other stations in the WPS) also differing from each other. This is consistent with the short residence time of Pb in surface seawater. The trend towards lower $^{206}\text{Pb}/^{207}\text{Pb}$ in the deep water over time is likely due to the larger contribution of anthropogenic Pb which penetrates into deeper water masses since the increase in coal use in Asia.

5. Conclusion

Several depth profiles of seawater Pb concentrations and isotopic composition in the WPS have been studied. Possible sources of Pb to this region have also been identified. Overall Pb concentration profiles are comparable to those reported for other locations in the North Pacific Ocean. The upper layer seawater Pb in the WPS has an anthropogenic signature related to a mixture of Pb from aerosol emissions from Asian countries rather than local aerosol from Taiwan. This anthropogenic input is also seen in deep water. Deep water isotopic signatures also suggest sediment transport from the continental arc and other land sources as an important source of Pb to deep water in the WPS. Overall, this study indicates that the Pb system in the Pacific Ocean is very dynamic, concentrations and isotopes change even in deep water on decadal scales. This rapid change should be considered in future Pb studies when sediment and coral materials are used to reconstruct past Pb signatures.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.marchem.2016.12.007>.

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Chapter Three

ATMOSPHERIC DRY DEPOSITION A SOURCE OF NUTRIENTS AND TRACE METALS TO LAKE TAHOE

Abstract

We present the first long term monitoring data set of aerosol nutrients and trace metals deposition and Pb isotopes signatures in the Tahoe basin. Five years of aerosol samples collected between the winter of 2005 and spring 2010 and lake water samples collected between Spring 2013 and Summer 2016 were analyzed. Our results indicate that aerosol concentrations in the air in the Tahoe basin are higher during the cold months (October – April) than in the warmer months of the year (May-September). Trace metal concentrations in aerosol samples are also higher in cold period; however, trace metal solubilities in aerosol samples are higher during the warm period, likely due to differences in aerosol sources or different atmospheric chemical transformation occurring during different seasons. Base on the correlation between various elements and Al and calculated elements' enrichment factors, most of the elements in the Tahoe basin are dominated by mineral dust sources, while Zn, Cu and Cd are contributed primarily by anthropogenic inputs. Among major nutrient concentrations $\text{NO}_3^- + \text{NO}_2^-$ in aerosols is higher during the cold period while NH_4^+ and soluble phosphate are higher in the warm period. Typically, the distribution of trace metal concentrations and Pb isotopic ratios is homogenous throughout the whole lake water column. This implies that the water mixing time is shorter than the residence time of trace metals in the lake. A triple-isotopes plot of Pb indicates that ground water discharge and riverine inputs are the major Pb sources, but aerosols still contribute Pb to the lake.

3.1. Introduction

Atmospheric deposition is an important source of nutrients and trace metal to remote water bodies like alpine lakes (Camarero et al., 2009; Mladenov et al., 2012). Studying the chemical composition of aerosols in comparison to that of receiving waters, can help us understand how aerosols deposition may influence water quality by contributing major and minor nutrients for phytoplankton growth and possibly affecting the trophic conditions in the lakes (Morales-Baquero et al., 2006). Temporal variability in aerosol sources will result in differences in aerosol chemistry and solubility and thus the ensuing impacts on water quality may differ seasonally (Dolislager et al., 2012; Zhang et al., 2013).

Lake Tahoe is a remote subalpine lake surrounded by mountains including the Carson Range and the Sierra Nevada. The unique characteristics of the watershed, including nutrient poor soils, erosion resistant substrate and dense forest, minimize terrestrial nutrient inputs to the lake. These watershed properties along with the large lake size compared to the size of the watershed make Lake Tahoe oligotrophic, resulting in very high water clarity. However, the clarity of Lake Tahoe has declined dramatically since the 1960s (TERC 2011). It is believed that increasing population and changes in land use and anthropogenic emissions all contribute to the decreasing water clarity (Fenn et al., 2008, 2003; Jassby et al., 1994). 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).

Because of the role atmospheric deposition may play in Lake Tahoe clarity several studies such as the Lake Tahoe Atmospheric Deposition Study (LTADS) by the California Air Resources Board (CARB) have been conducted. These studies monitored gases (Tarnay et al, 2005; Zhang et al., 2002), atmospheric particulate matter (Gertler et al., 2006; Sahoo et al., 2013; Zhang et al., 2002) and wet deposition (Jassby et al., 1994) at representative sites throughout the Lake basin and collected meteorology data as well. These studies provided important information on total particle deposition (Dolislager et al., 2012; Sahoo et al., 2013) as well as on nitrogen (Jassby et al., 1994; Tarnay et al., 2001) and phosphorous inputs (Dolislager et al., 2012; Jassby et al., 1994) and the size distribution of these constituents within atmospheric particulate matter (Dolislager et al., 2012; Tarnay et al., 2001). Other studies focused on organic compounds in aerosols in the region (Cahill, 2010; Datta et al., 1998). Based on data from previous studies (Bytnerowicz et al., 2013; Gertler et al, 2006), pollutants which influence water clarity mainly originate from within the Tahoe basin (e.g. pollutants from local vehicle, road dust, salts, soil and wood burning). However, to our knowledge none of the previous studies have reported long term seasonal variations of nutrients and trace metals in dry atmospheric deposition. Trace metals composition along with other information (for example Pb isotopic composition) can be used to identify possible aerosol sources (Véron and Church, 1997; Witt et al., 2006). Moreover, the soluble fractions of nutrients and trace metals

from aerosols are of particular importance when considering the impacts of aerosol deposition on water chemistry and aquatic ecosystems. Recently, an aerosol addition bioassay has been carried out to understand how atmospheric deposition may affect phytoplankton growth and ecosystem dynamics in Lake Tahoe (Mackey et al., 2013). This study showed that atmospheric aerosols provide nutrients with a high ratio of N:P and favor the growth of picoplankton thus can increase primary productivity without causing a large increase in chlorophyll (chl *a*) or biomass. The study demonstrated the importance of understanding nutrient inputs from aerosol and, more importantly, the fate of the aerosols after they are deposited onto the lake surface.

3.2 Materials and Methods

3.2.1 Aerosol Collection

Aerosol dry deposition samples were collected between 2005 and 2010. Weekly integrated samples were collected on quartz micro filters (10" x 8", Whatman[®]) using a Total Suspended Particle (TSP) sampler (High Volume Sampler, *Graseby* Anderson) which had an airflow rate of $\sim 85 \text{ m}^3 \text{ h}^{-1}$. Between November 2005 and May 2007, the sampler was located near the lake at the Tahoe City 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 from direct road dust

inputs by trees. Aerosols were collected at an airflow rate of $85 \text{ m}^3 \text{ hr}^{-1}$. All filters were kept frozen until further analyses.

For bulk composition of aerosols, a 15 mm x 10 mm sub-sample of each filter was digested by adding 2 mL concentrated HNO_3 and 1 mL HF in Teflon beakers 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 aerosol samples, a 47 mm circular subsample of each filter was placed on an acid-washed filter tower, and 100 mL MilliQ water was passed through the sample under gentle vacuum pressure exposing the sample for about 10 seconds to the water (Buck et al., 2006). 5 mL of the liquid was then added with 100 μL concentrated nitric acid for trace metal composition analysis and the rest of the sample was kept frozen for nutrient and ion chromatography analysis.

3.2.2 Lake Water Collection

Water depth profile samples from Lake Tahoe were collected seven times between Spring 2013 and Summer 2016. Niskin bottles were used for water collection at depths of 50, 100, 200, 250, 300, 350, 400 and 450 m and a one liter bottle attached to a 2.5 m long plastic stick was used to collect surface water samples. The sampling was done at the Mid-lake Tahoe Profile (MLTP) station. From each depth, a 40mL water sample was collected into a 50mL acid washed sample rinsed polypropylene centrifuge tube (Falcon™) for nutrient analysis and another

sample was collected in a one liter acid-washed sample rinsed LDPE bottle for trace metals and Pb isotope analyses. Ground water samples from two wells at Lake Tahoe fire station and three wells at the Tahoe Environmental Research Center (TERC) Hatchery, as well as river water samples from Third creek, Trout Creek, Upper Truckee creek, Ward creek, Incline creek, Blackwood creek and General Creek were collected for trace metal concentrations and Pb isotope analyses. All water samples were filtered with 0.45µm filters before nutrient, trace metal and Pb isotope analyses. Aerosol and water sampling locations are shown in Figure 3.1 and provided in Supplemental Material Table 3.1.

3.2.3 Nutrients, Trace Metals and Pb Isotopes Analyses

Nitrate+nitrite ($\text{NO}_3^- + \text{NO}_2^-$), ammonium (NH_4^+) and soluble reactive phosphorus (SRP) were analyzed using a nutrient autoanalyzer (QuikChem 8000 Flow Injection Analyzer). Detection limits of nitrate+nitrite, 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.

Aerosol total and soluble trace metal concentrations and water trace metal concentrations of Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sr, Cd, Pb and U were analyzed by Ion coupled Plasma Mass Spectrometry (ICPMS - Element XR); Na, Mg, Ca and P were also monitored in bulk aerosol and aerosol soluble fraction samples, while total concentration of Ba was determined in bulk aerosols. Details on trace metal analysis are given elsewhere (Chien et al., 2016). Detection limits typically

were at least two times smaller than sample concentrations, Cd and U concentrations in some samples were close to their detection limits. Lead concentrations in ground water and river samples were also determined.

In order to separate Pb from different sample matrices, samples were dried down and re-dissolved in 100 μ L of concentrated HBr (Optima grade, Fisher Scientific) three times. Pb separation was achieved using AG1-X8 resin (adapted from Kamber and Gladu, (2009)). Briefly, the matrix of the samples was eluted with 1N HBr and the Pb fraction was eluted by 6N double distilled HNO₃, this eluent was then dried down and brought up with 2% HNO₃ to ~2ppb for analyses (Chien et al., 2017).

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 ²⁰⁰Pb and ²⁰²Pb 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 2ppb Pb solution will result in a signal of about 4x10⁶ counts per second on ²⁰⁸Pb, external precision (2 σ) for ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁷Pb are 5.7‰, 3.7‰ and 2.2‰, respectively (n=33).

3.3 Results and Discussion

3.3.1 Temporal Variation of Aerosol Concentrations

During the period of December 2005 to February 2010, aerosol total suspended particles (TSP) concentrations in air at Tahoe basin ranged between 2.7 to 141 $\mu\text{g m}^{-3}$ of air, with an average and standard deviation of $26.3 \pm 14.2 \mu\text{g m}^{-3}$ (Table 3.1 and Fig. 3.2). In general, Tahoe basin has higher TSP concentration in the cold period during late Fall to early Spring (October to April) and lower TSP in the warm period during late Spring to early Fall (May to September), average concentrations are $29.8 \pm 16.1 \mu\text{g m}^{-3}$ and $20.6 \pm 7.6 \mu\text{g m}^{-3}$, respectively (Table 3.1). Shallower atmospheric mixing layer in cold seasons may cause the seasonal concentration variation.

The distributions of bulk metal composition within the TSP samples are listed in Table 3.1. Aluminum (Al) has the highest mean concentration ($1321 \pm 902 \text{ ng m}^{-3}$) among the trace metals, followed by Fe ($771 \pm 486 \text{ ng m}^{-3}$) and Ca ($669 \pm 471 \text{ ng m}^{-3}$), the metal with the lowest concentration is Cd ($0.031 \pm 0.031 \text{ ng m}^{-3}$). As expected like in the case of TSP concentrations in air, typically, trace metals also have higher concentrations in the cold period (October to April) and lower concentrations in the warmer period. For example, average concentrations of Al were $1674 \pm 1023 \text{ ng m}^{-3}$ and $827 \pm 285 \text{ ng m}^{-3}$ in the cold and warmer periods, respectively. However, some metals like Zn and Cd do not follow this seasonal trend, suggesting they have very different sources than the other trace metals (Table 3.1 and Fig. 3.3). Possible sources of trace metals can be determined by comparing their distribution to that of Al and assuming that Al mostly originates from crustal materials (mineral dust). Some of the

elements are highly correlated with Al, including V, Mn, Fe and Co (correlation coefficient > 0.96), indicating a common source of these elements, likely like for Al mineral dust. Cr, Ni and Pb on the other hand are less strongly correlated with Al (correlation coefficients are between 0.6 – 0.8), suggesting mixed origin, while Cu, Zn and Cd are poorly correlation with Al (correlation coefficient < 0.33) (Fig. 3.4). The high correlation between V, Mn, Fe and Co and Al suggests that these elements are coming primarily from mineral dust originating from the local soil and upper crust. The lower correlation of Al and Cr, Ni, Pb, Cu, Zn and Cd implies these elements may be contributed from anthropogenic sources in addition to mineral dust. These elements can come from vehicle emission (Cd, Pb, Zn and Cu) (Bilos et al., 2001) and road dust from non-exhaust activities (Ni, Cr, V, Zn, Ba) (Pant and Harrison, 2013), fertilizer (Cd, Cr, Pb, Ni and V)(Mortvedt, 1995) and industry (Pb, Ni, Cd, Cr, Cu, and Zn)(Chen et al., 2005). Biomass burning is another source of trace metals and can contain Mg, Al, Ca, Cr, Mn, Fe, Ni, Cu, Zn, and Ba. Considering the limited industrial and agriculture activities within the basin vehicle emissions, road dust and wood burning are the most likely sources, however, further studies need to be carried out in order to identify the specific sources within the basin.

