IS DISTANT POLLUTION CONTAMINATING LOCAL AIR?

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David Geng is a senior in the Department of Chemistry at Purdue University. His research interest peaked during his sophomore year, when David was presented with an opportunity to do environmental chemistry research with Dr. Greg Michalski. He then started a solo project that involved understanding local aerosol pollution. The analytical instrumentation used fueled a passion for analytical chemistry that continues today. In addition to research and classes, Geng is the vice president of the American Chemical Society, Purdue Student Affiliates. Geng’s plans for the future include finding a chemistry position in industry utilizing the skills that were developed during his research experience.

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Abstract

Understanding the origin of aerosols in the atmosphere is important because of visual pollution, climate impacts, and deleterious health effects due to the inhalation of fine particles. This research analyzed aerosols characterized by their chloride, sulfate, and nitrate content as a function of size over a 3-month period. Due to wind patterns over coal-burning power plants, a higher concentration of local sulfate pollution was expected. Aerosols were harvested on the Purdue University campus using a high-volume air sampler with glass fiber filters and a five-stage impactor that separates the aerosols into five sizes. The filters were extracted in water to dissolve anions and the solution was analyzed using high-pressure liquid ion chromatography. Only trace amounts of chloride with no distinct patterns in size were detected. In total, nitrate content ranged from 0.12 to 2.10 µg/m³ and sulfate content ranged from 0.44 to 6.45 µg/m³ over a 3-month period. As for fine particles, a higher concentration of sulfate was observed. The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model determines air mass origin, and in this study, higher total sulfate content was observed when the air mass moved out of the southwest, and higher total nitrate content was observed when the air mass originated from the southeast. The author concluded that small particles resulted in sulfate from sulfur dioxide, typically from gas to particle conversion. High sulfur dioxide levels are directly correlated with coal-burning power plant density. Small particulate sulfate found in West Lafayette, Indiana, was determined to originate primarily from power plants in southwest Indiana. Though the results do show a significant amount of potentially harmful aerosols in West Lafayette, there is still further research to be done concerning isotopic composition of those particles in attempts to better explain the chemical pathways.


Keywords

atmospheric aerosols, air sampling, coal, pollution, sulfates
INTRODUCTION

Every person on the planet breathes in air that contains very fine suspended particles known as atmospheric aerosols. Atmospheric aerosols have been a significant research topic since the early 20th century when scientists realized that people could become ill from inhaling air with a high particulate matter content. Now most research that is being conducted on aerosols is done utilizing technological advances in analytical chemistry and computer modeling to analyze aerosols thoroughly and with more certainty.

It is crucial to understand where aerosols come from because of the dramatic effect that particulate matter has on global climate, local air quality, and personal health. The effects of atmospheric aerosols on global climate have been studied since the 1970s, and research has shown that aerosols enhance the scattering and absorption of solar radiation. The physical characteristics of aerosols independently are mostly negligible, but when there are trillions of aerosols in the atmosphere, climatic effects may occur (Ramanathan, Crutzen, Kiehl, & Rosenfield, 2001). Some climatic effects that could occur include altering the solar radiation that enters the atmosphere by the “Twomey effect,” which is the ability of aerosols to reflect the radiation. Another way aerosols can affect climate is by modifying clouds by acting as cloud condensation nuclei, which may have an influence on the hydrological cycle (Lohmann & Leck, 2005). Though there is much scientific evidence to show that both of these physical phenomena are influenced by aerosols, there is a significant amount of uncertainty in whether or not anthropogenic aerosols are having a direct effect on the global-mean radiative forcing when compared to greenhouse gases (Schwartz & Andraee, 1996). The second implication of aerosols is the impact on visibility.

The United States has struggled with visual pollution for well over 100 years, since industrialization began emitting particles into the air. The United States Clean Air Act of 1963 sought to limit the extent of the air pollution and has had a significant impact on reducing visual air pollution; however, in other parts of the world, visual pollution continues to be a significant issue (see Figure 1).

