Atmospheric Cycling of Indium in the Northeastern United States

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Environmental Significance Statement

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Indium is a metal that is increasingly used in electronics and energy technologies, but whose environmental behavior and human health impacts are poorly understood. A better understanding of the concentrations of indium in the atmosphere over time and geographically is critical for assessing sources of indium to the atmosphere, whether humans have perturbed natural cycling, and ultimately if human exposure to indium is increasing. We conclude that the dominant releases of indium to the atmosphere in the northeastern United States are from nonferrous metal smelting and coal combustion, implying that human activities already dominate indium's natural atmospheric cycling.

Atmospheric Cycling of Indium in the Northeastern United States

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Abstract

Indium is critical to the global economy and is used in an increasing number of electronics and new energy technologies. However, little is known about its environmental behavior or impacts, including its concentrations or cycling in the atmosphere. This study determined indium concentrations in air particulate matter at five locations across the northeastern United States over the course of one year, in 1995. Historical records from a Massachusetts bog core showed that indium atmospheric concentrations in this region changed only modestly between 1995 and 2010. Atmospheric indium concentrations varied significantly both geographically and temporally, with average concentrations in PM_3 of 2.1 ± 1.6 pg/m^3 (1 standard deviation), and average particle-normalized concentrations of 0.2 ± 0.2 μg In/g PM_3. Peaks in the particle-normalized concentrations in two New York sites were correlated with wind direction; air coming from the north contributed higher concentrations of indium than air coming from the west. This correlation, along with measurements of indium in zinc smelter emissions and coal fly ash, suggests that indium in the atmosphere in the northeastern United States comes from a relatively constant low-level input from coal combustion in the midwest, and higher but more sporadic contributions from the smelting of lead, zinc, copper, tin, and nickel north of the New York sample sites. Understanding the industrial sources of indium to the atmosphere and how they compare with natural sources can lead to a better understanding of the impact of human activities on the indium cycle, and may help to establish a baseline for monitoring future impacts as indium use grows.

Introduction

Indium is an increasingly important metal in electronics and new energy technologies[1,2]. World production of indium has been increasing exponentially since the 1980s (approximate doubling time of 8 years)[3], most of which is used in light-transmissive conductive coatings (as ITO, indium tin oxide) for flat panel displays, LCD displays, and photovoltaic cells[1,2]. Releases of indium to the atmosphere are currently thought to be dominated by industrial sources, mostly by coal-fired power plants and non-ferrous smelters (Fig. 1;[1]). There is significant uncertainty about these estimates, however, and much of the present knowledge of atmospheric concentrations and cycling of indium comes from studies done in the 1970s[1,4], just as increased particulate control technologies for stationary sources came online in the United States and Canada[5–7].

The atmospheric cycling of metals is important for several reasons, including the fact that human health can be adversely impacted by inhalation of atmospheric particulate matter, which contains both organic matter and metals. Several studies have shown that inhaled indium can have serious health impacts[8–12], especially in occupational settings where indium concentrations in the air can reach levels a million times higher than ambient air[8]. Studies are lacking, however, about the health effects of chronic exposure to more modest elevations in concentration. Additionally, the physical and chemical form of indium in the atmosphere is poorly understood, and can be expected to influence its behavior, transport, and bioavailability; a better understanding of this speciation is important for a thorough understanding of indium's environmental impacts and toxicity.

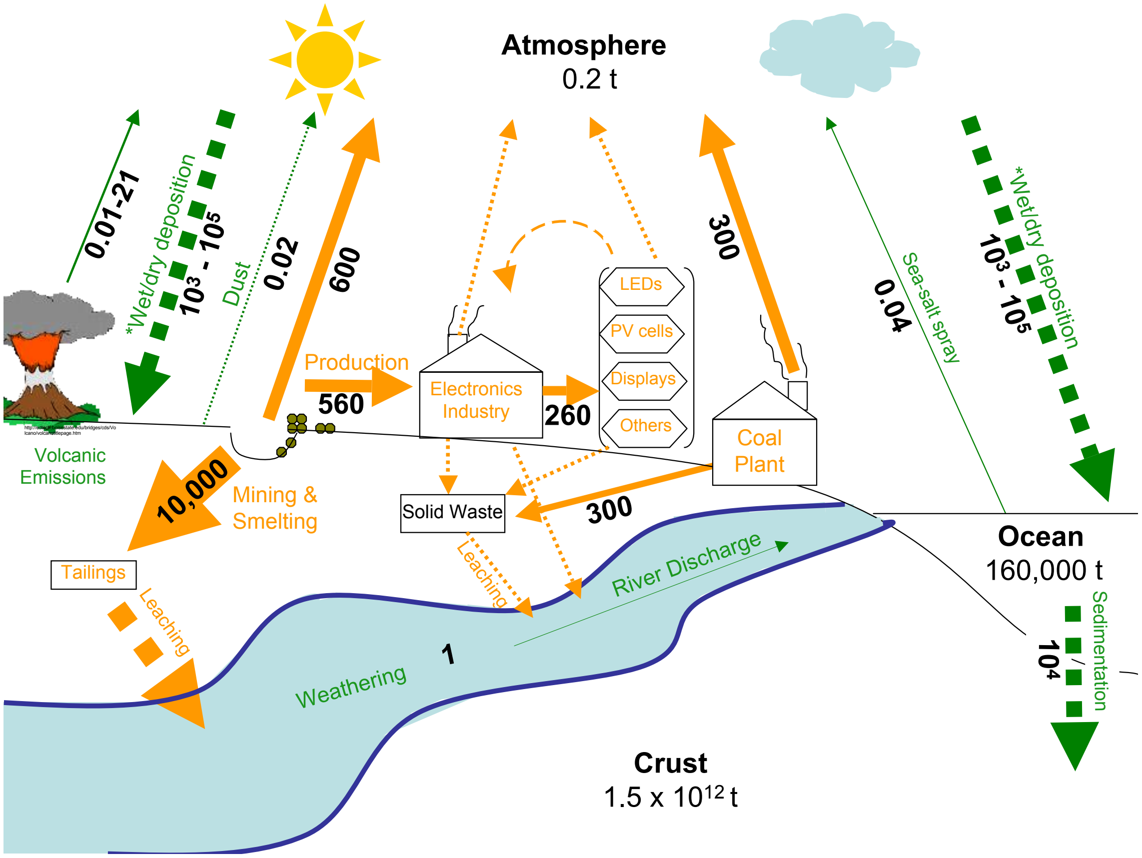

Figure 1: Indium's anthrobiogeochemical cycle is dominated by industrial fluxes, with coal-burning and smelting contributing the most indium to the atmosphere. Reservoir units = metric tons; flux units = metric tons/year; solid arrow = relatively well-known flux; dashed arrow = unknown flux; green arrow = natural flux; orange arrow = anthropogenic flux; arrow width = approximate relative magnitude. *Due to the method of estimation, wet/dry deposition fluxes may include both natural and industrial sources. Reprinted from White & Hemond 2012[1], with permission of the publisher, Taylor & Francis Ltd.

There are few measurements of indium in the atmosphere. Typical values reported for non-industrial air are on the order of 10 pg/m^3 for all particle size fractions (Total Suspended Particulate, or TSP)([4] and references therein). Indium concentrations in TSP have been measured from 0.053-4.3 pg/m^3 near the South Pole, Canada, and northern Norway[13,14], to 5-10 ng/m^3 near a lead smelter and a semiconductor-based industrial area[15,16]. Total Suspended Particulate includes indium that is bound in the crystal structure of large-diameter silicates, a fraction that does not likely contribute to significant human exposure. Respirable particles (those <2.5 μm in diameter), and indium that is sorbed to particles rather than bound in the crystal structure are more likely to lead to human exposure. Measurement of indium in the <2.5 μm particle fraction ($PM_{2.5}$) showed an average of 6.7 pg/m^3 from several sites in New York state during 1991 and 1993[17,18].