Enrichment factors (EF) can be another index to evaluate the source of various elements in the aerosol. EF are described as:

$$EF = \frac{\left(\frac{Element}{Al}\right)_{aerosol}}{\left(\frac{Element}{Al}\right)_{crust}} \quad (1)$$

where $(Element/Al)_{aerosol}$ is the mass concentration ratio of the trace element to Al in

the collected aerosol samples and $(\text{Element}/\text{Al})_{\text{crust}}$ is the ratio in upper continental crust (Taylor and McLennan, 1985) (Fig. 3.5). EF that are equal to one indicate that the specific constituent in the aerosol originated primarily from the upper continental crust (e.g. mineral dust, soil). Higher EFs suggest additional sources, specifically from anthropogenic activities, biogenic materials or wildfires. We also calculated EF of TSP based on metal compositions in California soils and regional volcanic rocks (Table 3.2). Among the aerosol samples collected in Tahoe basin, V, Co, and Fe have low EFs with average values lower than two, indicative of a major mineral dust source, while the enrichment factor of Zn, Cu and Cd is higher than five, implying that anthropogenic inputs could have contributed to these elements. Generally, the overall metal EF of TSP collected in Tahoe are low typically less than 10 while in urban polluted areas EF are much higher (>100) and even in areas dominated by mineral dust like the Gulf of Aqaba EF are higher (Chen et al., 2008). The low EF suggest that anthropogenic impacts are low in this region.

We also applied a principal component analysis (PCA) for metal bulk composition in the TSP samples. The results are given in Table 3.3. Overall, the majority of the metals have a common source (or combination of sources) base on the high first factor loadings among them. The common source is likely mineral dust based on the low EF of the metals and also the high correlations between these metals to Al. High factor loading of Cd in factor 2 and Cu and Zn in factor 3 indicate these metals are dominated by distinct anthropogenic sources as mentioned previously.

3.3.2 Aerosol Soluble Fraction

When considering the nutrients and metals input to lakes the soluble fractions of these nutrients and metals is what affects the water chemistry and biology. The soluble fractions of the various trace metals are largely controlled by their solubilities. For example, although the average bulk concentration of Al is 1321 ng m^{-3} , average concentration of its soluble fraction is only 3.3 ng m^{-3} , which is 0.25% of the bulk concentration consistent with the low solubility of metals such as Al and Fe in mineral dust (Trapp et al., 2010). On the other hand, the average bulk concentration of Zn is 7.3 ng m^{-3} , 180 times smaller than Al bulk concentration. However, 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 fraction of most trace metals in the aerosol is higher during the warm period (Table 3.1 and Fig. 3.6). This could be due to changes in the dry deposition sources between seasons and source dependent solubility stemming from changes in composition. Alternatively it is possible that some chemical transformation in the aerosols which is seasonally dependent, like air humidity or temperatures affects the solubilities. More work has to be done to determine the causes of the seasonal variations in metal solubility in the Tahoe region.

Concentrations of soluble $\text{NO}_3^- + \text{NO}_2^-$, NH_4^+ and SRP are $1.75 \pm 0.94 \text{ } \mu\text{mol m}^{-3}$, $2.97 \pm 2.24 \text{ } \mu\text{mol m}^{-3}$ and $0.05 \pm 0.03 \text{ } \mu\text{mol m}^{-3}$, with a N to P ratio 117 ± 70 (Table 3.1). Major nutrients extracted from the aerosol samples also showed seasonal

variations (Fig. 3.6). Overall, $\text{NO}_3^- + \text{NO}_2^-$ is higher in cold period ($1.93 \pm 0.92 \mu\text{mol m}^{-3}$) than in the warm period ($1.51 \pm 0.95 \mu\text{mol m}^{-3}$); while NH_4^+ and SRP are higher during warm period ($4.78 \pm 1.93 \mu\text{mol m}^{-3}$ and $0.08 \pm 0.02 \mu\text{mol m}^{-3}$) than in the cold period ($1.68 \pm 1.39 \mu\text{mol m}^{-3}$ and $0.03 \pm 0.02 \mu\text{mol m}^{-3}$, respectively). Like for the metals the causes for the seasonal variability could be seasonal changes in the aerosol sources and/or processes in the atmosphere that impact the solubility of these nutrients. The annual average N:P ratio, 117, is higher than the Redfield ratio of 16N:1P that phytoplankton generally need for growth, this ratio is even higher, reaching an average of 141 during the cold period (October to April). This is consistent with the report of Mackey et al., (2013). The high N:P ratio could impact the N:P ratio in lake water thus influencing growth of phytoplankton in Lake Tahoe. Indeed a nutrient addition experiments indicated that phytoplankton tend to be P limited during October through April when atmospheric N:P is higher (Goldman et al., 1993). Our long-term aerosol nutrient concentration data may be one of the reasons that at least seasonally the lake is P limited.

3.3.3 Nutrients and Trace Elements Fluxes from TSP to the Lake

Particle counts and size distributions vary at different locations within the Tahoe basin, the distributions are also different close to the shoreline and at offshore sites (VanCuren et al., 2012). Accordingly, we cannot use a single deposition rate for TSP to the lake surface. Deposition of trace metals to the lake in this study was

calculated based on previous modeling results of TSP deposition fluxes in 2003. (Dolislager et al., 2012). We calculated deposition fluxes of each element to the lake by multiplying element ratios in collected TSP sample with the model derived TSP deposition. This calculation is based on the over simplified assumption that all elements have the same deposition velocity. In order to independently check the model derived TSP deposition rates, we also applied a deposition rate of 2 cms^{-1} for TSP (Jacobson, 2005), which has been used for estimating aerosol deposition rate to the lake (Mackey et al., 2013) previously as well as a rate that is ten times smaller 0.2 cms^{-1} . (Table 3.4). TSP deposition modeled by Dolislager et al. [2012] is much lower than the deposition rate obtained using 2 cms^{-1} and is even lower than the deposition calculated with a 0.2 cms^{-1} deposition rate.

3.3.4 Lake Water Trace Metal Concentrations

Trace metal concentrations in the lake water did not show seasonal or depth variations (Fig. 3.7). Average Lake water concentration of Al, Fe, Co, V, Mn, Ni, Pb, Cr, Cu, Zn and Cd are 20.2, 11.4, 0.05, 9.8, 1.4, 0.7, 0.04, 0.59, 1.2, 12.7 and 0.05 nmolkg^{-1} , respectively. While metal concentrations in the north and south lake water collected in 2009 and 2010 (Romero et al., 2013) are typically higher than those measured in this study, the middle water concentrations in Romero et al. [2013] are similar to those in our study. Trace metal concentrations in Lake Tahoe are listed in Table 3.5.

The lack of seasonal or depth variation in trace metal concentrations is probably because except for the relatively short summer season when lake surface temperatures are relatively high, the lake water is well mixed every several years (TERC (Tahoe Environmental Research Center), 2016). This mixing of lake water distributes the trace metals evenly with depth and the net input or uptake of these metals over the summer months is not sufficient to change the distribution and result in any seasonal variation. The contribution of atmospheric deposition of trace metals was then calculated by dividing TSP annual deposition of dissolved trace metal by the of dissolved trace element inventories in the up 50 m of Lake Tahoe. The contributions typically are low, ranging from 0.02% in V to 3.6% in Mn and are consistent with the lack of surface maxima at this site. Although overall atmospheric deposition contribution is 20% for phosphorous, 57% of nitrogen and 16% of fine particles in the lake (Sahoo et al., 2013), atmospheric TSP contributions are much smaller for the soluble metals.

3.3.5 Pb Isotopic Composition

In order to better understand possible sources of trace metal to Lake Tahoe, we have analyzed the Pb isotopic composition in aerosol, lake water, river water and ground water samples. $^{206}\text{Pb}/^{204}\text{Pb}$, $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ of 24 aerosol samples were determined. Fig. 3.8 shows the variations of these three Pb isotopic ratios. No seasonal trends in the Pb isotopic ratios are seen suggesting that the sources of Pb

likely do not vary seasonally. The average and standard deviation of $^{206}\text{Pb}/^{204}\text{Pb}$, $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ are 18.11 ± 0.12 , 1.162 ± 0.006 and 2.428 ± 0.006 , respectively. There is also no seasonal variation in the depth distribution of Pb isotopes in lake water, consistent with the distribution of metal concentrations and the mixing of lake waters (Fig. 3.9). The average and standard deviation of $^{206}\text{Pb}/^{204}\text{Pb}$, $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ are 19.13 ± 0.15 , 1.199 ± 0.003 and 2.453 ± 0.003 , respectively. Annual atmospheric Pb input contributes only 2.8% to the upper 50m depth Pb inventory. Even when we considered a mixed layer depth of 20m based on the thermocline for the stratified period (Coats et al., 2006), we obtain a contribution from deposition of up to 3.5% since the stratification didn't last more than half a year. In either case the Pb from aerosols has little 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 sources. $^{206}\text{Pb}/^{204}\text{Pb}$, $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ in seven of the major rivers in Tahoe basin are 19.00 ± 0.27 , 1.215 ± 0.016 and 2.474 ± 0.017 , and ground water samples $^{206}\text{Pb}/^{204}\text{Pb}$, $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios are 18.87 ± 0.27 , 1.201 ± 0.012 and 2.459 ± 0.010 . We also assembled published Pb isotope ratios for additional potential sources in the region (Cousens et al., 2008; Cousens et al., 2011). We plotted all Pb isotope data in a $^{206}\text{Pb}/^{207}\text{Pb}$ vs $^{208}\text{Pb}/^{207}\text{Pb}$ tri-isotope plot (Fig. 3.10). The Pb isotopic composition in lake water are similar to those of ground water and some of the river water samples, suggesting that ground water and river water could be the major Pb sources to the

lake. In order to estimate the relatively contribution of soluble Pb from ground water, river water and atmospheric deposition, we used average ground water and river water Pb concentrations (0.133 and 3.43, respectively) and a ground water annual discharge $5.65 \times 10^7 \text{ m}^3$ per year (Thodal, 1997) and annual river discharge $3.83 \times 10^8 \text{ m}^3$ per year (Truckee River Chronology) to estimate contributions from the different sources. The annual Pb loads from rivers, ground water and atmospheric deposition were then estimated as 40.1, 10.5 and 5.5 kg, respectively. As a result, atmospheric deposition contributes only about 10% of Pb, this is also consistent with our Pb concentrations and isotope ratios in the lake.

3.4 Conclusion

Our results indicate that the TSP concentrations in the air in the Tahoe basin are higher during Oct – April than during the warmer months. Trace metal concentrations in aerosol samples are also higher in the cold period, however, trace metal solubilities in aerosol samples are higher during warm period. Base on the correlation between element and Al, element enrichment factors and PCA analyses, we can identify that most of the elements are dominated by mineral dust source, while Zn, Cu and Cd are contributed more by anthropogenic inputs. Overall based on EF the trace metals in the TSP in the Tahoe Basin are mostly of natural sources with limited anthropogenic contribution. Among major nutrient soluble concentrations in aerosols, $\text{NO}_3^- + \text{NO}_2^-$ is higher during cold period while NH_4^+ and SRP are higher in

warm period. Typically trace metal concentrations and Pb isotopic ratios are similar through whole water column, this implies that TSP is not a major source of soluble metals to the lake. Based on our estimation using Pb isotope ratios in aerosols, rivers and groundwater, TSP only contribute about 10% of soluble Pb assuming rivers and groundwater are the only other two sources.

