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Urban dust and central Ohio precipitation

Anne E. Carey^{*}, Susan A. Welch, W. Berry Lyons

School of Earth Sciences, The Ohio State University, Columbus, USA

^{}carey.145@osu.edu*

Abstract

Herein we examine the solubility of dust collected during a long-term study of the stable isotopic composition of precipitation in Columbus, Ohio, the 15th largest city in the United States. Samples were collected in a stationary, open, exposed rain collector so that between rain events dry deposition was obtained. Rain and snow samples collected during 2014–2016 were analyzed for Ca²⁺ and anions (Cl⁻ and SO₄²⁻) by ion chromatography. Chloride concentrations are low, ranging from >1 μM L⁻¹ to 26 μM L⁻¹, and are uncorrelated to Ca²⁺. Soluble, sea salt-corrected Ca²⁺ concentrations ranged from 6 to 124 μM L⁻¹. Our results are compared to a longer term dataset (1999–2015) from the National Atmospheric Deposition Program (NADP) of wet deposition samples collected 50 km southwest of Columbus. Mean sea salt-corrected Ca²⁺ concentration in our samples was 26 μM L⁻¹. Mean sea salt-corrected Ca²⁺ concentrations in NADP samples was significantly lower (p=0.0001), at 5.6 μM L⁻¹ with a range of 0.23–75 μM L⁻¹. Dry deposition between precipitation events plays a major role in Ca²⁺ input to the city landscape. It is unclear whether this soluble calcium is from a local urban source or a regional agricultural source. SEM analysis is used to determine mineralogy of dust input to our samples and possible source of the dissolved calcium observed.

Keywords: Urban deposition; Calcium; Columbus, Ohio, USA

1. Introduction

The role of dust in urban settings has been largely studied in relation to human health and to the quantification of urban emissions associated with pollution problems (e.g., Harrison and Yin, 2000). Although these two issues are extremely important to the overall understanding of dust transport and deposition in urban areas, they are not the only significant issues for the quantification of dust inputs into cities. In this paper we present a two-year time series of dust deposition in Columbus, Ohio, USA. As in numerous

investigations over the past few decades, in our work we use the measurement of water soluble calcium as a surrogate for dust (Witherow et al., 2006). We compare our data to those collected at Deer Creek State Park in Pickaway County, Ohio, some 50 km south of Columbus. This was done in order to access differences in urban versus rural dust deposition. Our study is part of ongoing hydrological investigations that seek to elucidate the stable isotopic composition of precipitation in Columbus, done to assess the seasonality of surface water distribution and management (Leslie et al., 2014) and groundwater recharge in greater Columbus.

Columbus is the 15th largest city in the United States with 1.25 million residents estimated in 2015 and with a population density of ~850 people km⁻². The city is situated on glacial till plains deposited during the Last Glacial Maximum. The local bedrock is Paleozoic sedimentary rocks including both carbonates and dolomites. Hence the local geology could be a major source of Ca-rich dust to the city.

1.1 Potential sources of Ca²⁺

There are numerous potential sources of Ca-rich dust in urban settings and these include both natural and anthropogenic ones. Natural sources include the erosion and transport of soil and other geologic materials from both local or even much longer-travelled sources. For examples, other investigations have demonstrated that Ca-rich dust deposited in the western and Midwestern portion of the USA can be attributed to distant sources (Gatz & Prospero 1996; Naiman et al., 2000; Bozlaker et al., 2013). In addition, both marine aerosols and forest fires can contribute to the overall dust burden. A major source of moisture to precipitation in Columbus is associated with air masses originating in the Gulf of Mexico and hence has the potential of contributing marine salt to the dust deposition (Leslie et al., 2014). Anthropogenic sources include industrial emissions, inputs through combustion of fossil fuels and the decay and erosion of urban infrastructure. The majority of electric power in the Ohio region is generated through the burning of coal. Hence CaSO₄ produced by the neutralization of SO₂ in the flue gases could potentially contribute to the Ca²⁺ atmospheric contribution in Ohio. The degradation of urban infrastructure such as concrete structures and roads and highways may also contribute Ca-rich particles to the local, urban atmosphere (Chambers et al., 2016).