Several studies have tried to determine the main sources of indium to the atmosphere. Ames et al.[18] used factor analysis to attribute the mass of indium at several sites in New York to the most probable sources during the course of the 2 year study. Depending on the site, they attributed from 35-79% of the $PM_{2.5}$ indium to smelter sources, 0-25% to a 'Canadian Regional' source that originates from the north and northwest (N/NW), 0-27% to a 'US Regional' source that originates from the west and southwest (W/SW), and 0-12% to a crustal source (i.e. dust). Sturges and Barrie[19] measured indium concentrations in Dorset, Ontario, and showed that peaks of up to 20 pg In/m^3 were associated with wind coming from a smelter region in eastern Canada, and were correlated with high ^{207}Pb/^{206}Pb ratios, a marker of those smelter emissions. Non-smelter-influenced air at this site showed concentrations of <10 pg/m^3 indium. Rahn and Lowenthal[20] determined that indium concentrations were 20–100x higher in air particles traveling from the nonferrous smelter region of Ontario and Quebec than from other wind directions.

Our own studies of historical indium deposition to a bog in Massachusetts suggest that coal combustion and the smelting of lead, zinc, copper, and tin sulfides have contributed indium to the atmosphere in the northeastern United States during the past century[21]. Fluxes to the bog increased beginning in the late 1800s, which correlated with increases in both coal consumption and nonferrous metal smelting. The indium flux to the bog peaked in the 1970s, then decreased dramatically to the present. This decrease correlated with decreases in particulate emissions from fuel combustion and nonferrous metal smelting. Thus it appears that both sources may have contributed to changing historical indium concentrations, though it is difficult to distinguish between the sources.

In the current study we analyze atmospheric particulate matter in the northeastern United States, with the objective of assessing the relative contributions of coal combustion and smelting as important sources of indium to the atmosphere in this region. Atmospheric particulate samples from five locations in the northeastern United States over the course of a year (1995) are analyzed for indium to constrain variations spatially and temporally. From our bog study cited above, atmospheric deposition of indium to the bog, and thus atmospheric concentrations of indium, appear not to have changed greatly between 1995 and 2010, the year the bog was sampled[21]. This suggests that conclusions drawn about the sources and cycling of indium in 1995 are relevant to present-day sources and cycling of indium. In order to constrain the source of indium to the sample locations, atmospheric back trajectories are modeled to determine the wind directions contributing to peaks in indium concentration, the chemistry of air from differing regions is analyzed, and enrichment factors are calculated. Additionally, indium concentrations in zinc smelter emissions and in coal fly ash are measured to help determine overall indium emissions from these sources. These data show that peaks in particle-normalized concentrations are brought to two New York sites from the north, and suggest that indium in the atmosphere in the northeastern United States comes from a relatively constant low-level input from coal combustion in the midwest, and higher but more sporadic contributions from the smelting of lead, zinc, copper, tin, and nickel north of the New York sample sites. Lastly, we use the data from this study to contribute to knowledge of global fluxes of indium to and from the atmosphere (Fig. 1).

Methods

Indium in Air Filters

Site description and sample collection

Archived particulate samples from a network of air monitoring stations in the northeastern United States were used for this study. These samples were collected in 1995 as described by Pedersen and colleagues[22–25]. High volume samplers pulled 300 L/min air, while a dichotomous virtual impactor separated the particles into a 3–10 μm and <3 μm fraction. (<2.5 μm is the typical operational cutoff for respirable particles; in the following discussion we refer to the <3 μm fraction as PM_3, and the 3-10 μm fraction as PM_{3-10}.) Samples were taken for 24 hours (12am to 12am) every sixth day over the course of a year, and particles were collected on quartz fiber filters that had been pre-combusted at 550°C. Indium was analyzed in approximately 30% of the PM_3 samples and a small number of the PM_{3-10} samples.

The locations of the samples reflect urban, rural, and background settings in two separate airsheds[22] (Fig. 2). Boston, MA and Rochester, NY are urban areas. Reading is a suburban area 20 km north of Boston, and Brockport is an agricultural community 35 km west of Rochester. The Quabbin site, in a protected watershed in central Massachusetts, reflects regional background conditions.

Sample Preparation

PM_3 filters were previously subsampled by Pedersen and colleagues[22–25] using razor blades on a plexiglass template. PM_{3-10} filters were subsampled for this study with razor blades using a glass template. One third of each filter was digested and analyzed with an Inductively-Coupled Plasma Mass Spectrometer (ICP-MS), based on a slightly modified EPA Method 3050B. Air filters were refluxed on a hotplate with 20 mL concentrated nitric acid (Malinckrodt Chemical reagent grade) and 10 mL 70% perchloric acid (Alfa Aesar reagent grade) for approximately 8 hours. (Warning - use extra caution when working with perchloric acid.)

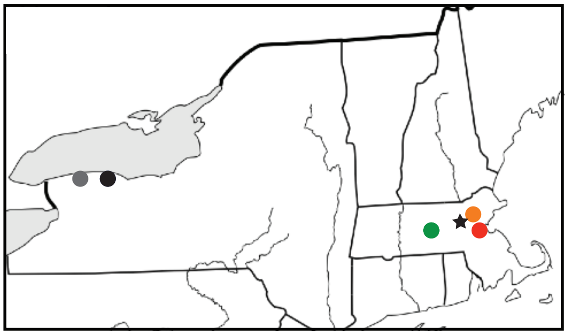

Figure 2: Air samples (circles) were taken in five locations across the northeastern United States. From left to right: Brockport, NY (grey); Rochester, NY (black); Quabbin Reservoir, MA (green); Reading, MA (orange); and Boston, MA (red). Colors in subsequent data figures correspond to this color scheme. Peat core discussed (star) was taken from Thoreau's Bog, MA.

After holding at room temperature overnight, the samples were taken to dryness; perchlorate was driven off with the addition of 5 mL nitric acid, followed by again taking to dryness. Each sample was dissolved in 10 mL 2% nitric acid, left for 30 minutes, then the acid decanted into a 15 mL polypropylene vial. After addition of indium spikes (discussed below), samples were filtered using an acid washed Whatman or VWR brand polypropylene 0.45 μm syringe filter, and a non-acid-washed Normject 10 mL polypropylene syringe. Reagent blanks and acid blanks were filtered in the same manner and showed no significant indium contamination from this process, and standards showed that indium was not lost significantly during filtration. This acid digestion should liberate all of the indium in oxides, sulfides, sulfates, carbonates, and organic fractions[26,27], leaving only what is bound in silicates, and the silicate fraction of indium is thought to be small[28–30].

Acid-washed teflon beakers and watchglasses were used for these digests, along with acid-washed glass-ribbed watchglasses for taking the samples to dryness. Reagent blanks were run with each sample set, and in most cases were less than 10% of the indium signal. Field blanks – filters collected as though they were samples, but the pump to the air sampler was not run – were digested three separate times and analyzed. Field blanks had comparable signal to reagent blanks, indicating that any contamination came during and after the digestion process, rather than during sampling. Indium signals were corrected by subtracting the reagent blank signal.

Source Emissions Characterization

Zinc smelter emissions

Particulate emissions from a hydrometallurgical zinc smelter in Canada (name not provided by request) were sampled by Environment Canada and supplied to us for the measurement of indium. The samples were collected with a sampling train as described in the EPA Method for Sampling Particulate Matter from a Stationary Source (201A). A single cyclone was used to separate >2.5 μm particles from <2.5 μm particles. The >2.5 μm particles were collected from a catch cup and the interior surfaces of the cyclone walls. The <2.5 μm particles were collected from the probe and filter of the sampling train, downstream of the cyclone, by rinsing these surfaces with deionized water and acetone into glass jars. Samples were then dried.