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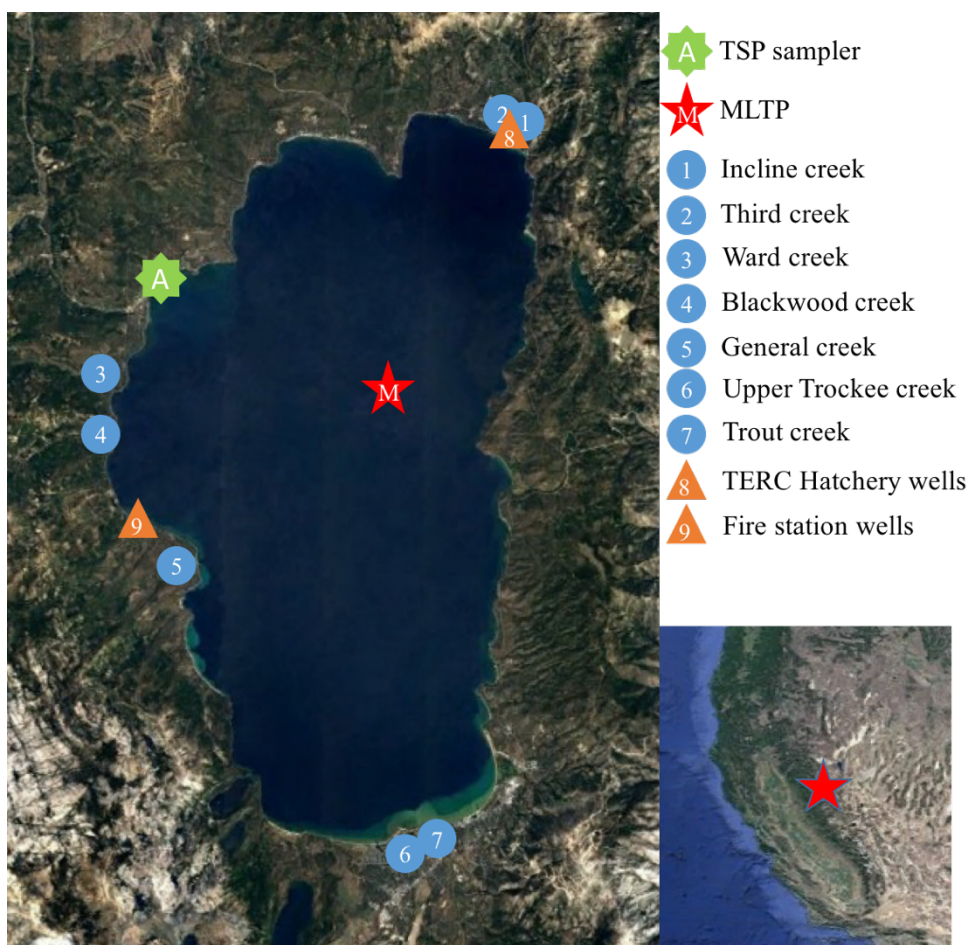


Figure 3.1 Sampling locations

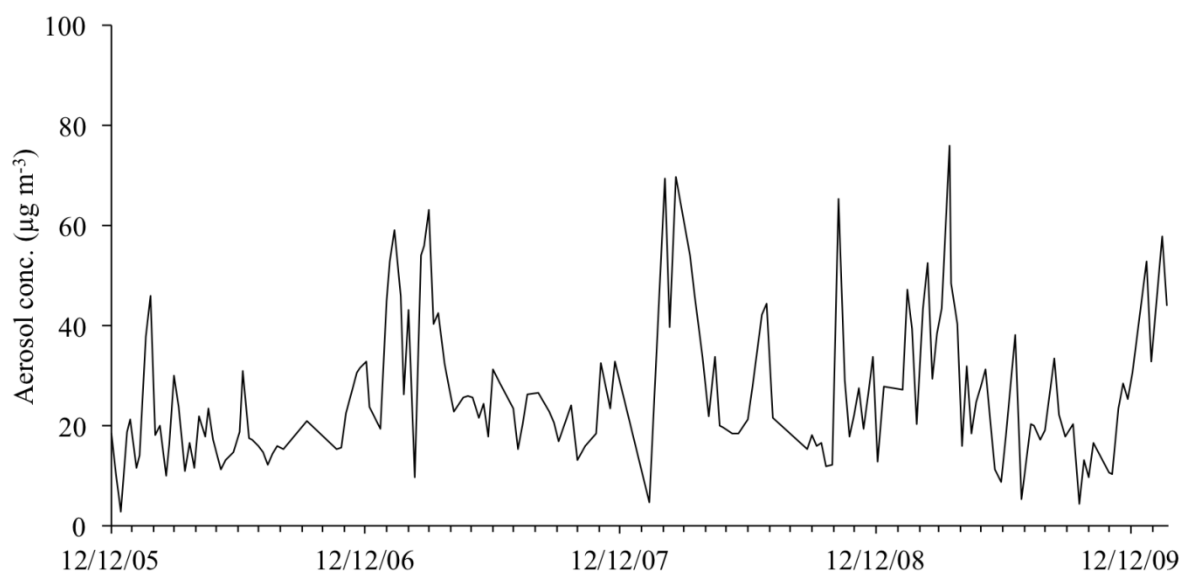


Figure 3.2 Aerosol concentration ($\mu\text{g m}^{-3}$) records from 12/12/2015 to 2/2/2010

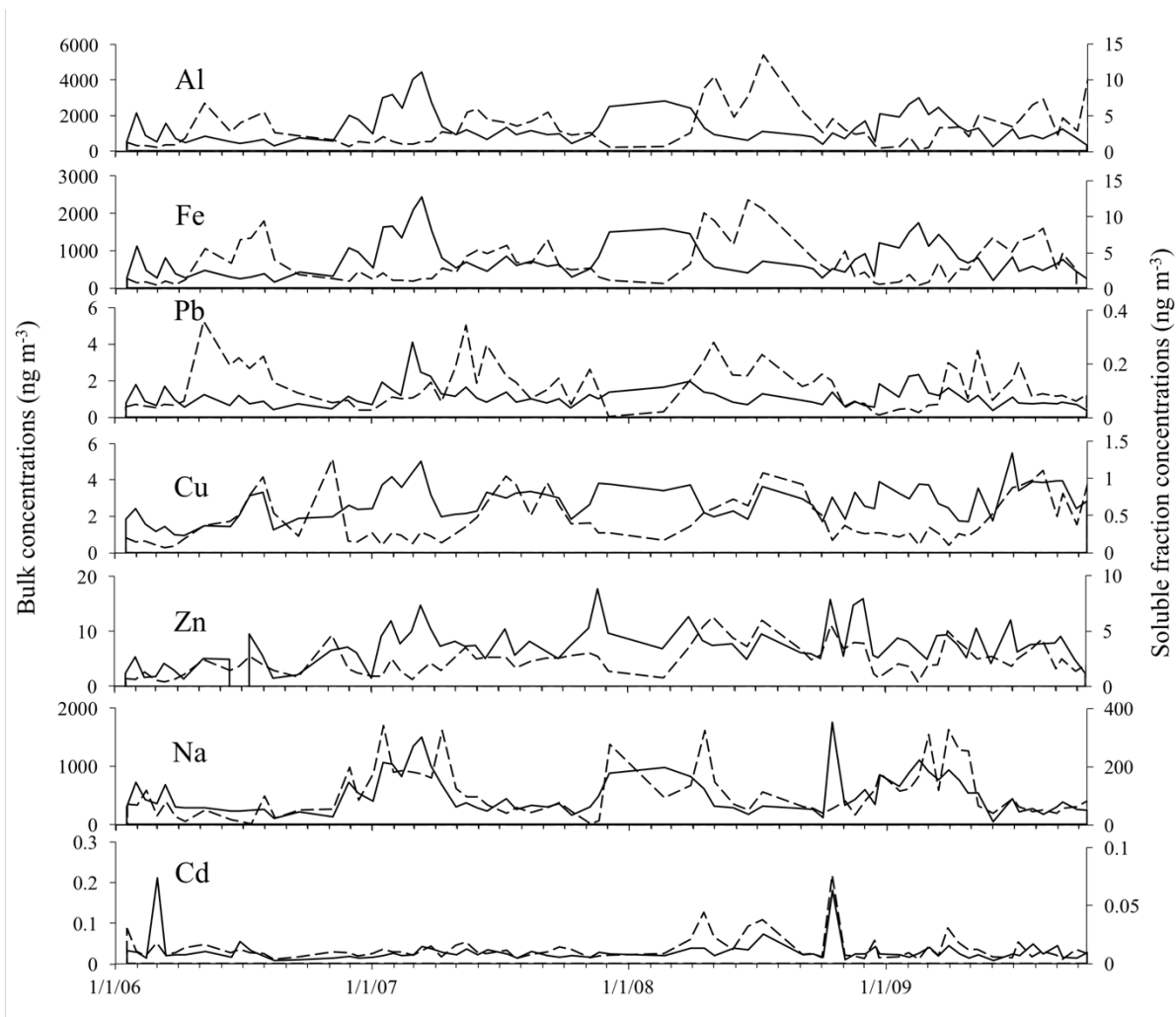


Figure 3.3 Trace metal bulk (solid lines) and soluble fraction (dash lines) concentrations in TSP (ng m^{-3}), the concentrations were normalized to air volume.