Recent work describing depositional variations in rainfall collected as part of the U.S. National Atmospheric Deposition Program (NADP) during 1994–2010 indicates there has been little to no measurable change in Ca²⁺ in the Columbus region during this period (Brahney et al., 2013). This result is unlike that observed in sample locations in the western, Midwestern and mid- to northern Atlantic coast portions of the USA, where Ca²⁺ deposition has increased in some locations by as much 200% as over this 15-year time interval (Brahney et al., 2013).

1.2 Importance of dust to urban ecosystems

Due to the production and deposition of “acid rain” in the mid to late 20th century, there are soils in the eastern USA that have had their acid-neutralizing capacity decreased, in part through the solubilisation of alkaline ions such as Ca²⁺ and Mg²⁺ (Likens et al., 1996). In addition, the use of N-rich fertilizers on urban residential lawns and gardens can also produce acid via ammonium oxidation thereby depleting soils of their alkaline metals and lowering the soil pH (Fortner et al., 2012). Dust rich in Ca²⁺ may aid in buffering soil pH

and adding Ca^{2+} to urban soils. Thus the deposition of Ca-rich dust may serve as a positive attribute in urban regions.

2. Methods

Columbus samples were collected by the open-bucket method in an open area away from vegetation in a residential area 4 km north of The Ohio State University campus. The collection was made in Pyrex[®] glass vessel that was thoroughly washed and dried between sample collections. The collector was sampled only immediately after the cessation of an individual rain event, hence our samples contained the materials associated with the discrete rain event and any dry deposition deposited between the rain event and the previous event. Samples were placed into pre-cleaned polyethylene vials that were rinsed three times with sample before filling with sample, capping, and storage at 4 °C. Prior to analysis, the precipitation samples were filtered using auto sampler filter caps (20µm pore size) and analyzed with a Dionex model ICS 2100 or DX-120 ion chromatograph for anions and a Dionex model DX-120 for cations. Ca^{2+} , SO_4^{2-} , Cl^- , and NO_3^- were analysed by ion chromatography using the techniques described by Welch et al. (2010). The precision of these measurements as attained by replicate standards was generally within 5%, and often reproducibility for replicate analysis for samples or standards is within 1%. In addition to our in-house quality assurance measures, our laboratory participates in a calibration study run annually by the U.S. Geological Survey (USGS). In that calibration, we analysed the USGS standards and compared to the most probably value. Our accuracies for these analytes were 7.1%, 3.4%, 7.2%, 7.6% respectively.

Selected precipitation samples were filtered using 0.2 µm pore-size Nuclepore filters, and the filter was then air dried for analysis of suspended particulate material. Sections of the filters were mounted on aluminium stubs with carbon tape, coated with gold-palladium, and analysed using an FEI Quanta FEG Field Emission scanning electron microscope (SEM) using both secondary and back scattered electron detectors (BSE and SE). The SEM is equipped with a Bruker energy dispersive spectroscopy detector (EDS) which allows for semiquantitative spot chemical analysis. Geochemistry and mineralogy of particulate material on the filters were inferred from the spot chemical analysis and grayscale intensity in the BSE images.

The samples for the rural site were collected and analyzed by the NADP and they represent wet deposition only. Those samples were collected in a wet bucket that was open only during rain events. The samples were collected weekly and shipped to the Illinois State Water Survey for analysis. The weekly data utilized herein can be found at <http://nadp.sws.uiuc.edu/data/sites/siteDetails.aspx?net=NTN&id=OH54>.