The sample masses were reported by Environment Canada, and the entire mass of $PM_{2.5}$ supplied was transferred to teflon beakers by rinsing with deionized water. These samples were then dried on a hotplate while covered with acid-washed glass ribbed watchglasses. The samples were digested similarly to the air filters, but double distilled concentrated nitric acid and 70% trace-metal grade perchloric acid (Fisher Chemical TraceMetal Grade) were used. The indium concentration in a reagent blank was less than 7% of the sample indium concentration, and was subtracted during data analysis.

Coal combustion emissions

Several types of coal fly ash samples, representing bituminous, subbituminous, and lignite coal from the U.S. (see Table 2), were obtained from E. Sholkovitz (Woods Hole Oceanographic Institution) and W. Linak (U.S. Environmental Protection Agency). In the potential source areas for our study site (the Midwestern, Mid-Atlantic, and New England states), the primary types of coal burned in 1995 were bituminous (67%) and subbituminous (32%)[31]. The coal fly ash samples were generated by combustion in controlled experiments using a down-fired, refractory-lined furnace rated at 50 kW. The combustion process and sample collection are described in detail in Linak and Miller[32], and were designed to create conditions similar to those in full-scale utility furnaces. Size segregated particulate matter was collected by passing flue gas through a cyclone for size segregation, followed by dilution with clean filtered ambient air to reduce temperature, then collection on teflon-coated glass fiber filters (see Linak et al. 2000 for complete details). These samples have previously been characterized for a variety of metals, but have not been analyzed for indium[32].

These coal fly ash samples were analyzed by Standard Laboratories, Inc., for indium, lead, zinc, and copper using Inductively-Coupled Plasma Mass Spectrometry after digestion with nitric and hydrofluoric acids. ASTM Method D6357 was used for the digestion. In order to account for matrix effects and instrument drift, indium was used as an internal standard during the measurement of lead, zinc, and copper, and rhodium was used as an internal standard for the measurement of indium. Laboratory error of ∼20% relative standard deviation (RSD) was reported, and measurements of lead and copper in NIST Standard 1633b (coal fly ash) were within 5% and 11% of the certified values, respectively, and zinc was within 14% of the reported, but non-certified value. Indium concentrations in this NIST standard have not been certified or published. Concentrations for lead, zinc, and copper in three of these samples were previously measured by Linak et al.[32]. Lead concentrations reported here differ from the Linak et al. values by 3-66% (41% mean RSD); zinc concentrations differ by 13-51% (33% mean RSD); and copper concentrations differ by 11-82% (37% mean RSD). These values are not consistently biased higher or lower than the Linak values.

ICP-MS Analysis

A Fisons PlasmaQuad 2+ Quadrupole Inductively-Coupled Plasma Mass Spectrometer (ICP-MS) was used for metals analysis, with argon as the carrier gas. A 1 ppb indium solution typically shows about 200,000 counts per second (CPS) at a mass to charge ratio of 115, and the instrument has approximately unit mass resolution. Indium occurs naturally as ^{115}In (95.7%) and ^{113}In (4.3%). Sample introduction is via free draw, using a 1000 μL/min nebulizer with attached frit to prevent clogging, and the instrument is run in peak-jumping, pulse counting mode with 200 sweeps per measurement. In order to account for matrix effects and drift of the instrument signal over time, the method of standard additions was used for quantification of total indium[33]. In this method, each sample is split in two, one of those samples is spiked with 0.1 ppb indium, and the samples are run back-to-back on the ICP-MS. Mass to charge ratio 115 was monitored, and testing of potential polyatomic interferences at 115 has shown that there were none present for these sample matrices. There is, however, an isobaric interferent in ^{115}Sn (0.34% of total Sn). The interference is linear and predictable, therefore we monitored ^{117}Sn and ^{118}Sn in order to subtract this interference out of the signal at mass to charge ratio 115[34]. Calculations using the two Sn isotope corrections agree to better than 1%, indicating that this is a reasonable correction and that there are no other important interferences present. The correction for ^{115}Sn were as high as 50% of the total counts at mass to charge ratio 115 for air filters, and <1% for zinc smelter emissions. Samples with a range of concentrations of tin spiked into them showed that indium concentrations could still be analyzed accurately even when ^{115}Sn counts were high relative to ^{115}In.

HYSPLIT Analysis

In order to determine the direction of air that was influencing indium concentrations at the Boston and Rochester locations, the HYbrid Single Particle Langrangian Integrated Trajectory model (HYSPLIT4) from the National Oceanographic and Atmospheric Administration (NOAA)[35–37] was used to generate back trajectories for each day for which indium was measured. A complete description of the model is given in Draxler and Hess[38],[39]. The online version was used to generate back trajectories that ran for 48 hours, each starting at 12:00 PM for the indium measurement date and at a height of 500 m. Trajectories were run starting both at a 10 m height and a 500 m height. The direction of each is the same, although the distance traveled by the 500 m height trajectory is much farther. The 500 m trajectory height is presented here, with the assumption that stack heights of the most likely emitters are > 150 m, and the Sudbury Super Stack, a possible source of indium to these samples, is 380 m. Archived meteorological data from the Nested Grid Model (NGM) database were used, except for several dates when data were missing from this database, at which time the REANALYSIS database was used. Tests showed that these two databases produced similar results.

Indium removal during atmospheric transport (e.g. by gravitational settling or washout by rain) was not taken into consideration when analyzing back trajectories, although rainfall was qualitatively monitored. Here the time of the back trajectory is limited to 48 hours to minimize the influence of settling of the PM_3 fraction.

Correlation of indium with other metals in PM_3

Please see supplementary information for details on the calculations comparing indium:other metal ratios in PM_3 samples.

Results

The average concentration of indium in PM_3 particles in air sampled in this study in the northeastern United States is 2.1 ± 1.6 pg/m^3 (1 standard deviation), with peaks up to 8 pg/m^3 (Fig. 3), and is of a similar magnitude as previous studies of indium in $PM_{2.5}$[17,18]. Normalizing to the total PM_3 mass in the sample, average particle concentrations are 0.2 μg In/g PM_3, with deviations in the New York sites up to 0.95 μg/g. By contrast, Wedepohl[40] reports average indium concentrations in the earth's crust of 0.052 μg/g.