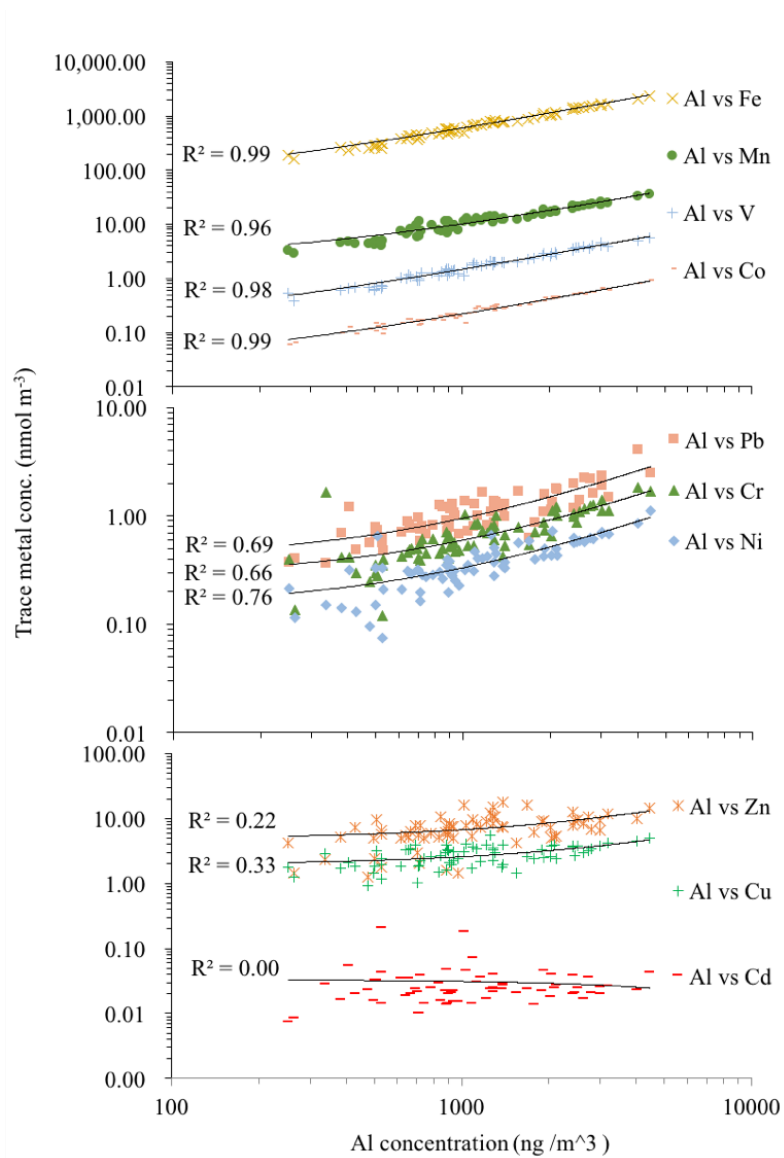


Figure 3.4 Linear relationships of trace metals to Al

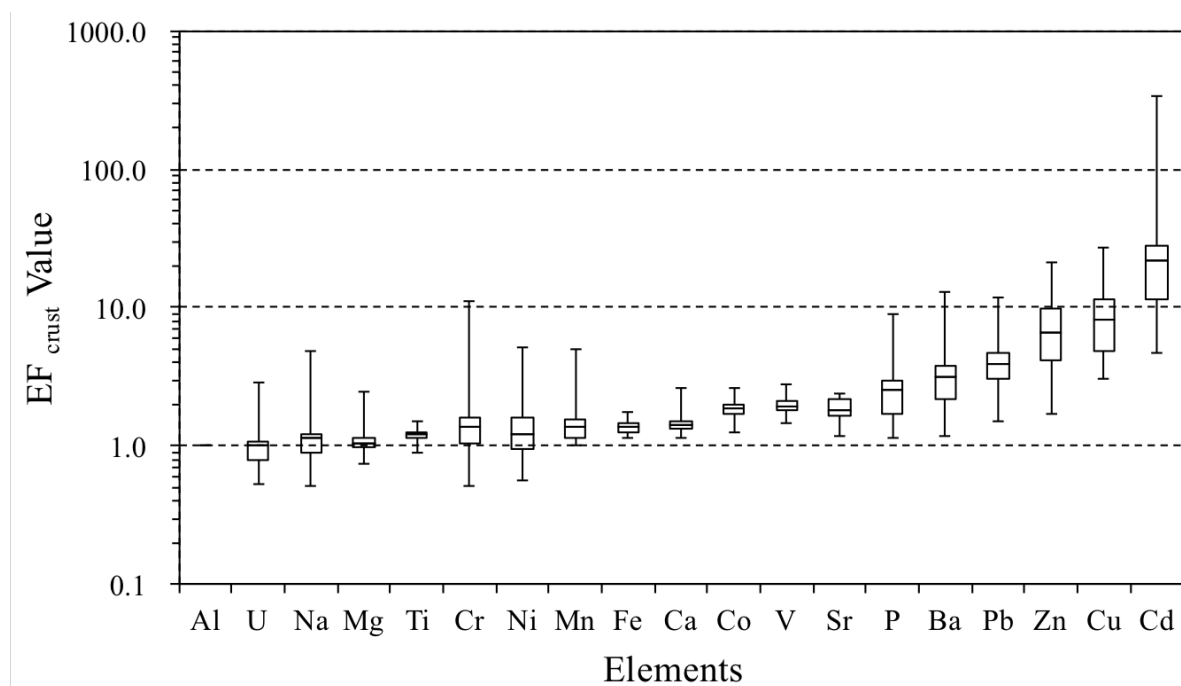


Figure 3.5 Upper crust enrichment factor values for various trace elements in aerosols collected in Tahoe Basin. The bottom and the top of each box are located at the 25 and 75 percentiles, central horizontal line is drawn at the sample median.

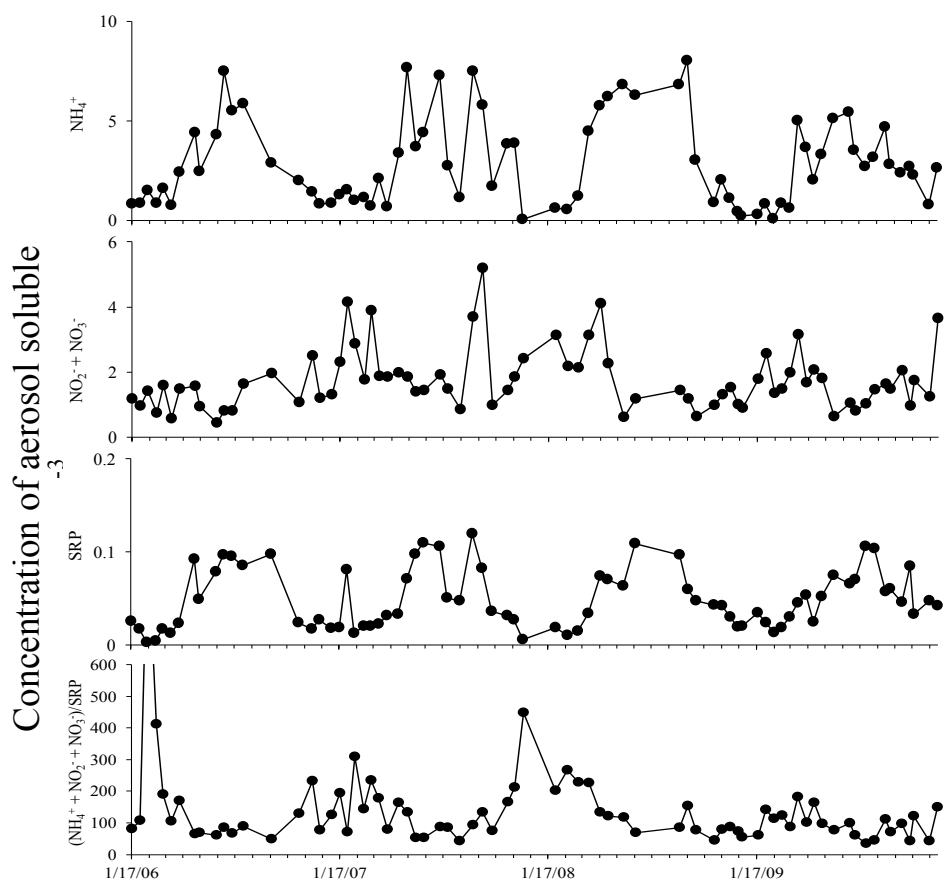


Figure 3.6 NH_4^+ , $\text{NO}_2^- + \text{NO}_3^-$, SRP and $(\text{NH}_4^+ + \text{NO}_2^- + \text{NO}_3^-)/\text{SRP}$ ratio in aerosol soluble fraction between 2006 to 2009

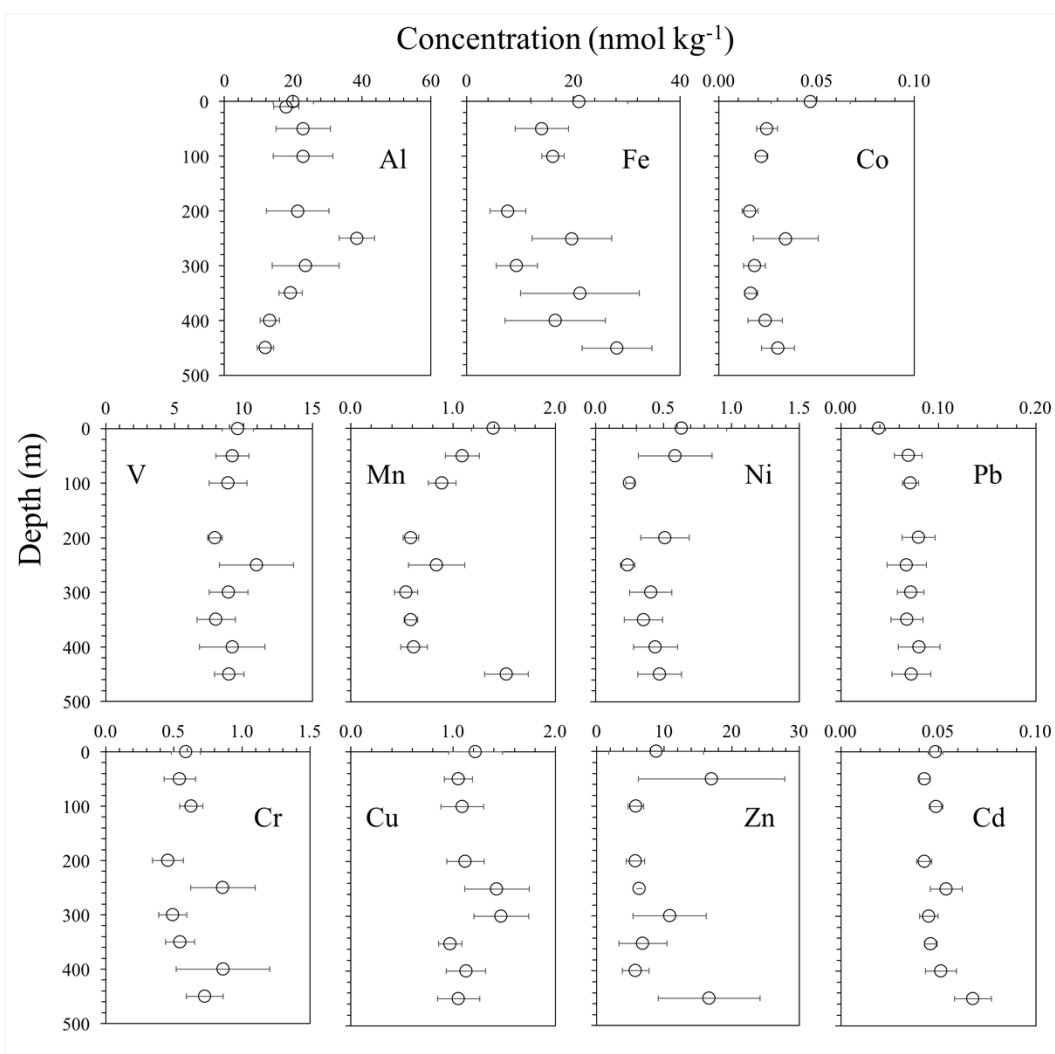


Figure 3.7 Trace metal concentration depth profiles. Samples were collected at MLTP at mid-lake. Mean values and one standard deviations are from seven depth profiles collected during Spring 2013 and Summer 2016.

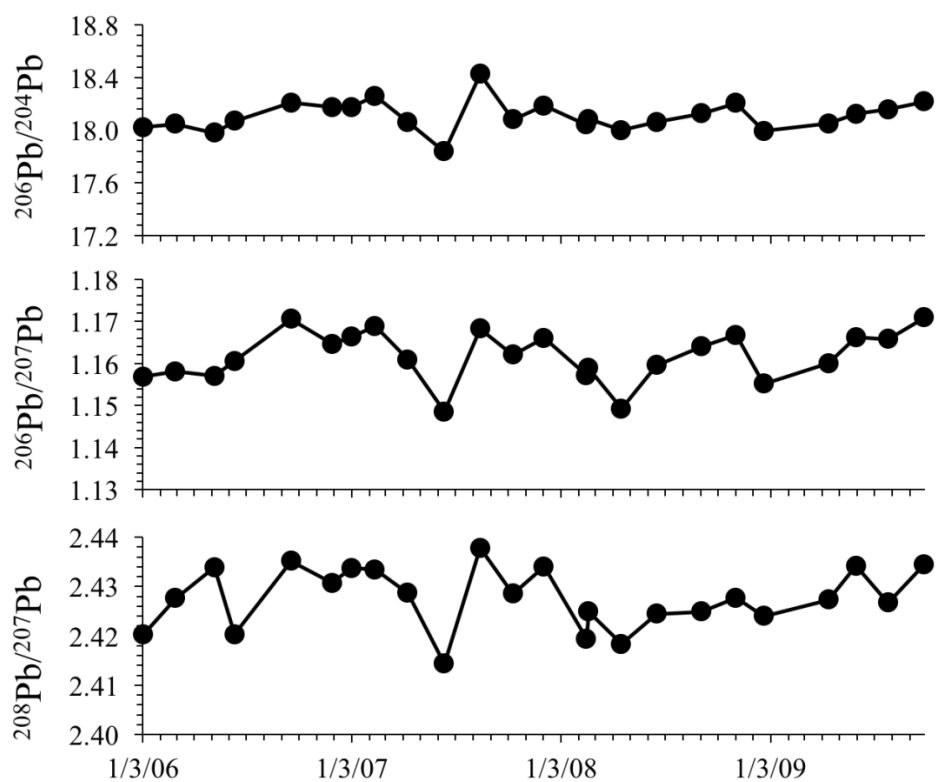


Figure 3.8 $^{206}\text{Pb}/^{204}\text{Pb}$, $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ in 24 TSP samples collected during Jan 2006 to Sep 2009.