A more important implication of high concentrations of aerosols is the detriment to human health (Kinney & Ozkaynak, 1991). Research has shown that continued exposure to aerosols can damage respiratory tissues and, depending on the chemistry of the particulate matter, may even cause cancer (Avol et al., 1979). Additionally, fatalities due to respiratory issues increase during times of elevated aerosol concentration. The primary hurdle with studying these health effects is that the experiments...
are difficult to control because there are too many
variables (Vincent, 1990). Negative health effects are the
main motivation for studying pollution aerosols and, in
particular, sulfate aerosols. There is a clear correlation
between coal-burning power plants and sulfur dioxide
\( \text{SO}_2 \) emissions because gas-phase oxidation can result in
elevated concentrations of sulfate aerosols (Hewitt, 2001).
Coal-burning power plants are important to understand
because \( \text{SO}_2 \) has shown to be a direct cause of degrading
pulmonary function (Clarke et al., 1998).

The purpose of this research is to understand what the
quantity, size, composition, and origin of atmospheric
aerosols are in West Lafayette, Indiana. This research
is unique because it combines cutting-edge particle
transport modeling with analytical chemistry techniques to
understand the origin of local air pollution. Though both the
chemistry of aerosols and the transportation of particulate
matter have been studied, the combination of both in
Indiana has not been done before. The main goal of the
research was to sample aerosols and to better understand the
source of the collected aerosols using scientific inference.
At the beginning of the research it was unclear what trends
could be seen in the local air pollution and where those
aerosols originated from. The hypothesis, based on previous
research, was that the highest sulfate concentrations
stemmed from air masses moving over coal-burning power
plants depositing sulfur aerosol pollution downwind.

**METHODOLOGY**

In order to test the hypothesis, the initial step was to collect
local pollution aerosols. A Tisch-Environmental TE-5000
High Volume Total Suspended Particulate Air Sampler
was installed on the roof of the Civil Engineering building
on the campus of Purdue University (Figure 2). The TE-
5000 has a five-stage cascade impactor that size segregates
particles by causing aerosols to impact on a series of glass
fiber filters. The dynamic range of the size segregation was
20–8.0 \( \mu \text{m} \) (stage 1), 8.0–3.5 \( \mu \text{m} \) (stage 2), 3.5–1.8 \( \mu \text{m} \) (stage 3),
1.8–0.95 \( \mu \text{m} \) (stage 4), 0.95–0.4 \( \mu \text{m} \) (stage 5), and backup
filter that captured particles < 0.4 \( \mu \text{m} \). The purpose of the
size segregation was to better understand how the smaller
particles (< 2.5 \( \mu \text{m} \)), which can penetrate the human lungs,
differ in concentration and composition relative to the larger
particles. To better understand the size segregations, the
data was broken down into three segregations: filters 1 and
2 in the large segregation, 3 and 4 in medium segregation,
and filter 5 and backup in the small segregation. The air
sampler was operated at a flow rate of 1.25 m\(^3\)/min for
24- to 72-hour intervals from May 20 to August 20, 2010.
The filters were collected and rinsed with deionized water
in order to dissolve the soluble fraction of the aerosols.
The aerosol’s soluble anion composition, including sulfate
\( \text{SO}_4^{2-} \), nitrate (\( \text{NO}_3^- \)), and chloride (\( \text{Cl}^- \)), was analyzed
by ion chromatography (IC) using a high-pressure liquid
 chromatography (HPLC) instrument. The IC trapped anions
on an anion exchange column that was then eluted using a
carbonate/bicarbonate buffer system of 14.3 g/L \( \text{NaHCO}_3 \)
and 19.1 g/L \( \text{Na}_2\text{CO}_3 \). Anions were pushed off of the resin at
different rates, allowing for separation. The ion content was
then calculated for each of the desired anions as a function
of the area under the curve (see Figure 3).

**Figure 2.** The IC-HPLC is a mass of tubes and a controller (A)
that separates the anions. The TE-5000 is located on top of Civil
Engineering Building (B) and within the air sampler is a series of
three main components: glass-fiber filters (C), a five-stage impactor
with slots for the air to pass through (D), and a vacuum motor (E).
Anion calibration was carried out using predetermined concentrations of sulfate, nitrate, and chloride in solution to calculate a calibration curve. The range of anion standard concentrations was from 0.5 parts per million (ppm) to 25 ppm concentration. After calibration the resulting concentration of each sample was found in ppm with a standard deviation (SD) of 5% of the total anion concentration. This SD is due to the accuracy of the instrument and the amount of human error involved in sampling. The resulting concentration measurements were then converted to micrograms per cubic meter (µg/m$^3$) by normalizing the concentrations with respect to flow time. The resulting value was in units of µg/m$^3$, which is a common unit for air particle concentrations.