There are significant differences in indium concentrations both geographically and temporally (Fig. 3). One metric of temporal variation at each site is the standard deviation of

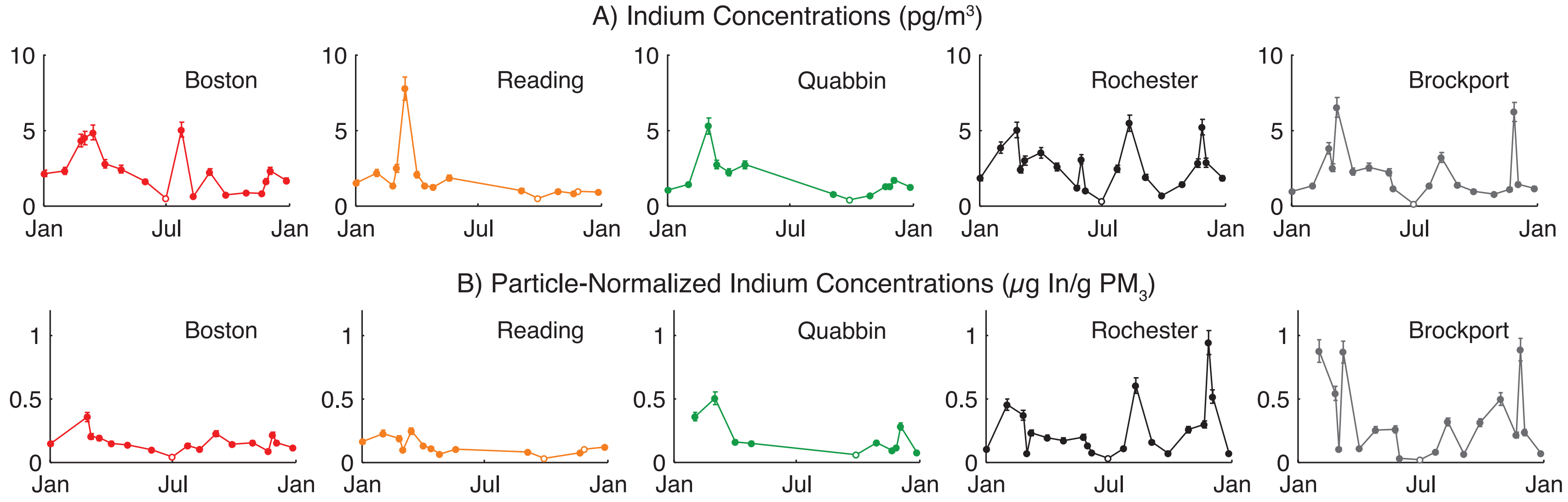

Figure 3: Indium air concentrations (A) and fine particle-normalized indium concentrations (B) vary significantly across five locations in the northeastern United States, and over the course of a year. Colors as in Figure 2: Red = Boston, MA; Orange = Reading, MA; Green = Quabbin Reservoir, MA; Black = Rochester, NY; Grey = Brockport, NY. Hollow data points indicate samples that were below the detection limit. Error bars reflect the method uncertainty of 20%, based on multiple digestions of the same sample.

all data for one location divided by the mean of that data. For air concentrations (pg/m^3) at each location, this relative change in concentrations over the course of a year is at least 56% of the mean (65%, 97%, 73%, 81% and 56% respectively for Boston, Reading, Quabbin, Brockport, and Rochester.) For particle-normalized concentrations (μg/g) at the Massachusetts locations, this relative change is slightly less (46%, 50%, and 74% respectively for Boston, Reading, and Quabbin), while at the New York sites the relative change is slightly higher (93% and 90% for Brockport and Rochester, respectively).

Air concentrations in Boston, Reading, and Quabbin, (urban, suburban, and background locations in Massachusetts) correlate relatively well with one another (Supplementary Fig. S2), suggesting that the major source of indium to these locations is not local, but instead comes from long-range transport. (r = 0.81 for Boston and Quabbin; 0.69 for Boston and Reading; and 0.44 for Reading and Quabbin, low due to one outlier. The correlation coefficient used here, r, is the Pearson product-moment correlation coefficient, which is the covariance normalized by the product of the standard deviation of each sample. An r of 1 denotes perfect correlation. This correlation coefficient is symmetric, meaning that it does not change if the x and y variables are interchanged.) Particle-normalized concentrations for these locations correlate less well than the air concentrations (r = 0.54, 0.42, and 0.48, respectively), as is expected due to less significant deviations from the mean for these normalized concentrations. There are several peaks in the air concentration in Massachusetts samples, in March and July, but they reflect only a small change in particle-normalized concentration. As an example, one can compare each peak to a mean concentration, m*, where * denotes that the mean was calculated excluding the point of interest. For the peak in Reading in March, the air concentration is more than $11\sigma^*$ from m*, where σ^* is the standard deviation calculated excluding the point of interest, whereas the particle-normalized value on the same day is within $2.5\sigma^*$ of m$*$. While peaks in indium concentration suggest that the intensity of the source(s) is changing, this conclusion is not supported when the peak concentrations are normalized by particle mass.

Air concentrations in Rochester and Brockport (urban and rural locations in New York) correlate relatively well with one another ($r = 0.62$), but show a different pattern from the Massachusetts sites ($r = 0.23$) (Supplementary Fig. S2). Particle normalized concentrations for the New York sites also correlate relatively well with one another ($r = 0.64$), and interestingly show some correlation with the eastern Massachusetts sites ($r = 0.51$). The concentration of particulate indium (pg/m^3) in these sites varies significantly throughout the year, and upon normalization to fine particle mass (μg/g), most of these peaks are retained. Peaks in the particle-normalized indium concentration suggest that there is a different source of indium to this area on the peak days. Alternatively, the low particle-normalized concentrations could reflect a dilution of high particle-normalized source contributions with low particle-normalized source particles.

There is no apparent seasonality to these data, unlike was found for other components of these samples such as organic carbon and mutagenicity[22]. Additionally, even at the smallest sampling interval of 6 days, data points are not well autocorrelated (correlations typically <0.25, except for Quabbin air concentrations (0.31) and Reading particle-normalized concentrations (0.39)), indicating that meteorological conditions that affect indium concentrations change more quickly than 6 days.

Source emissions characterization

Zinc smelter emissions

Zinc smelter emissions of $PM_{2.5}$ from a hydrometallurgical smelter operation have an indium concentration of 52 μg/g (Table 1). This is similar to average indium concentrations in sphalerite ((Zn,Fe)S) of 1-100 μg/g[4]. This is significantly higher than even the peak concentrations of indium seen in New York of 1.1 μg/g.

Table 1: Metal composition of zinc smelter $PM_{2.5}$ emissions (concentrations in μg/g).

	Process A <2.5 μm
In	52
V	<39
Mn	4000
Cu	<2600
Zn	96400
As	209
Cd	255
Ba	<19
Pb	<66

Coal fly ash

Coal fly ash has concentrations of indium of 0.14-0.34 μg/g in the <2.5 μm fraction and 0.03-0.09 μg/g in the >2.5 μm fraction (Table 2). Uncombusted coal has an average indium concentration of 0.1 μg/g[4]. Lignite, subbituminous, and bituminous coal fly ash only differ in their indium content by a factor of 3. In the potential source areas for our study site (the Midwestern, Mid-Atlantic, and New England states), the primary types of coal burned in 1995 were bituminous (67%) and subbituminous (32%)[31]. The indium concentration in these fly ashes is comparable to mean concentrations of indium seen in New York and Massachusetts of 0.2 μg/g.

Discussion

Tracking the source of indium to atmosphere

Source Tracking: Concentration Patterns and Wind Direction

For the Rochester and Brockport data, atmospheric back trajectories show air to be coming from the north or northwest on 6 out of 7 of the days when indium concentrations are highest

Table 2: Metal composition of coal fly ash (concentrations in μg/g)

	W. KY - Bituminous		OH - Bituminous		MT - Subbituminous		ND - Lignite		PA - Bituminous		UT - Bituminous		NIST 1633b Coal Fly Ash	NIST 1649a Urban Dust
μg/g	<2.5 μm	>2.5 μm	<2.5 μm	>2.5 μm	<2.5 μm	>2.5 μm	<2.5 μm	>2.5 μm	<2.5 μm	>2.5 μm	<2.5 μm	>2.5 μm		
Cu	86	61	82	65	208	118	107	46	73	134	75	193	97	370
In	0.17	0.08	0.28	0.08	0.34	0.09	0.14	0.06	0.26	0.06	0.15	0.03	0.17	0.35
Pb	76.6	44.2	153	50.7	62.5	21.5	60.9	18.4	71	32.1	41.9	12.2	63.4	11600
Zn	655	336	269	107	218	57	166	66	139	249	68	20	173	1390
From Linak et al. 2000:														
As	132	68.4			62.7	45.3					89	59.6		
Cd	8.7	3.3			<1.0	<1.0					<1.0	<1.0		
Cr	132	108			17.5	19.6					110	78.7		
Cu	73.5	51.9			96.7	55.6					95.8	51.5		
Fe	76500	88300			4000	3810					16000	14400		
Pb	34.5	16.1			93.2	48.4					40.2	<12.3		
Ni	110	86.2			41.5	29.3					109	39.4		
S (wt %)	1.12	0.46			0.74	0.01					0.68	0.27		
V	356	330			111	84.9					186	123		
Zn	548	265			141	31.9					144	40.3		