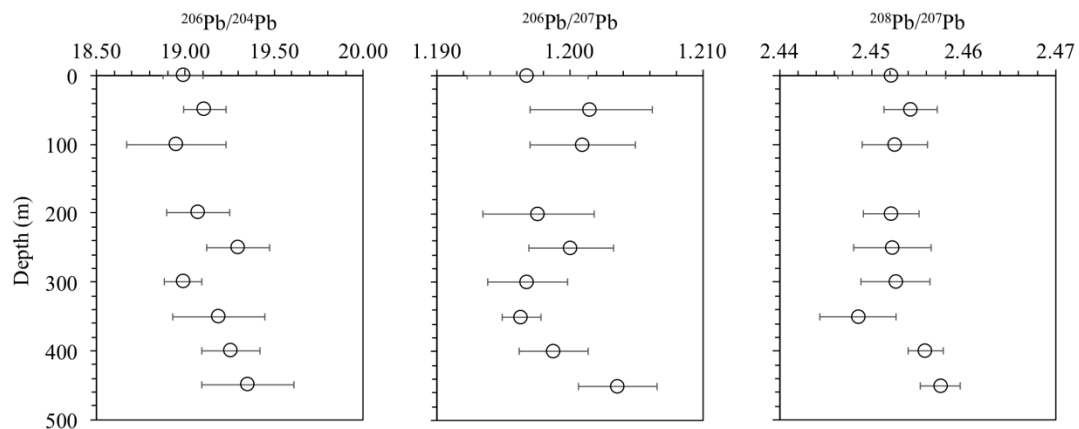


Figure 3.9 $^{206}\text{Pb}/^{204}\text{Pb}$, $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ depth profiles.

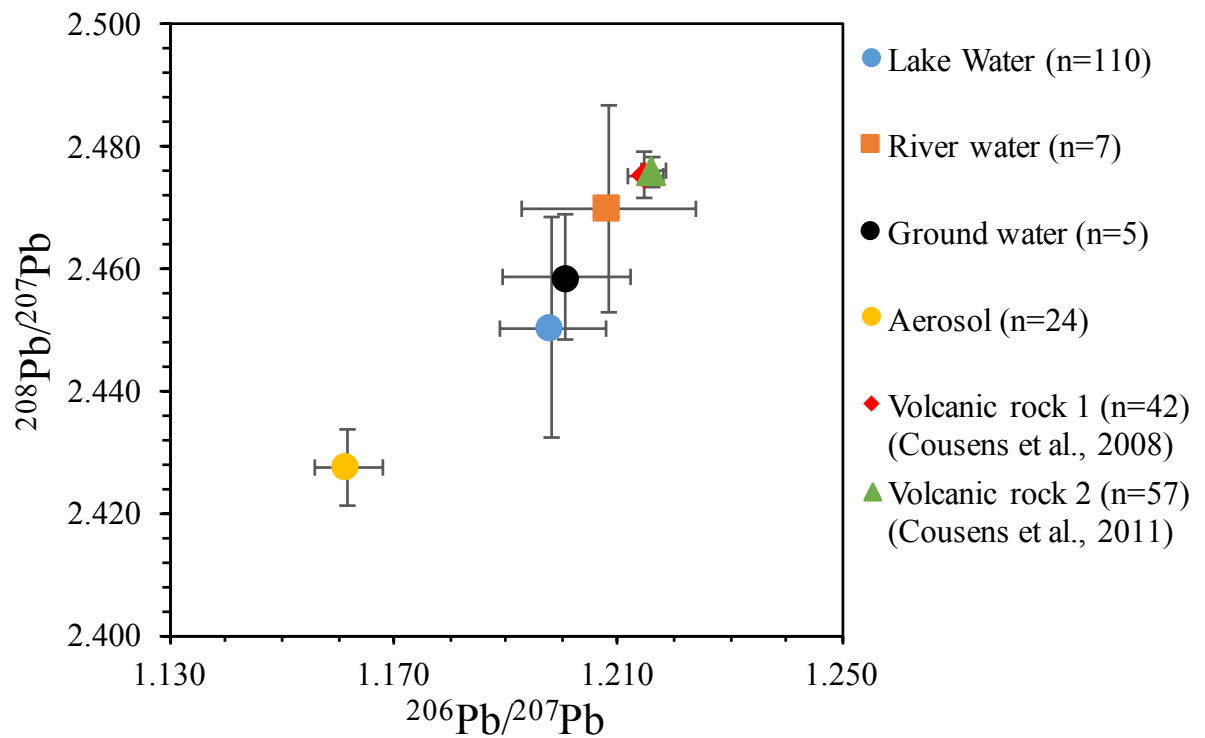


Figure 3.10 Triple-isotope plot of Pb in lake water, river water, ground water, aerosol and volcanic rocks (1 and 2 are mean values of Pb isotopes from (B. Cousens et al., 2008) and (B.L. Cousens et al., 2011), respectively.). Numbers in parentheses are data sizes. Note the river water ratio is an average of weighted ratios base on their individual annual discharges.

Table 3.1 Annual, May to September and October to April of aerosol total suspended particles ($\mu\text{g m}^{-3}$), nutrients (nmol m^{-3}) and trace metals (ng m^{-3}) bulk and and soluble fraction concentrations.

	May to September		October to April		Annual	
	Bulk	Soluble	Bulk	Soluble	Bulk	Soluble
TSP	20.6 ± 7.6	1.51 ± 0.95	29.8 ± 16.1	1.93 ± 0.92	26.3 ± 14.2	1.75 ± 0.94
NO ₃ ⁻ +NO ₂ ⁻		4.78 ± 1.93		1.68 ± 1.39		2.97 ± 2.24
NH ₄ ⁺		0.08 ± 0.02		0.03 ± 0.02		0.05 ± 0.03
SRP		83 ± 29		141 ± 80		117 ± 70
N:P		5.1 ± 2.4		2.1 ± 2.0		3.3 ± 2.6
Al	827 ± 285	5.8 ± 2.5	1674 ± 1023	2.0 ± 1.7	1321 ± 902	3.6 ± 2.8
Fe	527 ± 184	82 ± 55	945 ± 518	70 ± 37	771 ± 486	75 ± 45
Ca	422 ± 166	61 ± 30	898 ± 371	140 ± 96	699 ± 471	107 ± 107
Na	282 ± 98	14 ± 8	672 ± 156	10 ± 6	509 ± 348	12 ± 7
Mg	159 ± 53	0.10 ± 0.04	286 ± 56	0.05 ± 0.10	233 ± 138	0.07 ± 0.09
Ti	48 ± 17	—	92 ± 13	—	74 ± 49	—
Ba	22 ± 13	—	28 ± 13	—	25 ± 13	—
Mn	9.7 ± 3.3	2.5 ± 3.2	14.8 ± 8.5	1.1 ± 0.7	13 ± 7	1.7 ± 2.2
Sr	5.9 ± 2.5	0.5 ± 0.3	15.9 ± 10.3	0.4 ± 0.2	12 ± 9	0.4 ± 0.2
Zn	6.8 ± 2.4	2.7 ± 1.2	7.7 ± 4.1	2.2 ± 1.4	7.3 ± 3.6	2.4 ± 1.4
Cu	2.9 ± 1.0	0.7 ± 0.3	2.7 ± 1.0	0.3 ± 0.2	2.8 ± 1.0	0.4 ± 0.3
V	1.30 ± 0.46	0.088 ± 0.039	2.32 ± 1.38	0.020 ± 0.020	1.9 ± 1.2	0.049 ± 0.045
Pb	0.91 ± 0.28	0.16 ± 0.08	1.29 ± 0.71	0.08 ± 0.06	1.13 ± 0.60	0.11 ± 0.08
Cr	0.56 ± 0.18	0.03 ± 0.02	0.8 ± 0.42	0.034 ± 0.043	0.70 ± 0.36	0.032 ± 0.035
Ni	0.34 ± 0.13	0.028 ± 0.011	0.43 ± 0.22	0.013 ± 0.007	0.39 ± 0.19	0.019 ± 0.012
Co	0.20 ± 0.07	0.017 ± 0.005	0.35 ± 0.21	0.009 ± 0.005	0.28 ± 0.18	0.013 ± 0.006
U	0.028 ± 0.010	0.0013 ± 0.0005	0.043 ± 0.025	0.0004 ± 0.0004	0.037 ± 0.021	0.0008 ± 0.0007
Cd	0.027 ± 0.015	0.012 ± 0.008	0.033 ± 0.038	0.012 ± 0.008	0.031 ± 0.031	0.012 ± 0.008

Table 3.2 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), California Soil (EF soil) and the Volcanic Rocks for Trace Elements in Aerosols Collected in This Study.

	Element/Al ratio			Calculated Enrichment Factors			Reference
	Upper crust, Taylor and McLennan 1985	California soil, Bradford et al. 1996	Lake Tahoe–Reno region volcanic rocks, Brian Cousens et al. 2008	EF upper crust	EF California soil	EF volcanic rocks	Gulf of Aqaba, Chen et al., 2008. EF upper crust
Al	1	1	1	1	1	1	1
Fe	0.44	0.51	0.42	1.35	1.17	0.72	1.16
Na	0.36	0.22	0.20	0.97	1.61	1.42	4.13
Mg	0.17	0.14	0.45	1.07	1.33	0.41	1.57
Ca	0.37	0.20	0.79	1.41	2.65	0.66	8.86
Ti	0.04	0.06	0.09	1.20	0.87	0.66	–
P	8.7	5.6	13.3	2.11	4.42	1.88	10.3
Mn	7.5	8.8	13.8	1.33	1.13	0.72	1.97
Ba	6.8	7.0	10.9	2.88	2.79	1.78	–
Sr	4.4	1.8	8.3	1.98	5.00	1.05	3.1
Zn	0.88	2.04	–	7.42	3.20	–	16.7
V	0.75	1.53	2.04	1.96	0.96	0.72	6.88
Cr	0.44	1.67	0.83	1.29	0.34	0.68	6.23
Cu	0.31	0.39	–	8.18	6.33	–	10.5
Ni	0.25	0.78	0.30	1.30	0.40	1.05	11.2
Pb	0.25	0.33	0.09	3.87	2.88	10.04	28
Co	0.12	0.20	–	1.80	1.06	–	2.44
U	0.03	0.06	–	0.86	0.43	–	–
Cd	0.0012	0.0049	–	17.14	4.29	–	97.3

Table 3.3 The rotated principal component matrix of annual TSP deposition of metals in Lake Tahoe, factor loading 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
Cu	0.656	0.121	0.633
Zn	0.543	0.408	0.532
Sr	0.963	-0.139	-0.131
Cd	0.022	0.918	-0.300
Ba	0.732	0.021	0.248
Pb	0.857	-0.041	-0.216
U	0.939	0.200	-0.024

Table 3.4 Calculated fluxes of TSP (kg), nutrients (kmole) and trace metals (kg) in Summer/Fall, Winter/Spring and annual periods to Lake Tahoe, base on TSP annual deposition from Dolislager et al., 2012 and particle deposition rate 0. 2cms⁻¹ and 2cms⁻¹.

	June to November			December to May			Annual		
	Dolislager et al., 2012	0.2cm/s	2cm/s	Dolislager et al., 2012	0.2cm/s	2cm/s	Dolislager et al., 2012	0.2cm/s	2cm/s
TSP	3x10 ⁵	4.1x10 ⁵	4.1x10 ⁶	2.8x10 ⁵	4.1x10 ⁵	4.1x10 ⁶	5.8x10 ⁵	8.2x10 ⁵	8.2x10 ⁶
NO ₃ ⁻ + NO ₂ ⁻	22	13	131	18	15	147	40	28	278
NH ₄ ⁺	58	34	343	19	16	157	77	50	500
SRP	1.0	0.6	6.0	0.3	0.3	2.5	1.3	0.8	8
Al	63	89	891	23	32	319	86	121	1210
Fe	72	102	1020	22	31	315	94	133	1335
Ca	971	1373	13733	758	1071	10712	1729	2444	24445
Na	841	1189	11889	1375	1944	19435	2216	3132	31324
Mg	166	235	2349	106	150	1504	273	385	3853
Ti	1.2	1.8	18	0.6	0.8	7.8	1.8	2.5	25
Mn	47	66	663	24	33	333	71	100	997
Sr	12	17	168	8	12	117	20	29	285
Zn	78	111	1105	39	56	557	118	166	1662
Cu	19	26	263	4.7	6.7	67	23	33	330
V	2.1	2.9	29	0.5	0.7	7	2.6	3.7	37
Pb	3.6	5.1	51	1.9	2.6	26	5.5	7.8	78
Cr	1.1	1.5	15	0.5	0.7	7	1.6	2.3	23
Ni	0.7	1.0	9.6	0.3	0.4	4.1	1.0	1.4	13.8
Co	0.4	0.6	5.8	0.2	0.3	2.9	0.6	0.9	8.7
U	0.03	0.04	0.40	0.01	0.01	0.15	0.04	0.05	0.55
Cd	0.3	0.5	4.8	0.2	0.3	3.5	0.6	0.8	8.3

Table 3.5 Trace metal concentrations of Lake Tahoe water. Units are nmol L⁻¹.