3. Results

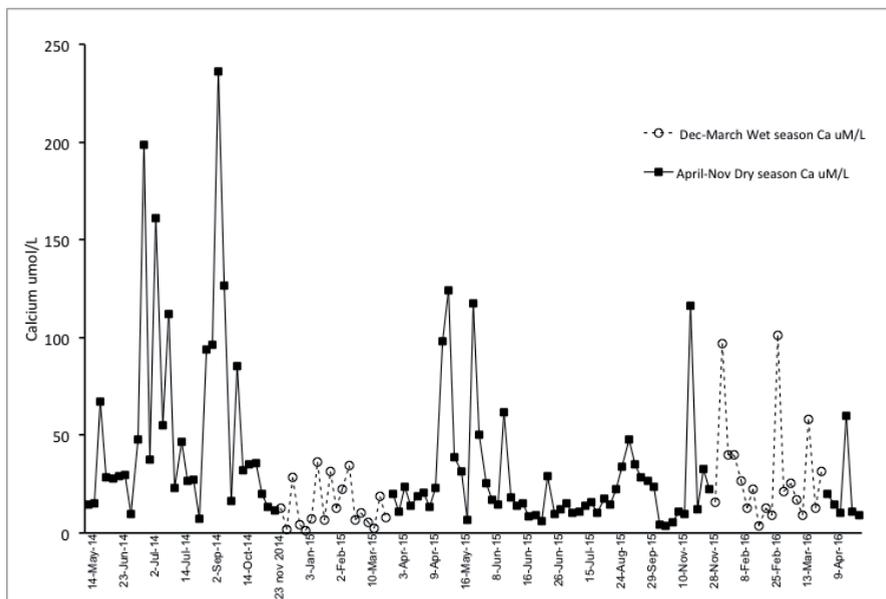


Fig. 1. Time series of dissolved Ca^{2+} concentrations in urban deposition, May 2014–April 2016. Wet season samples are shown in filled squares and dry season samples are shown in open circles

The time series for the Ca^{2+} concentrations in the Columbus precipitation samples is shown in Fig. 1 and the statistics of the Ca^{2+} concentrations for both sampling sites are given in Table 1.

The climate of Columbus is continental in character with cold winters and warm summers but mean monthly precipitation data demonstrate a seasonality in precipitation amount with higher monthly totals in December through March and lower average monthly precipitation for April through November (data obtained from <http://forecast.weather.gov/product.php?site=NWS&product=CLM&issuedby=CMH>). For the sake of discussion, December to March is denoted as the wet season and April through November termed the dry season. In general our time-series data reflect this seasonality with higher Ca^{2+} in the dry season and lower values in the wet season (Fig. 1). The dry season has 64% higher mean soluble calcium concentrations than the wet season (Table 1). Although there are relatively high values observed during the wet season, the 8 highest calcium concentrations observed were in the dry season (Fig. 1). Our data analysis of the rural site shows a similar seasonal relationship with higher concentrations in the dry season, even though these data represent wet precipitation deposition only (i.e., no dry deposition). Thus the two datasets, even though they represent different sampling protocols, demonstrate higher concentrations during the drier portions of the year (Table 1). Clearly our data reflect the importance of either the dry deposition of Ca^{2+} or our urban location, or perhaps both, as the dissolved Ca^{2+} concentrations are much higher in Columbus (a factor of approximately six-fold greater in Columbus than in Pickaway County during the dry season).

Table 1. Descriptive statistics for dissolved calcium in urban deposition and rural precipitation

Descriptive statistic	Urban		Rural	
	Wet season	Dry season	Wet season	Dry season
	$\mu\text{mol L}^{-1}$	$\mu\text{mol L}^{-1}$	$\mu\text{mol L}^{-1}$	$\mu\text{mol L}^{-1}$
Mean	22.4	37.2	4.75	6.2
Median	14.4	22.4	3.07	4.0
Mode	N/A	N/A	3.74	2.0
Standard deviation	22.9	42.7	6.17	7.57
Minimum	1.3	3.9	0.30	0.25
Maximum	101.3	236.4	59.13	75.58
n	36	89	227	428

4. Discussion

4.1 Possible sources of Ca^{2+}

We have used the Cl^- values measured in our samples and the $\text{Ca}:\text{Cl}$ ratio of seawater (Bruland, 1983) to estimate the amount of Ca^{2+} contributed by the marine aerosol. Our calculations yield an average seawater input value of 1.1% of the total calcium, with seawater contributions ranging 0.1%–13%. In many of our samples there is a marine aerosol contribution to Ca^{2+} but in none of the samples is the contribution a major one.

Figure 2 demonstrates the relationship between Ca^{2+} and SO_4^{2-} in the Columbus urban samples. The relationship is not a strong one. The 1:1 line in Figure 2 would represent the contribution of CaSO_4 to our samples and, although this, too, is not a strong relationship, the plot might suggest that some of the Ca^{2+} , especially at low total Ca^{2+} concentrations, could be derived from CaSO_4 . This would indicate a source either from coal burning emissions, long-range evaporate transport, or perhaps even a specific urban construction material source, wallboard.