(Figs. 4, 5(a)). (0.35 μg/g is used as a somewhat arbitrary cutoff for a 'peak' value, based on the average concentrations for Rochester and Brockport of 0.25 and 0.3 μg/g respectively). The days when particle-normalized concentrations are <0.35 μg/g in both locations, back trajectories show that air is coming from the west, southwest, or south on 9 of 11 of the days. Based on the source map in Figure 4 (reproduced larger in Figure S1), a trajectory from the N/NW suggests smelter influence, whereas a trajectory from the W/SW suggests coal influence. Note that Canada does not rely heavily on coal-fired power plants; in eastern Canada, Quebec uses primarily hydropower (>94%), and Ontario relies on nuclear (50-60%) and hydropower ($\sim$20%)[41]. The coal-fired power plants that were in operation in Canada in 1995 are mapped in Figures 4 and S1.

For the Boston site, back trajectories show air coming from the north/northwest and the west/southwest/south on a roughly equal number of days, although there are only three days that have an indium concentration >0.35 μg/g (Fig. 5(b)). Two of these days show air coming from the northwest, whereas one shows air coming from the southwest. The latter sample does not support the hypothesis that elevated In concentrations are always associated with smelter emissions, and we note the presence of a secondary smelter and a coal-fired power plant directly southwest of Boston, on the border of Massachusetts and Rhode Island, as well as multiple incinerators along the east coast (Fig. 4). If smelters are contributing to indium in these samples, the lack of peak concentrations may be due to the further distance of these sites from Canadian smelters, allowing particles emitted from these sources to disperse sufficiently to blend in with the background signal. The presence of peaks in air concentration at the Massachusetts sites despite the relatively constant particle-normalized concentrations suggest that significant variations in these source(s) can occur.

For all 5 sites, these data are consistent with the hypothesis that coal contributes relatively constant low-level concentrations of indium to the atmosphere, due to the predominance of west-to-east wind directions and the large volume of coal consumed. When wind blows from the north, however, smelters can contribute a high concentration of indium to

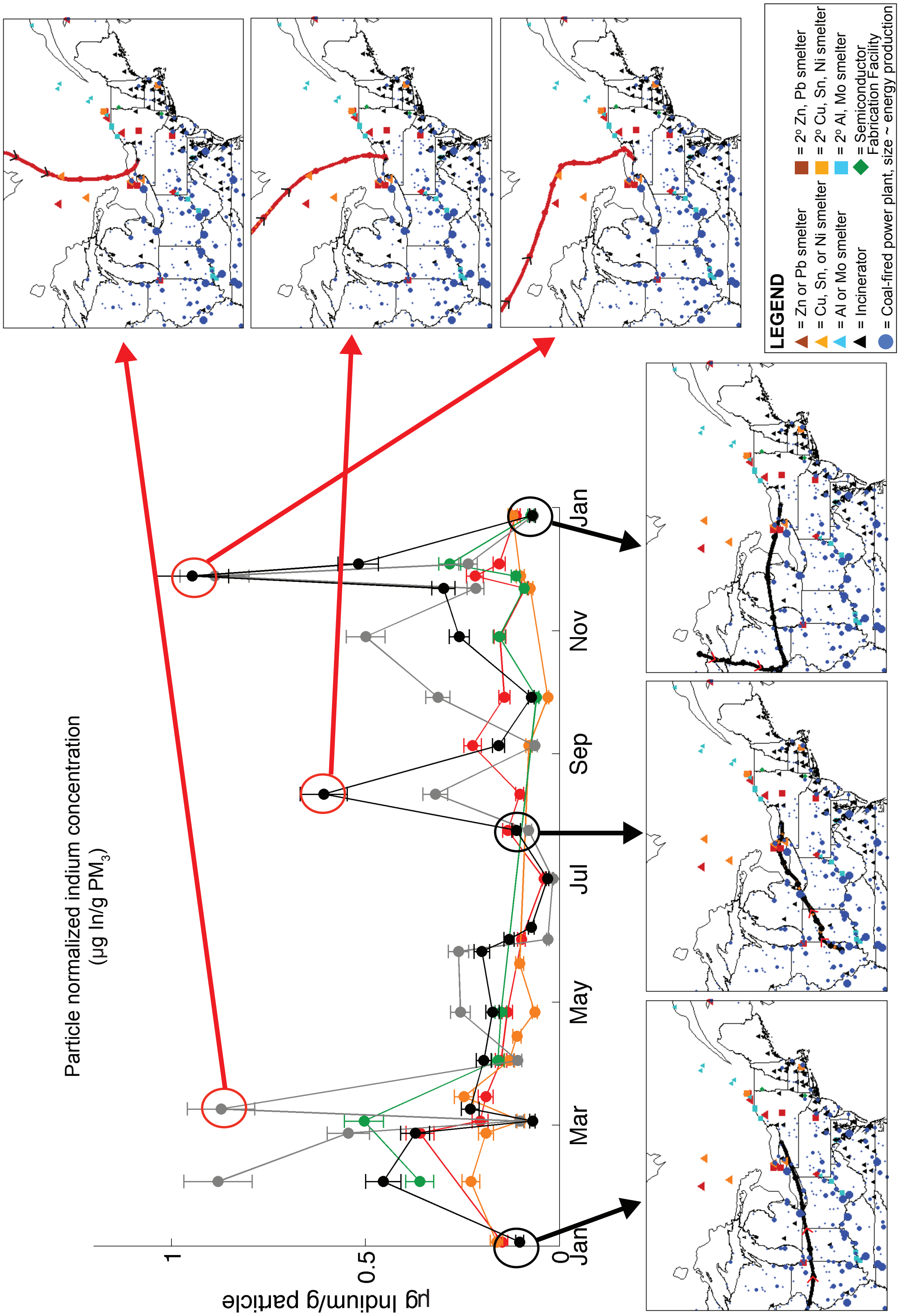

Figure 4: Atmospheric back trajectories generated with the HYSPLIT model show that peaks in particle-normalized indium concentration occur on days when air is coming from the north/northwest. Data point colors consistent with previous figures: Red = Boston, MA; Orange = Reading, MA; Green = Quabbin Reservoir, MA; Black = Rochester, NY; Grey = Brockport, NY. The size of the circles representing coal-fired power plants roughly denote the scale of their energy production. Note that Canada does not rely heavily on coal-fired power plants; those in operation in 1995 are mapped. For enlarged map see Figure S1.