	This study	North lake, Romero et al., 2013	South lake, Romero et al., 2013	Mid lake, Romero et al., 2013	Mid lake, Chang et al., 1992
Cd	0.05	0.04	0.04	0.08	—
Pb	0.04	0.09	0.25	0.01	—
Al	20.2	25.8	48.5	5.6	—
V	9.8	12.5	10.5	13.0	—
Cr	0.59	—	—	—	—
Mn	1.4	3.3	9.6	0.8	—
Fe	11.4	11.1	135	2.3	22.8
Co	0.05	0.10	0.11	0.02	—
Ni	0.7	1.0	3.5	0.7	—
Cu	1.2	4.1	10.9	0.8	8.9
Zn	12.7	—	—	—	—

Table 3.6 Trace metal inventories per square meter in 0-50m water column, TSP trace metal fluxes and flux to inventory ratios. Units of trace metal inventories and fluxes are μg

	Metal inventory	TSP metal flux	Flux to inventory
	0-50m	Annual	Annual
Cd	276	1.2	0.4%
Pb	391	11	2.8%
Al	27286	171	0.6%
V	25002	5.2	0.02%
Cr	1550	3.2	0.2%
Mn	3968	141	3.6%
Fe	32053	189	0.6%
Co	135	1.2	0.9%
Ni	1991	1.9	0.1%
Cu	3859	47	1.2%
Zn	41110	235	0.6%

CONCLUSIONS

In this thesis 3 studies were presented that show the diverse and complex impacts of dry atmospheric deposition on marine biology and seawater chemistry contributing to the increasing scientific body of work that illustrates the importance and close interactions between the atmosphere and hydrosphere. These studies also emphasized the importance of understanding controls on aerosol chemistry and solubility, as well as time series data on dry atmospheric deposition at various regions, as directions for future studies.

APPENDICES

Chapter 1

A1 Model supporting information

In the supporting information, we provide detailed information regarding the calculation of the amount of dust added in the dust bioassay treatments and on our modeling of aeolian fluxes of phosphate and iron.

Dust addition in the bioassay incubations

The amount of dust added to the low dust bioassays (0.03mg in 500ml) was calculated based on the annual average dust deposition of $10 \text{ g m}^{-2} \text{ yr}^{-1}$ at the study area mixed into a 10m water column (mixing depth) over 20 days (residence time). That is 10g into 10,000 L or 1mg of dust deposited into 1L over 365 days and $\sim 0.055 \text{ mg}$ per liter over 20 days of deposition. We added 0.03mg of dust into 500ml seawater (0.06 mg/L) slightly more than the average deposition over 20 days.

For the high dust additions, we assumed a deposition rate of $150 \text{ g m}^{-2} \text{ yr}^{-1}$ (this is 15 times the average and is seen in extreme dust storm events); hence we added 0.5mg (15 times 0.03mg).

Modeling of Aeolian Fluxes of P and Fe

Phosphorus was modeled following *Mahowald et al.* [2008] with some small differences, which we describe here. Dust emissions, concentrations and AOD are tuned to match observations following the methodology of *Albani et al.* [2014]. Preindustrial

dust is likely to be lower in most regions, and the deposition ratios from *Mahowald et al.* [2010] are used to tune the emissions in different source areas to represent these changes. Industrial combustion sources of P in both the fine and coarse fraction are modeled following *Mahowald et al.* [2008], which uses emission factors and the spatially explicit emissions from the Speciated Emission Wizard (SPEW) [*T Bond et al.*, 2007; *T C Bond et al.*, 2004; *Mahowald et al.*, 2008]. For preindustrial times we assume 10% of industrial emissions in the current climate occur in preindustrial time periods. Biomass burning aerosols are assumed to have a phosphorus to black carbon (P/BC) ratio of 0.0029 and 0.02 in fine and coarse modes respectively, with 20% of the BC occurring in the coarse mode, based on observations from the Amazon [*Mahowald et al.*, 2008; *Mahowald et al.*, 2005]. Biomass burnings emission from GFEDv3 are used, but tuned to better match observations of aerosols using the methods of Ward et al. [2012], as described in the main text for N emissions (using exactly the same methodology and datasets for P, Fe and N). Biofuel emissions are based on the same emission factors of P/BC as for biomass burning, since there is no data, and the biofuels emission map of *Lamarque et al.* [2010] are used. We modeled these emissions with the same mechanism as the dust, using 4 size bins. For preindustrial times we assume 10% of emissions of P in biofuels as the current climate. P in primary biogenic particles was modeled as a function of simulated above ground biomass in *Mahowald et al.* [2008], while here we wish to use more observation-based estimates and thus use the satellite retrieved leaf area indices [*Zhu et al.*, 2013]. LAI and above ground vegetation are roughly linear in relationship (e.g. [*Madugundu et al.*, 2008]), although they may not be linear across all ecosystems. We adjust the emission rate of primary biogenic particles to match the observation that

approximately 30% of the aerosol mass less than 10 μm over the Amazon is primary biogenic particles (similar to *Mahowald et al.* [2008]), and obtain a similar global emission rate as seen in *Mahowald et al.* [2008], although there is more mass in higher latitudes than in that study. This is consistent with P data in high latitudes, so this is likely to be an improvement in our simulation compared to *Mahowald et al.* [2008]. We distribute the P throughout the 4 bins, using a similar size distribution as dust. Assuming a similar size distribution as dust is a large assumption, but we have no other information. We do not include a change in leaf area index between preindustrial and current, as this should be a small change, and is not well constrained. Sea salts are a small source of P to long range transport [*Graham and Duce*, 1979; *Mahowald et al.*, 2008], so we make a simplifying assumptions that P concentrations in sea water are $8\text{e-}8$ kgP/kg sea salts and use the prognostic sea salt algorithm in the CAM [*Mahowald et al.*, 2006]. Volcanoes emit P aerosols as well, and we use the same methodology as in *Mahowald et al.* [2008], based on emissions of sulfur from volcanoes in the fine mode. Following *Mahowald et al.* [2008], dust sources of P are assumed to have a lower solubility than other sources (10% vs. 50%).

Iron is modeled following *Luo et al.* [2008] and consistent with N and P, as much as possible. Dust is assumed to contain 3.5% iron on average. Biomass burning is assumed to have a ratio of 0.2 gFe/gBC in the fine mode, and 1.4 gFe/gBC for the coarse mode [*Luo et al.*, 2008]. Industrial sources of Fe are emitted following *Luo et al.* [2008]. Changes in dust, biomass burning and industrial sources of Fe are done in the same manner as P. Not all Fe is equally soluble [*Baker et al.*, 2006; *Mahowald et al.*, 2009; *Sedwick et al.*, 2007; *Sholkovitz et al.*, 2009]. Combustion sources of Fe are thought to be

more soluble than dust sources (4% vs 0.4%) [*Luo et al.*, 2008]. In addition, Fe can be processed in the environment by acids (e.g. [*Mahowald et al.*, 2009]). Here we use the solubility calculations conducted in *Luo et al.* [2005] and *Mahowald et al.* [2009] for preindustrial and current conditions, and apply them to simulations of dust from the CAM4 model. This will cause a slight inconsistency between the solubility calculations of Fe and the distribution, which, due to not having a set of simulations with soluble Fe calculated, is currently unavoidable. Because of the uncertainties in the exact processes causing solubilization, the inconsistency in model simulations is not likely to be the largest uncertainty in our estimates. The simulations of N and P used here are consistent with the simulations included in *Brahney et al.* [2015], and the N and P ratios are compared to available observations in that study.

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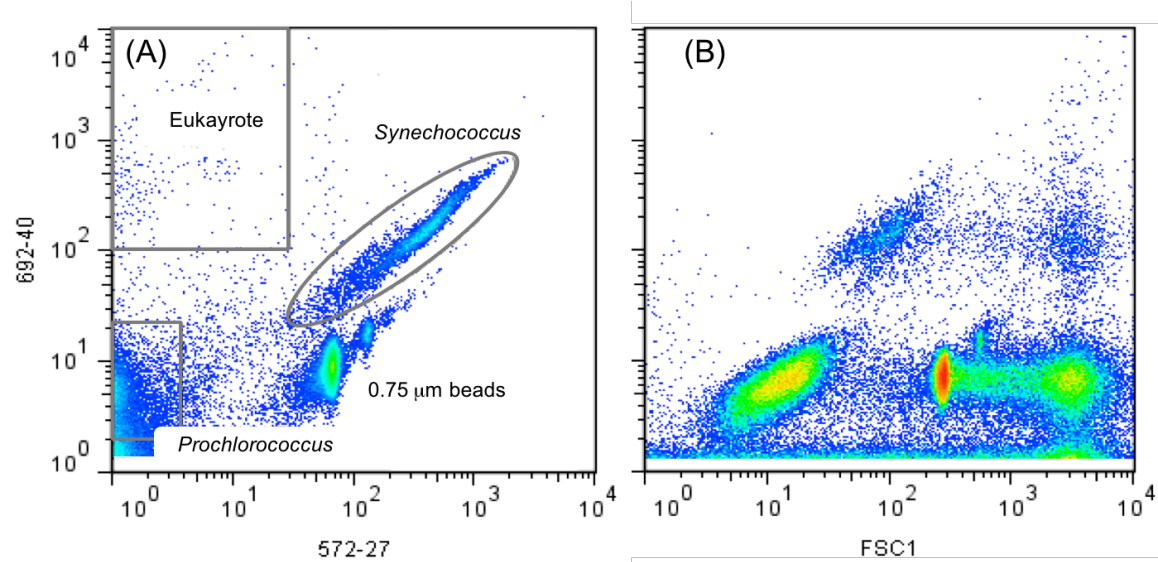


Figure S1.1 (A) Distributions of *Prochlorococcus*, *Synechococcus* and picoeukaryote based on red fluorescence (692/40nm) and orange fluorescence (572/27nm). (B) Cell distribution based on red fluorescence (692/40nm) and forward scatter.

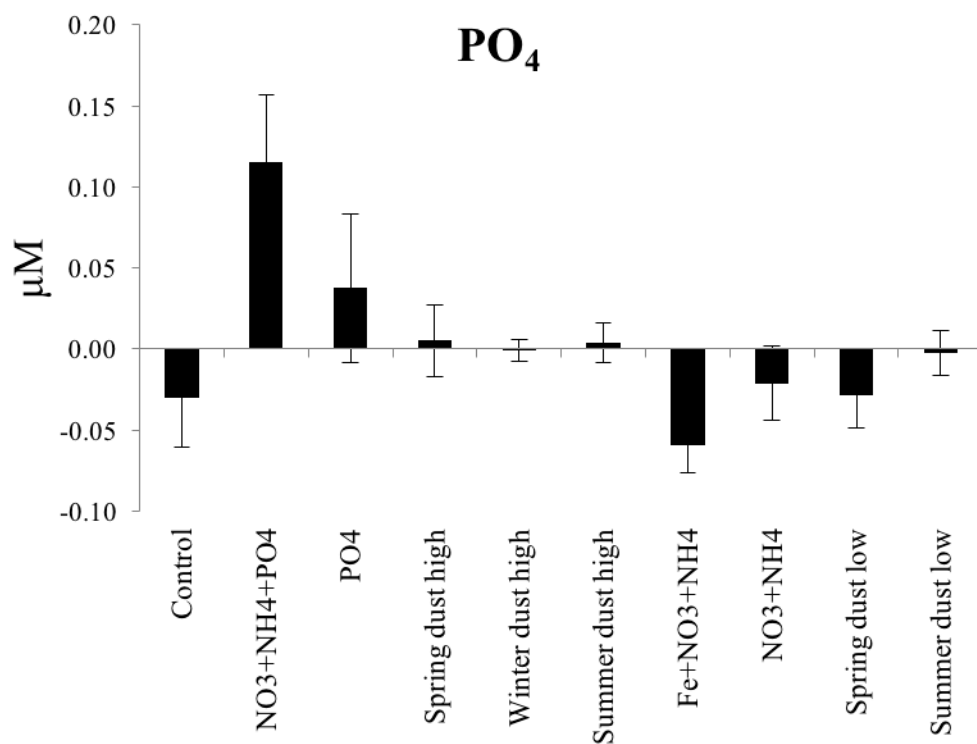


Figure S1.2 Phosphate drawdown in the various treatments, calculated by subtracting concentrations in day 3 from those of day 0. Positive values indicate that P was consumed.