The origin of the air mass containing the aerosols was determined using a back-flight trajectory model, HYSPLIT. The HYSPLIT model is a free, Internet-based air dispersion model from the National Oceanic and Atmospheric Administration (NOAA), which takes meteorological data from sites across the United States and inputs the data into the model (Draxler & Rolph, 2012). The HYSPLIT model then calculates and displays the backward trajectory of the air mass for a given sampling day.

This shows where an air mass was 6, 12, 18, 24, 30, 36, 42, and 48 hours prior to the sampling time. A quadrant system was employed to divide the resulting trajectories into four possible directions (Figure 4) to determine if aerosols of certain size or composition came from unique regions. HYSPLIT data was collected for each of the sampling periods.

RESULTS AND DISCUSSION

The main anions present in the aerosols were chloride, nitrate, sulfate, and some oxalate. Sulfate (SO$_4^{2-}$) aerosols had the highest concentrations, ranging from 0.44 to 6.45µg/m$^3$ total during the 3-month period. The total nitrate (NO$_3^{-}$) content ranged from 0.12 to 2.10µg/m$^3$ and was usually lower than the sulfate content on a given day. Chloride content was near the ion chromatograph’s detection limit, making the data not useful for this experiment. Oxalate was only present in three of the sampling periods and will not be discussed.

The highest amount of sulfate was found in the < 0.95 µm (small) size fraction (Figure 5), suggesting that the majority of the sulfate was formed by gas to particle conversion. Sulfur dioxide (SO$_2$) is a gas at normal atmospheric conditions and is a natural component of the atmosphere. Some natural SO$_2$ sources include volcanic eruptions, biological organisms that release sulfur as a byproduct, sea spray, and dying phytoplankton in the ocean that emit dimethylsulfide (DMS) that is converted to SO$_2$ in the atmosphere. A large majority of the SO$_2$ in the atmosphere is from anthropogenic sources such as coal burning, petroleum refining, and metal smelting (Cullis & Hirshler, 1980). Sulfur dioxide is oxidized in the atmosphere to sulfuric acid [SO$_2$ + H$_2$O + ½ O$_2$ = H$_2$SO$_4$(aq)] that quickly becomes hydrated, forming very small particles (< 0.1 µm). Once the particle becomes hydrated, other particles then coagulate around the original sulfuric acid particle. Though the oceans are a large contributor of natural SO$_2$, they are significantly far from Indiana, making oceans an unlikely contributor of the sulfate aerosols recorded. The second largest contribution of SO$_2$ is volcanic activity, but like the ocean, volcanic activity is very far from the sampling site. This suggests that the sulfate collected originates mostly from anthropogenic sources like coal-burning power plants, petroleum-refining processes, smelting operations, and paper manufacturing. The source that is most common near the sampling site, and therefore most likely to be contributing to the sulfate pollution, is Midwestern coal-burning power plants (Figure 6).

![Figure 3. IC chromatogram that shows each of the anions as a function of time. Specific anions are represented by each curve. From left to right: chloride, nitrate, and sulfate.](image)

![Figure 4. An example of a HYSPLIT model image displaying the origins of air particles at three different altitudes 48 hours prior to reaching Lafayette, Indiana. A superimposed quadrant system is shown to categorize air mass source numerically.](image)
To test the hypothesis that coal-burning power plants near Purdue are the source of the sulfate pollution, the HYSPLIT model evaluated the directions from which the air originated. The HYSPLIT model showed that more that 55% of the runs came from the southwest. Air masses out of the southwest are typical during the summer months with wind currents moving out of the Gulf of Mexico into the interior of the continent. The highest average total of sulfate originated out of the northwest with a concentration average of 4.35 µg/m³. This higher average is most likely due to the poor air quality associated with the industry and coal-burning power plants around Chicago, Illinois, and Gary, Indiana. The lowest average totals originated out of the northeast, which is logical due to the lower concentrations of industry and coal plants relative to the other quadrants. Overall, the largest amount of total sulfate originates out of the southwest due to both the high probability of the air mass coming from the southwest in the summer and a large abundance of coal-burning power plants to the southwest. However, the air quality appears to be worse when the air originates from the northwest, most likely due to large urban centers.