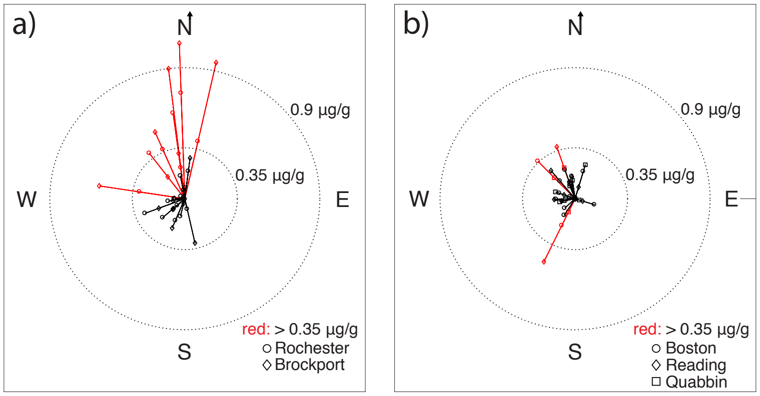

Figure 5: Atmospheric back trajectories generated with the HYSPLIT model for the New York sites (a) show that peaks in particle-normalized indium concentration occur on days when air is coming from the north/northwest. Trajectories generated for the Massachusetts sites (b) show that few peaks occur in particle-normalized indium concentration in these sites, and there is no strong correlation between indium concentration and wind direction. The length of each ray is equal to the magnitude of the particle-normalized indium concentration; red denotes concentrations > 0.35 μg/g. The direction of the ray is the angle from which the wind is traveling at a time of -24 hours.

the atmosphere in the New York sites, and a lower level to the Massachusetts sites, where it has dispersed and been diluted by lower concentration sources. One explanation of the lack of seasonality of indium in atmospheric particles is that, even if coal consumption is mildly seasonal, with as much as 20-25% more consumed during summer and winter than during spring and fall[42], the change in wind direction that brings higher indium concentrations to these sites from smelters is not seasonal, and obscures any small seasonal trends that may be present.

These hypotheses are supported by measurements of indium in coal fly ash and in zinc smelter emissions. The indium concentrations reported for coal fly ash $PM_{2.5}$ (0.14-0.34 μg/g for all types analyzed; 0.15-0.34 μg/g for bituminous and subbituminous, the two main types burned in the study area[31] (Table 2)) are similar to the average indium concentrations of 0.2 μg/g seen in all five locations in this study. Other source emissions will contribute to the overall $PM_{2.5}$ concentration, but coal emissions can be dominant. For example, 30-80% of the total $PM_{2.5}$ in the atmosphere in 16 sites in the eastern United States was attributed to coal combustion[43], suggesting that our hypothesis that coal emissions may account for the low levels seen may not be unreasonable. However, a higher concentration source is required to explain the peaks of indium concentrations. Indium in zinc smelter emissions are of the order of 150-370x higher than in coal fly ash. While the indium concentrations of 52 μg/g in $PM_{2.5}$ (Table 1) are 50x higher than the peak concentrations of indium seen in the New York sites (1.1 μg/g), the mixing of smelter emissions with other lower particle-normalized concentration sources may account for the peak concentrations seen in this study.

Source tracking: Enrichment Factors

In order to determine if these average concentrations are due to dust from direct erosion and transport of crustal material, or whether they come from high-temperature sources, e.g. volcanic activity or industry such as coal-burning or smelting, one can examine indium's enrichment relative to aluminum. Enrichment factors (EF) for indium in our samples ($EF = (In/Al)_{sample}/(In/Al)_{crust}$) are greater than 15 in all but one case (Brockport, July 2), and >1000 in one case, indicating a predominately high-temperature source of indium to the atmosphere in this region rather than dust (Supplementary data, Fig. S3). The enrichment factors in our study are comparable or higher than those found in a study of 6 European cities and one US city that found enrichment factors of 4–140 relative to soil values[30].

For comparison, incinerator emissions have shown enrichment factors for indium of 120–2300[44], lead smelting can result in EFs of 10^5[45,46], and coal fly ash has shown enrichment factors of 3–5 (present study). Indium has been shown to be enriched in volcanic emissions[47–50], although enrichment factors have not been reported. This may be further evidence that the highest concentrations of indium seen in these samples, which have the highest enrichment factors, may be associated with a smelter source, whereas the bulk of the samples with moderate concentrations and moderate enrichment factors, may be associated with a source such as coal emissions.

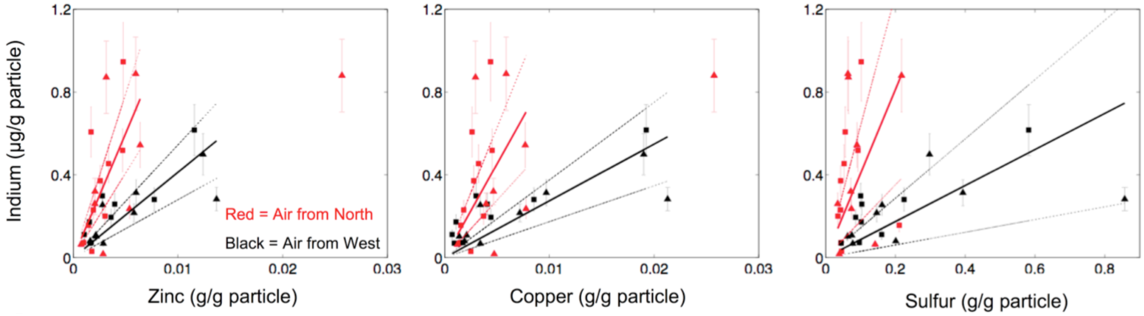

Figure 6: Air from the north has a distinctly different chemical makeup than air from the west. This can be seen in a correlation plot (this figure), in cumulative distribution functions (Fig. S4), and by computing a Kolmogorov-Smirnov statistic (Supplementary Information Methods and Table S2). Solid lines are means for all Monte Carlo-generated regression lines, as described in Supplementary Information. Dotted lines are $\pm 1\sigma$ standard deviations of those regression lines.

Source Tracking: Correlation of Indium with other metals in PM_3

Using the New York sites, and distinguishing between when air is coming from the north (defined as the angle made from a trajectory at -24 hours being between 292.5°and 22.5°, if due north is 0°) and from the west (all other angles, since winds from the south or east are extremely rare), shows that these two air directions carry PM_3 of distinctly different chemical makeup (Fig. 6). Representative plots are shown for Zn, Cu, and S. Pb, Fe, and Ag show similar differences. Plotted are the mean regression for each set of data, forcing the intercept to be zero, and the 1σ standard deviation of this slope.

Cumulative distribution functions for the In:metal (In:M) mass ratios for each of the two air types highlight the difference in distribution between air from the north and air from the west (Supplementary Information Fig. S4). Using these cumulative distribution functions, the Kolmogorov-Smirnov test shows that the two populations are different from one another with more than 85% probability for In:Zn, In:Cu, In:Pb, In:S, In:Fe, and In:Ag mass ratios (Supplementary Methods and Supplementary Information Table S2).

Comparing In:M (where M = Cu, Pb, and Zn) mass ratios from northern air versus western air shows that differences, while statistically significant, are small (Table 3). These

In:M mass ratios are higher in northern air than in western air, but are significantly lower than both zinc smelter emissions and coal fly ash ratios. This suggests that dilution of these emissions with other low In:M particles is occurring. (The In:Cu and In:Zn mass ratios in zinc smelter emissions are significantly higher than in coal fly ash).

Table 3: A comparison of the In:M ratios seen in air samples, source $PM_{2.5}$, and another atmospheric study[19].

	North	West	Zn smelter emissions $PM_{2.5}$	Coal fly ash $PM_{2.5}$	Ratios in Sturges & Barrie N	Ratios in Sturges & Barrie W
In:Cu	0.00006	0.00003	> 0.02	0.002	-	-
In:Pb	0.0003	0.0002	> 0.8	0.003	0.002	0.006
In:Zn	0.00007	0.00005	0.001	0.001	0.003	0.006

Also presented is a comparison of ratios from a detailed study by Sturges and Barrie[19] of indium and other metals in atmospheric particulate matter in Dorset, Ontario. They found high indium concentrations associated with air traveling from the Canadian smelter region north of the study site. The Sturges and Barrie In:M mass ratios are 1–2 orders of magnitude higher than the ratios in the samples for our study. This could be due to Dorset's closer proximity to the smelter sources, differences in the ore smelted at the time of each study, and changes in emissions controls that could alter the size distribution of emitted particles (which may in turn have different metal ratios associated with them).