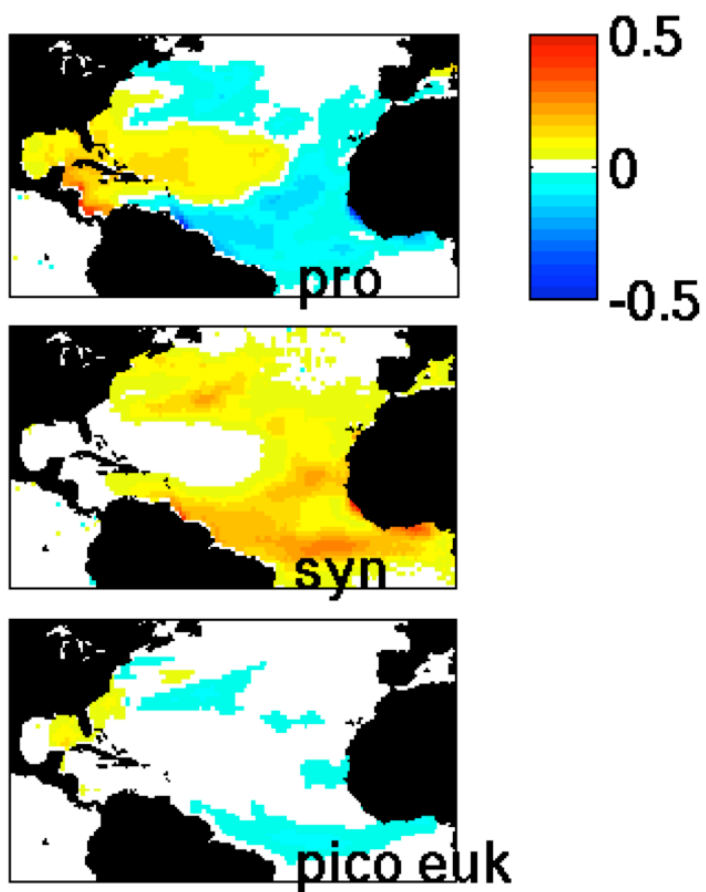


Figure S1.3 Difference in biomass (mg Cm⁻³) between EXP2 described in the main manuscript and a model run with the same parameters but with only Fe input from dust. Note that the scale here is one tenth that of the scale in Figures 5D, E and F in the main manuscript.

Metal	Detection limit*	Recovery (%)	CASS5 analyses**		SAFe-S (n=6)***	
			Measured	Certified	Measured	consensus
			av $\pm$ SD	av $\pm$ SD	av $\pm$ SD	
Mn	0.023	102 $\pm$ 2	38.2 $\pm$ 1.6	46.6 $\pm$ 3.6	0.84 $\pm$ 0.05	0.79 $\pm$ 0.06
Fe	0.74	103 $\pm$ 1	26.4 $\pm$ 0.7	25.1 $\pm$ 2.0	BD	0.093 $\pm$ 0.008
Co	0.005	101 $\pm$ 2	1.4 $\pm$ 0.1	1.6	0.003 $\pm$ 0.002	0.005 $\pm$ 0.001
Ni	0.11	102 $\pm$ 0	5.1 $\pm$ 0.2	5.5 $\pm$ 0.4	2.45 $\pm$ 0.17	2.28 $\pm$ 0.09
Cu	0.013	101 $\pm$ 1	5.8 $\pm$ 0.2	5.8 $\pm$ 0.4	0.37 $\pm$ 0.02	0.52 $\pm$ 0.05
Cd	0.0004	99 $\pm$ 0	0.22 $\pm$ 0.01	0.19 $\pm$ 0.15	0.0017 $\pm$ 0.0008	0.0011 $\pm$ 0.0003
Pb	0.0009	100 $\pm$ 2	0.042 $\pm$ 0.002	0.053 $\pm$ 0.010	0.044 $\pm$ 0.001	0.0480 $\pm$ 0.0022

* Detection limit calculated as 3 $\times$ standard deviation of the blank.

** Results from multiple analyses over the period samples were analyzed.

*** w/o UV treatments

Table S1.1 Detection limit and CRM analyses. Units are nmol/kg if not mentioned otherwise.

Table S1.2 Elemental ratios of C:N:P:Fe used for the model were based on mid-range values from aggregated laboratory and field collected data for different phytoplankton functional groups as listed in this table.

Functional group	Species	Strain or location	C:N	C:P	N:P	Fe:C (μmol/mol)	Condition	Reference
Coccolithophore	<i>Emiliana huxleyi</i>					4.1	Total[Fe]=1.2	Sunda and Huntsman 1995
Coccolithophore	<i>Emiliana huxleyi</i>					22.2	Total[Fe]=101	Sunda and Huntsman 1995
Coccolithophore	<i>Emiliana huxleyi</i>	371	6.69	117	17.5		20C, low light	Feng 2008
Coccolithophore	<i>Emiliana huxleyi</i>	371	6.86	108	15.7		24C, low light	Feng 2008
Coccolithophore	<i>Emiliana huxleyi</i>	371	6.11	91	15		20C, high light	Feng 2008
Coccolithophore	<i>Emiliana huxleyi</i>	371	5.83	82	14.2		24C, high light	Feng 2008
Coccolithophore	<i>Emiliana huxleyi</i>		7.1					Pedrotti et al., 2012
Coccolithophore	<i>Calcidiscus leptoporus</i>		5.9					Pedrotti et al., 2012
Coccolithophore	<i>Syracosphaera pulchra</i>		7.7					Pedrotti et al., 2012
Coccolithophore	<i>Emiliana huxleyi</i>		6.6			2-10		Shi et al., 2010
Diatom	<i>Thalassiosira weissflogii</i>	CCMP1336	6.9	97	14	33.4	Total[Fe]=100nM, NH ₄ or NO ₃	Price 2005
Diatom	<i>Thalassiosira weissflogii</i>	CCMP1336	7	70	10	9.46	Total[Fe]=10nM, NH ₄ or NO ₃	Price 2005
Diatom	<i>Thalassiosira weissflogii</i>					7.2	Total[Fe]=1.2	Sunda and Huntsman 1995
Diatom	<i>Thalassiosira weissflogii</i>					9.8	Total[Fe]=101	Sunda and Huntsman 1995
Diatom	<i>Thalassiosira pseudonana</i>					12.5	Total[Fe]=9.5	Sunda and Huntsman 1995
Diatom	<i>Thalassiosira pseudonana</i>					149	Total[Fe]=1023	Sunda and Huntsman 1995
Diatom	<i>Thalassiosira weissflogii</i>					13.1	Total[Fe]=11	Sunda and Huntsman 1995
Diatom	<i>Thalassiosira weissflogii</i>					101	Total[Fe]=1025	Sunda and Huntsman 1995
Diatom	Diatom assemblage/ bloom	Monterey Bay				~50		Bruland et al., 2001
Diazotroph	<i>Trichodesmium</i>	culture				8	NH ₄ as N source	Kustka et al., 2003
Diazotroph	<i>Trichodesmium</i>	culture				38	N ₂ as N source	Kustka et al., 2003
Diazotroph	<i>Trichodesmium</i>	Australia transect		79-310; ave=185	14-52; ave=29	18-78; ave=35	Australia transect	Kustka et al., 2003
Dinoflagellate	<i>Prorocentrum</i>					10.7	Total[Fe]=9.3	Sunda and Huntsman 1995

	<i>minimum</i>							
Dinoflagellate	<i>Prorocentrum minimum</i>					74.5	Total[Fe]=2968	Sunda and Huntsman 1995
<i>Prochlorococcus</i>	<i>Prochlorococcus</i>	MED4	5.7	121	21.2		P replete	Bertilsson et al., 2003
<i>Prochlorococcus</i>	<i>Prochlorococcus</i>	SARG	8.8	215	24.4		exponential	Heldal et al., 2003
<i>Prochlorococcus</i>	<i>Prochlorococcus</i>	NATL-MIT	9.2	206	22.6		exponential	Heldal et al., 2003
<i>Prochlorococcus</i>	<i>Prochlorococcus</i>	GP2	9.2	190	21		exponential	Heldal et al., 2003
<i>Prochlorococcus</i>	<i>Prochlorococcus</i>	SB	9.9	156	15.9		exponential	Heldal et al., 2003
<i>Prochlorococcus</i>	<i>Prochlorococcus</i>	EQPAC1	8.5	160	19		exponential	Heldal et al., 2003
<i>Prochlorococcus</i>	<i>Prochlorococcus</i>	PCC9511	9.5	190	20		exponential	Heldal et al., 2003
<i>Prochlorococcus</i>	<i>Prochlorococcus</i>	NGI surface	4.04	277	75		AMT field samples	Grob et al., 2013
<i>Prochlorococcus</i>	<i>Prochlorococcus</i>	NGI 142m deep	5.83	1073	185		AMT field samples	Grob et al., 2013
<i>Prochlorococcus</i>	<i>Prochlorococcus</i>	NGII surface	7.82	737	99		AMT field samples	Grob et al., 2013
<i>Prochlorococcus</i>	<i>Prochlorococcus</i>	NGI 127m deep	5.62	1150	206		AMT field samples	Grob et al., 2013
<i>Synechococcus</i>	<i>Synechococcus</i>	WH8102	5.4	130	24		P replete	Bertilsson et al., 2003
<i>Synechococcus</i>	<i>Synechococcus</i>	WH8103	5	165	33.2		P replete	Bertilsson et al., 2003
<i>Synechococcus</i>	<i>Synechococcus</i>	WH8103	10	150	15		PCR-S11 medium; exponential	Heldal et al., 2003
<i>Synechococcus</i>	<i>Synechococcus</i>	WH7805	8.9	113	13.3		PCR-S11 medium; exponential	Heldal et al., 2003
<i>Synechococcus</i>	<i>Synechococcus</i>	WH7805	7	115	16.4			Cuhel and Waterbury 1984
<i>Synechococcus</i>	<i>Synechococcus</i>	DC2				35.7-38.5	Fe replete, NH ₄ or NO ₃	Kudo and Harrison 1997
<i>Synechococcus</i>	<i>Synechococcus</i>	DC2				34.5	Fe limited, NO ₃ only	Kudo and Harrison 1997
<i>Synechococcus</i>	<i>Synechococcus</i>	DC2				14.9	Fe limited, NH ₄ only	Kudo and Harrison 1997
<i>Synechococcus</i>	<i>Synechococcus</i>	NGII surface	5.48	1150	100		AMT field samples	Grob et al., 2013
<i>Synechococcus</i>	<i>Synechococcus</i>	NGI 127m deep	4.41	621	135		AMT field samples	Grob et al., 2013

Chapter 2

A2 Pb analysis supporting information

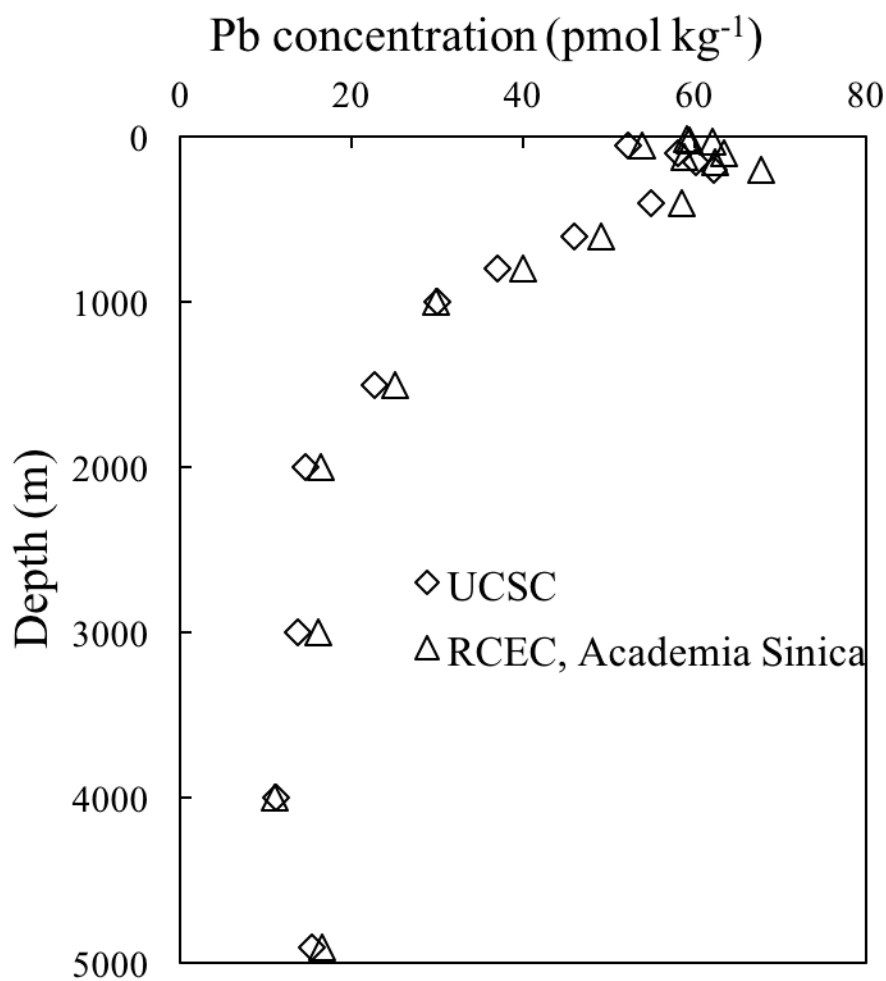


Fig. S2.1 Comparison of two Pb concentrations profiles at station 7, results are from independently determination by UCSC and RCEC, Academia Sinica.