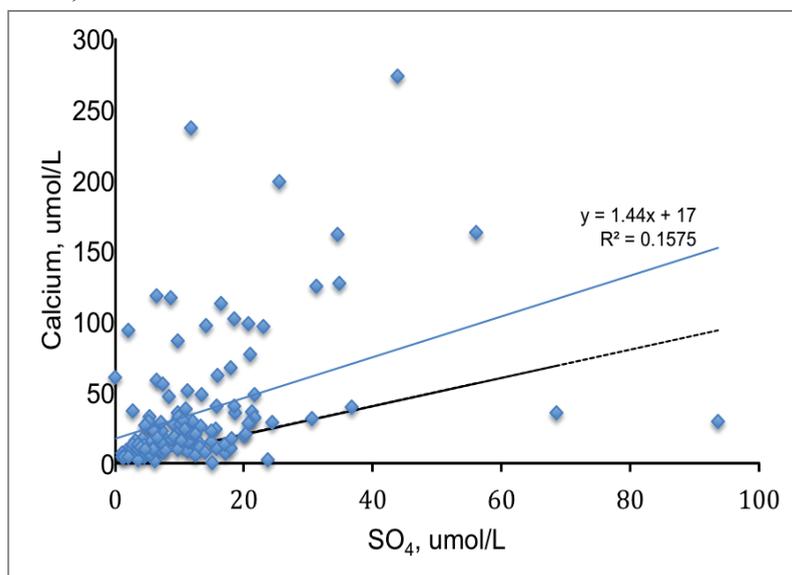


Fig. 2. Dissolved total concentrations of dissolved Ca^{2+} and SO_4^{2-} in ($\mu\text{mol/L}$) in urban precipitation. Solid blue line is the best fit line. Black dashed line indicates the 1:1 molar concentrations

A more likely source of Ca^{2+} is from CaCO_3 - or $\text{Ca,Mg}(\text{CO}_3)_2$ -rich dust that is common in the local soils and geological materials and is also a global dust compound that can be transported long distances (Legrand & Mayewski, 1997). SEM images of material filtered from these urban samples demonstrate abundant aluminosilicate and CaCO_3 -rich particles. SEM analysis of filtered precipitation samples showed a complex assemblage of inorganic and biogenic material. Rock and mineral particles ranged in size from submicron to several hundreds of microns. EDX spot analysis of individual mineral grains showed chemistry consistent with quartz, alkali and plagioclase feldspars, illite/muscovite, biotite, goethite, pyrite, calcite and dolomite. However, the most abundant lithic fragments observed on the filters were carbonate-rich micritic shale particles. These often showed evidence of extensive dissolution of the carbonate phases, revealing fine grained illitic clay at the surface. Our on-going work seeks to elucidate the sources of Ca^{2+} to these samples and to qualify and quantify these sources.

4.2 Ecological and landscape implications

As noted above, the soils affected by either acid deposition or enhanced fertilizer usage can be depleted in base cations. The input of Ca^{2+} derived from dust may aid in neutralizing acid, either directly in the precipitation itself, or in the soilwater after deposition. The effect on urban landscapes is unknown. Our mean soil Ca^{2+} value in Columbus deposition was $35.6 \mu\text{mol L}^{-1}$. The Ca^{2+} concentration in first order urban streams in Columbus was found to range from 1020 to $3680 \mu\text{mol L}^{-1}$ (Stucker, 2013). The mean Ca^{2+} values from these first-order streams are equal to or higher than concentrations observed in the Olentangy River, a major river in Columbus into which they flow. This would suggest that the mean contribution of dust dissolution to the Columbus landscapes is only 1–3.5%. The stream data represent only base flow conditions and currently there is no way to ascertain the importance of Ca-rich dust on the ecology or the landscape biogeochemistry of the Columbus urban environment. Our future work will focus on quantifying this contribution.

5. Conclusions

The mean concentration of soluble Ca from dust deposition and precipitation in Columbus, Ohio, the 15th largest city in the USA is $36.5 \mu\text{mol L}^{-1}$. Higher concentrations were observed during the dry season and probably represent larger contributions of Ca^{2+} from dry deposition between rainfall events. The concentrations in Columbus precipitation are higher than observed in a nearby rural area but this difference is probably a reflection of difference in sample collection techniques. Marine aerosol contributes a minor fraction of the total Ca^{2+} while CaSO_4 produced through coal burning may also contribute a minor but measureable fraction of the measureable Ca. The primary source of Ca^{2+} to this urban deposition is probably derived from either local or longer-range transport of CaCO_3 and $\text{Ca,Mg}(\text{CO}_3)_2$ -rich dust or a combination of these. Currently it is unclear whether this Ca^{2+} addition to the urban landscape has a positive ecological effect. Our future research will focus on these last two aspects of the work.

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