As a caveat, some care must be taken in comparing these ratios across studies and even across samples, due to differences in method of analysis (e.g. 'partial' digest with nitric and perchloric acids versus 'total' digest with hydrofluoric acid). Nonetheless, the comparison of these ratios is useful, and error induced by the differences in analysis method are likely no higher than uncertainties in these ratios caused by natural variation in source composition, which is significant [e.g. 46].

Constraining indium's fluxes to the atmosphere and deposition

The atmospheric concentrations and source concentrations reported here can be used to further understand the sources and sinks of indium to and from the atmosphere, which remain highly uncertain (Fig. 1).

The indium concentrations measured in coal fly ash and in zinc smelter emissions can be used to estimate total indium emissions from coal combustion and zinc smelting. Estimates for Canada and the United States can be calculated. $PM_{2.5}$ emissions for coal combustion in the United States were estimated to be 85,000 t/yr in 2005[51,52]. In the same year, Canadian $PM_{2.5}$ emissions from all electric utilities were estimated at 8,100 t/yr[53]. Multiplying this by the average indium concentration measured in $PM_{2.5}$ coal fly ash, 0.22 μg In/g $PM_{2.5}$, and doing the same for PM_{10} estimates (Canada + US emissions = 186,000 in 2005 x 0.07 μg In/g PM_{10}) results in an estimate of 33 kg/yr of indium released to the atmosphere from coal combustion in the US and Canada. Global $PM_{2.5}$ emissions estimates for coal are 16 Mt/yr, multiplied by the average indium concentration in $PM_{2.5}$ coal fly ash, 0.067 μg In/g $PM_{2.5}$, suggests a release of 1.1 t/yr. PM_{10} emissions estimates are needed in order to compare this number to the global estimate of indium emissions from coal combustion of 300 t/yr[1], but this 300 t/yr number appears to be an overestimate.

For non-ferrous smelting, $PM_{2.5}$ emissions in the United States were estimated to be 15,803 t/yr in 2011[54]. In 2010, Canadian emissions from non-ferrous smelting and refining were estimated at 1750 t/yr[53]. Assuming that the indium concentration of 52 μg/g measured in $PM_{2.5}$ emissions from a zinc smelter is representative of all non-ferrous smelting (based on typical ore concentrations[4]), then 0.9 tons of indium is released per year with the $PM_{2.5}$ fraction. Concentrations of indium in PM_{10} released from zinc smelting are not yet available, but adding the release associated with PM_{10} will likely not change this estimate by more than 2-3x. Global $PM_{2.5}$ and PM_{10} emissions estimates are needed in order to compare this number to the global estimate of indium emissions from smelting processes of 600 t/yr[1].

Caution must be used when estimating emissions from coal combustion using coal fly ash.

The coal fly ash samples measured for this study may not be representative of actual emitted particles. These samples were collected upstream of emissions controls. Emissions controls tend to remove particles with diameters above 1 μm with better than 99% efficiency, while smaller diameter particles (< 1 μm) are more likely to escape (control efficiencies of 80-90% have been reported)[55]. This smaller size fraction is typically formed by volatilization and subsequent nucleation of coal constituents, which may enrich some metals in this fraction, compared to the bulk $PM_{2.5}$, which can have a makeup more typical of the uncombusted coal[55]. Therefore some care should be taken when extrapolating the concentrations measured for $PM_{2.5}$ fly ash to actual emissions estimates. The smelter stack sample was collected downstream of particulate matter controls, and so should be representative of the chemical makeup of actual emissions.

Deposition is made up of both wet and dry forms, and is calculated by $J = V_d C_a + V_w C_a = C_a(V_d + V_w)$, where J is the total depositional flux (ng/(cm^2-yr)), V_d is the dry depositional velocity, V_w is the wet depositional velocity, C_a is the air concentration, and the total deposition velocity, $V_t = V_d + V_w$. Indium is expected to deposit in a similar way to ^{210}Pb, and ^{210}Pb total depositional velocities of 0.6-1.9 cm/s have been reported, with a 1 cm/s V_t for the northeastern United States[56,57]. Using this range of deposition velocities and an average air concentration for 1995 (the year air filter samples were collected) of 2.3 pg/m^3, an indium flux of 40–140 pg/(cm^2-yr) can be calculated. The indium deposition observed to Thoreau's Bog, a peat bog in Massachusetts near the sites sampled in the present study, was 150 pg/(cm^2-yr) in the year 1995[21]. However, PM_{10} should be included in this calculation, and analysis of a limited number of PM_{3-10} samples show that indium concentrations are roughly equal to those in PM_3 (Fig. S5, Supplementary Information). If PM_{3-10} concentrations are used in this calculation, such that total $C_a = PM_{3-10} + PM_3$ $\sim$5 pg/m^3, an indium flux of 90–300 pg/(cm^2-yr) is calculated. The estimated flux to Thoreau's Bog (150 pg/(cm^2-yr)) falls within this range.

The deposition rates suggested from the peat core can also be used to inform the wide range of depositional estimates (1,000-100,000 t indium/yr) in Fig. 1. Assuming that the deposition seen in Thoreau's Bog is applicable globally (although this is likely a poor assumption), multiplying by the surface area of the earth results in a global flux of ∼770 t/yr. This is slightly less than the lowest box model estimate, and may be due to this core not being representative globally—particulate emissions controls in the US and Canada may cause the northeastern United States to have lower indium concentrations than less-developed countries—or due to an overestimation of atmospheric inputs and depositional fluxes in the box model.

As indium-containing particles are deposited to surface waters, their aqueous behavior will depend on a variety of factors, including the chemistry of the water and the speciation of indium deposited. Indium's aqueous behavior is relatively poorly understood[1,58,59]. In general, one would expect indium to primarily remain associated with particles due to its relatively low solubility and high particle-reactivity, except at low pH (<4.5) or high concentrations of ligands such as humic substances, F^-, or Cl^-[1,59].

Future Research Needs

There is still much to be learned about natural and industrial sources of indium to the atmosphere, and its subsequent cycling and deposition. The most pressing need is a method to track the source of indium to environmental samples collected. This may require more in-depth investigations of the composition of particles emitted from various sources, including other chemical constituents and the chemical speciation of indium in these particles. Source tracking may also be aided by an investigation of indium's isotopic system – its two isotopes are 5% and 95% abundant, making them well-suited to isotopic studies. However, scarcely nothing is known about the extent to which indium may fractionate in various environmental and industrial processes, and only large differences in isotopic fractionation will be measurable due to the low concentrations of indium in environmental samples. Ultimately, better source-tracking methods will allow us to determine what impact humans have had on the natural cycling of indium. Finally, it is important to understand the influence of indium deposition on aquatic indium concentrations to fully assess the impact of human activities on the environment.

Conflicts of Interest

There are no conflicts to declare.

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References

(1) White, S. J. O.; Hemond, H. F. The Anthrobiogeochemical Cycle of Indium: A Review of the Natural and Anthropogenic Cycling of Indium in the Environment. *Critical*

Reviews in Environmental Science & Technology **2012**, *42*, 155–186.