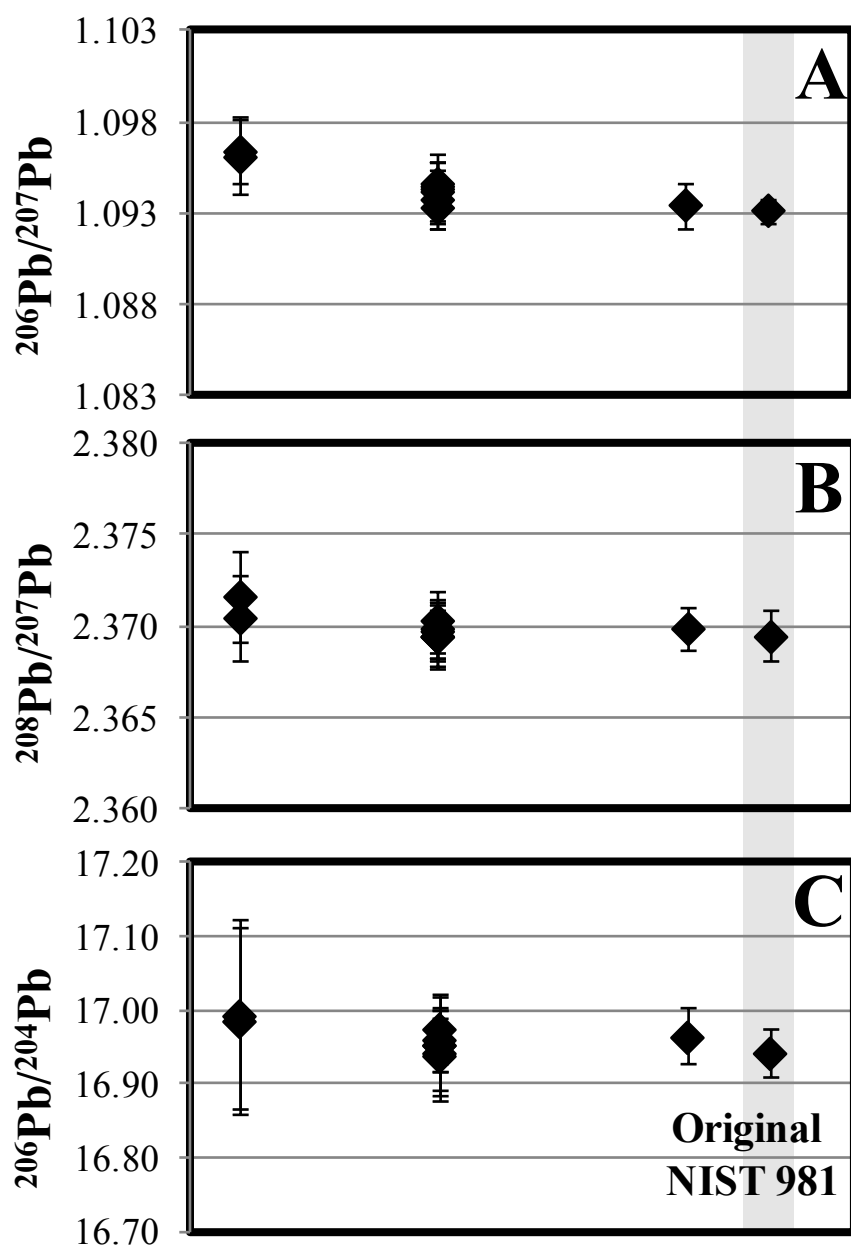


Fig. S2.2 Pb isotope ratios of NIST 981 in 1L of trace metal free seawater at concentration of 15 to 150 pmol/kg Pb (seawater was purified by Nobias Chelate-PA1 resin). (A) $^{206}\text{Pb}/^{207}\text{Pb}$. (B) $^{208}\text{Pb}/^{207}\text{Pb}$. (C) $^{206}\text{Pb}/^{204}\text{Pb}$. The error bar represented ± 2 s.d..

Table S2.1 Pb detection limit and concensus samples analyses.

CRM	Detection limit*	measured	consensus
	pmol/kg	pmol/kg (av $\pm$ SD)	
SAFe_S (n=6)	0.5	44.0 $\pm$ 1.0	48.0 $\pm$ 2.2
SAFe_D1 (n=4)		27.2 $\pm$ 1.3	27.7 $\pm$ 2.6

* Detection limit calculated by 3 $\times$ standard deviation of 26 blanks.

Table S2.2 Pb concentrations and isotopic compositions at each station. * at station 6 represented mean and standard error of isotope results from duplicate samples.

Depth (m)	Concentration (pmol kg ⁻¹)	²⁰⁶ Pb/ ²⁰⁷ Pb	2SD	²⁰⁸ Pb/ ²⁰⁷ Pb	2SD	²⁰⁶ Pb/ ²⁰⁴ Pb	2SD
ST1 23.5°N 121.74°E							
10	36.2	1.1698	0.0002	2.4492	0.0003	18.27	0.02
30	38.4	1.1683	0.0003	2.4499	0.0008	18.24	0.03
48	42.5	1.1701	0.0003	2.4505	0.0006	18.27	0.02
100	52.2	1.1657	0.0003	2.4500	0.0006	18.21	0.02
600	35.8	1.1673	0.0003	2.4527	0.0008	18.22	0.03
800	35.8	1.1674	0.0002	2.4526	0.0006	18.22	0.03
1000	29.9	1.1675	0.0004	2.4504	0.0006	18.23	0.03
1500	21.0	1.1710	0.0003	2.4489	0.0006	18.29	0.03
2000	17.7	1.1716	0.0002	2.4549	0.0006	18.31	0.02
3000	31.2	1.1788	0.0005	2.4697	0.0009	18.46	0.06
3237	36.7	1.1839	0.0003	2.4709	0.0007	18.51	0.03
ST3 23.5°N 122.25°E							
70	43.4	1.1674	0.0001	2.4468	0.0002	18.22	0.01
100	41.5	1.1648	0.0001	2.4448	0.0004	18.19	0.01
150	43.4	1.1636	0.0001	2.4477	0.0003	18.18	0.01
200	47.5	1.1648	0.0002	2.4466	0.0004	18.19	0.01
600	30.3	1.1648	0.0002	2.4508	0.0004	18.17	0.02
800	24.6	1.1664	0.0003	2.4514	0.0005	18.20	0.03
1000	23.7	1.1684	0.0002	2.4542	0.0004	18.26	0.02
1500	23.4	1.1692	0.0002	2.4535	0.0005	18.25	0.02
2000	21.9	1.1708	0.0003	2.4528	0.0006	18.30	0.02
3000	26.4	1.1805	0.0002	2.4618	0.0004	18.45	0.02
4000	37.8	1.1738	0.0002	2.4575	0.0004	18.34	0.01
4500	46.1	1.1797	0.0003	2.4689	0.0006	18.45	0.02
ST4 23.5°N 123°E							
100	52.1	1.1655	0.0003	2.4475	0.0008	18.21	0.02
200	49.3	1.1634	0.0003	2.4469	0.0005	18.17	0.01
400	45.6	1.1630	0.0002	2.4486	0.0005	18.16	0.01
600	39.0	1.1635	0.0002	2.4488	0.0004	18.16	0.01
800	35.0	1.1649	0.0003	2.4506	0.0006	18.20	0.01
1000	29.2	1.1675	0.0003	2.4527	0.0006	18.24	0.01
ST5 23.5°N 124°E							
30	52.2	1.1631	0.0001	2.4474	0.0003	18.17	0.01

65	58.0	1.1634	0.0003	2.4474	0.0006	18.18	0.02
100	60.1	1.1635	0.0002	2.4480	0.0006	18.18	0.01
150	62.2	1.1626	0.0002	2.4479	0.0005	18.16	0.01
200	54.8	1.1631	0.0002	2.4487	0.0006	18.17	0.01
600	46.0	1.1631	0.0003	2.4496	0.0005	18.16	0.02
1000	30.0	1.1682	0.0002	2.4518	0.0006	18.25	0.02
1500	22.7	1.1705	0.0002	2.4558	0.0006	18.28	0.02
2431	13.7	1.1772	0.0006	2.4571	0.0027	18.43	0.20
ST6 23.5°N 125°E							
30	62.2	1.1652	0.0003	2.4482	0.0009	18.21	0.02
67*	66.0	1.1641	0.0008	2.4478	0.0003	18.18	0.03
100*	65.4	1.1640	0.0006	2.4476	0.0003	18.18	0.00
150	59.1	1.1632	0.0003	2.4477	0.0005	18.16	0.02
200*	59.7	1.1632	0.0001	2.4485	0.0005	18.15	0.00
400*	48.2	1.1616	0.0003	2.4497	0.0005	18.17	0.00
600	44.5	1.1621	0.0004	2.4482	0.0007	18.14	0.02
800	37.3	1.1653	0.0003	2.4499	0.0008	18.20	0.02
1000*	21.9	1.1663	0.0011	2.4533	0.0004	18.26	0.01
1500	22.7	1.1660	0.0002	2.4512	0.0004	18.21	0.02
2000*	16.4	1.1695	0.0014	2.4513	0.0009	18.24	0.03
3000	17.9	1.1704	0.0003	2.4555	0.0007	18.28	0.02
4000*	11.4	1.1742	0.0005	2.4520	0.0009	18.22	0.07
4500*	19.5	1.1723	0.0020	2.4522	0.0006	18.24	0.03
ST7 23.5°N 126°E							
50	52.2	1.1628	0.0002	2.4469	0.0005	18.16	0.01
95	58.0	1.1647	0.0000	2.4474	0.0006	18.18	0.00
150	60.1	1.1625	0.0003	2.4472	0.0005	18.17	0.04
200	62.2	1.1623	0.0003	2.4479	0.0004	18.16	0.01
400	54.8	1.1616	0.0002	2.4491	0.0004	18.14	0.01
600	46.0	1.1617	0.0002	2.4476	0.0005	18.14	0.01
800	36.9	1.1640	0.0002	2.4487	0.0006	18.18	0.01
1000	30.0	1.1664	0.0002	2.4517	0.0006	18.22	0.01
1500	22.7	1.1674	0.0002	2.4516	0.0005	18.23	0.01
2000	14.6	1.1698	0.0004	2.4562	0.0007	18.33	0.03
3000	13.7	1.1752	0.0002	2.4623	0.0004	18.38	0.02
4000	11.2	1.1721	0.0004	2.4575	0.0010	18.33	0.03
4909	15.3	1.1762	0.0004	2.4617	0.0008	18.42	0.03
ST8 23.5°N 128°E							
10	47.4	1.1638	0.0003	2.4469	0.0004	18.19	0.02

30	42.4	1.1641	0.0003	2.4471	0.0008	18.19	0.02
80	53.0	1.1640	0.0003	2.4489	0.0006	18.24	0.02
110	51.5	1.1642	0.0003	2.4476	0.0008	18.18	0.03
150	48.1	1.1651	0.0003	2.4465	0.0005	18.19	0.02
200	55.8	1.1627	0.0002	2.4477	0.0005	18.16	0.02
400	49.9	1.1633	0.0003	2.4497	0.0005	18.16	0.02
600	43.9	1.1622	0.0002	2.4481	0.0007	18.16	0.02
800	40.8	1.1634	0.0003	2.4484	0.0005	18.13	0.02
1000	30.3	1.1646	0.0004	2.4489	0.0007	18.17	0.03
2000	19.1	1.1703	0.0003	2.4512	0.0009	18.29	0.05
3000	16.3	1.1716	0.0003	2.4537	0.0007	18.31	0.02