Nitrate is another aerosol component that is important to study, especially in the Midwest where there is an abundance of agriculture and automobiles. Nitrate aerosols, like sulfate, have many possible sources including inorganic nitrate fertilizer applied to local croplands and fossil fuel combustion that produces nitrogen oxides (NOₓ) that can be oxidized to nitrate (NO₃⁻). Similarly to sulfate, high amounts of small nitrate aerosols are likely to be caused by gas to particle conversion. However, unlike sulfate, a high concentration of nitrate was recorded in the large segregation.

Why are there two aerosol modes with high nitrate but only one mode that has high sulfate? The gas–particle equilibrium reaction \([\text{HNO}_3(g) + \text{NH}_3(g) \rightarrow \text{NH}_4\text{NO}_3(s)]\) is known to be sensitive to temperature and would produce fine particles. Nitrate in the larger segregation could be indicative of another reaction pathway where nitric acid reacts with an existing aerosol: \([\text{HNO}_3 + \text{M} + \text{OH}^{-} \rightarrow \text{NO}_3^{-} + \text{H}_2\text{O}]\). The air sampler was run over the summer when temperatures were high, causing the reaction to be pushed toward the gaseous reactants. This reaction gives a plausible explanation for the high concentration in the smaller filters, but since there is a backup filter to catch the aerosols from 0.4 µm to 0 µm, there would be a bias for collecting all nitrogen. Though this bias would add to a
higher concentration in the backup overall, the fraction of nitrate collected is still representative of the given reaction schemes. The aerosol-dependent pathway for creating nitrate is a high surface area reaction that is not as likely in the middle of the summer. For this reaction to proceed there needs to be a surface on which the nitric acid can react. In an agriculture-rich area, that surface is typically ammonium or some other dust particle usually produced by agriculture. The need for high surface area particles makes the aerosol pathway logical during either tilling or harvesting seasons, but is an interesting observation for the summer months. The inference from the size segregation is one strategy for sourcing, but another way to source aerosols is by looking at the movement of air masses, which is where HYSPLIT trajectory can supply clues. The highest average total of nitrate originated from the southeast and had a concentration average of 1.50 µg/m³. The southeast is a prime candidate for high nitrate due to the abundance of reaction aerosols from urban environments like Indianapolis and even large cities in southern Ohio, which explains the high concentration of large particle nitrate. The highest nitrate concentration for the small-sized particles originated out of the southwest, which is also logical because of the ammonia affiliated with agriculture from states to the southwest like Arkansas, Tennessee, and Missouri. The lowest concentrations for nitrate were seen when the air mass moved from the northeast, which is the same as the sulfate, because of the lower agriculture and less urban concentration from the northeast than the other three quadrants. Overall, there is more nitrate on large particles from urban areas, but since most of the air is originating out of the southwest, there is a greater total of nitrate from the southwest.

CONCLUSIONS
The discovery of the highest sulfate totals in the respirable (< 0.95 µm) particles is alarming due to the discussed damaging effects of sulfate aerosols on the lungs. Equally concerning is the fact that the air quality out of the northwest is even worse than out of the southwest. Overall, there is much less nitrate than sulfate, meaning that there is less nitrification from ammonia in the summer months and most likely more gas-phase nitrogen than aerosol nitrogen due to the higher temperatures, which agrees with observations from the Clean Air Status and Trends Network (CASTNet) (Spak & Holloway, 2009). For this research only the soluble anions were studied, which is only half an aerosol, but assuming the counter cation is mostly ammonium the concentration of pollution would be about 11.6 µg/m³. The 11.6 µg/m³ is the soluble fraction and, considering that only 75% of the aerosols are soluble, the resulting maximum aerosol concentration is 15.4 µg/m³ compared to the particle pollution maximum set by the EPA as 35 µg/m³ (U.S. Environmental Protection Agency, 2006). The city of West Lafayette is a typical Midwestern small city with minimal visual pollution. However, the research suggests there is a significant amount of aerosol pollution even though the concentrations are lower than the EPA’s pollution maximums. A problematic situation has arisen considering that most of the pollution seen on Purdue’s campus is likely not from the city, but from coal-burning power plants over a hundred miles to the southwest. These aerosols mean that there are potentially thousands of people at risk in the college town. In the future, isotopic analysis will better explain the chemical pathways by which the anions are produced. Particulate matter has been a significant scientific research topic for over 100 years and will continue to be a pertinent research concentration until the aerosol pollution is fully regulated. Though the pollution maybe coming from elsewhere, in the future similar research could have a serious impact on the way humans pollute.

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