(2) U.S. Geological Survey, In *Historical statistics for mineral and material commodities in the United States (2014 version): U.S. Geological Survey Data Series 140, accessed 2019 at http://minerals.usgs.gov/minerals/pubs/historical-statistics/*; Kelly, T. D., Matos, G. R., Eds.; Indium end-use statistics [through 2003; last modified September 1, 2005]; US Geological Survey, 2014; p 4.

(3) U.S. Geological Survey, In *Historical statistics for mineral and material commodities in the United States (2014 version): U.S. Geological Survey Data Series 140, accessed 2019 at http://minerals.usgs.gov/minerals/pubs/historical-statistics/*; Kelly, T. D., Matos, G. R., Eds.; Indium statistics [through 2015; last modified January 19, 2017]; US Geological Survey, 2014; p 4.

(4) Smith, I. C.; Carson, B. L.; Hoffmeister, F. *Trace metals in the environment: Volume 5 - Indium*; Ann Arbor Science Publishers: Ann Arbor, Mich., 1978; p 552.

(5) EPA, History of PM Standards, Available online: epa.gov/pm/history.html. 2012.

(6) EPA, History of the Clean Air Act. 2012.

(7) Minerals and Metals Division, National Office of Pollution Prevention, Environment Canada, *Multi-pollutant Emission Reduction Analysis Foundation (MERAF) for the Base Metals Smelting Sector*; Final Report, 2002.

(8) Homma, T.; Ueno, T.; Sekizawa, K.; Tanaka, A.; Hirata, M. Interstitial pneumonia developed in a worker dealing with particles containing indium-tin oxide. *Journal of Occupational Health* **2003**, *45*, 137–139.

(9) Homma, S.; Miyamoto, A.; Sakamoto, S.; Kishi, K.; Motoi, N.; Yoshimura, K. Pulmonary fibrosis in an individual occupationally exposed to inhaled indium-tin oxide. *European Respiratory Journal* **2005**, *25*, 200–204.

(10) Nakano, M.; Omae, K.; Tanaka, A.; Hirata, M.; Michikawa, T.; Kikuchi, Y.; Yoshioka, N.; Nishiwakii, Y.; Chonan, T. Causal Relationship between Indium Compound Inhalation and Effects on the Lungs. *Journal of Occupational Health* **2009**, *51*, 513–521.

(11) Chonan, T.; Taguchi, O.; Omae, K. Interstitial pulmonary disorders in indium-processing workers. *European Respiratory Journal* **2007**, *29*, 317–324.

(12) Hamaguchi, T.; Omae, K.; Takebayashi, T.; Kikuchi, Y.; Yoshioka, N.; Nishiwaki, Y.; Tanaka, A.; Hirata, M.; Taguchi, O.; Chonan, T. Exposure to hardly soluble indium compounds in ITO production and recycling plants is a new risk for interstitial lung damage. *Occupational and Environmental Medicine* **2008**, *65*, 51–55.

(13) Maenhaut, W.; Zoller, W. H. Determination of Chemical Composition of South Pole Aerosol by Instrumental Neutron-Activation Analysis. *Journal of Radioanalytical Chemistry* **1977**, *37*, 637–650.

(14) Rahn, K. A. *The Chemical Composition of the Atmospheric Aerosol*; Technical Report, 1976.

(15) Ragaini, R. C.; Ralston, H. R.; Roberts, N. Environmental trace metal contamination in Kellogg, Idaho, near a lead smelting complex. *Environmental Science & Technology* **1977**, *11*, 773–781.

(16) Chen, H.-W. Characteristics and risk assessment of trace metals in airborne particulates from a semiconductor industrial area of northern Taiwan. *Fresenius Environmental Bulletin* **2007**, *16*, 1288–1294.

(17) Olmez, I.; Gullu, G.; Ames, M.; Huang, X.; Keskin, S.; Che, J.; Wakefield, A.; Gone, J. K.; Beal, J. *Upstate New York Trace Metals Program, Vol. II ”Trace Metals”*; 1997.

(18) Ames, M. R.; Gullu, G.; Beal, J.; Olmez, I. Receptor modeling for elemental source contributions to fine aerosols in New York State. *Journal of the Air & Waste Management Association* **2000**, *50*, 881–887.

(19) Sturges, W. T.; Barrie, L. A. The use of Stable Lead 206/207 Isotope Ratios and Elemental Composition to Discriminate the Origins of Lead in Aerosols at a Rural Site in Eastern Canada. *Atmospheric Environment* **1989**, *23*, 1645–1657.

(20) Rahn, K. A.; Lowenthal, D. H. Pollution Aerosol in the Northeast - Northeastern-Midwestern Contributions. *Science* **1985**, *228*, 275–284.

(21) White, S. J. O.; Keach, C.; Hemond, H. F. Atmospheric Deposition of Indium in the Northeastern United States: Flux and Historical Trends. *Environmental Science & Technology* **2015**, *49*, 12705–12713.

(22) Pedersen, D. U.; Durant, J. L.; Penman, B. W.; Crespi, C. L.; Hemond, H. F.; Lafleur, A. L.; Cass, G. R. Seasonal and spatial variations in human cell mutagenicity of respirable airborne particles in the northeastern United States. *Environmental Science & Technology* **1999**, *33*, 4407–4415.

(23) Pedersen, D. U.; Durant, J. L.; Penman, B. W.; Crespi, C. L.; Hemond, H. F.; Lafleur, A. L.; Cass, G. R. Human-cell mutagens in respirable airborne particles in the northeastern United States. 1. Mutagenicity of fractionated samples. *Environmental Science & Technology* **2004**, *38*, 682–689.

(24) Pedersen, D. U.; Durant, J. L.; Taghizadeh, K.; Hemond, H. F.; Lafleur, A. L.; Cass, G. R. Human cell mutagens in respirable airborne particles from the Northeastern United States. 2. Quantification of mutagens and other organic compounds. *Environmental Science & Technology* **2005**, *39*, 9547–9560.

(25) Salmon, L. G.; Cass, G. R.; Pedersen, D. U.; Durant, J. L.; Gibb, R.; Lunts, A.;

Utell, M. *Determination of fine particle and coarse particle concentration and chemical composition in the north-eastern United States, 1995*; 1999.

(26) Deis, L. F. *CRC handbook of chemistry and physics (89th edition)*; CRC Press: Cleveland, Ohio, 2009.

(27) Schaider, L. A.; Senn, D. B.; Brabander, D. J.; McCarthy, K. D.; Shine, J. P. Characterization of zinc, lead, and cadmium in mine waste: Implications for transport, exposure, and bioavailability. *Environmental Science & Technology* **2007**, *41*, 4164–4171.

(28) Greenberg, R. R.; Gordon, G. E.; Zoller, W. H.; Jacko, R. B.; Neuendorf, D. W.; Yost, K. J. Composition of particles emitted from the Nicosia municipal incinerator. *Environmental Science & Technology* **1978**, *12*, 1329–1332.

(29) Greenberg, R. R.; Zoller, W. H.; Gordon, G. E. Composition and size distributions of particles released in refuse incineration. *Environmental Science & Technology* **1978**, *12*, 566–573.

(30) Heindryckx, R.; Dams, R. Chemical-Analysis of Atmospheric Aerosols by Instrumental Neutron-Activation. *Progress in Nuclear Energy* **1979**, *3*, 219–252.

(31) Energy Information Administration, *Electric Power Monthly, December 1996, accessed February 2019 at https://www.eia.gov/electricity/monthly/backissues.php*; December 1996.

(32) Linak, W.; Miller, C. Comparison of particle size distributions and elemental partitioning from the combustion of pulverized coal and residual fuel oil. *Journal of the Air & Waste Management Association* **2000**, *50*, 1532–1544.

(33) Thomas, R. *Chapter 13: Methods of Quantitation*, third edition ed.; Practical Guide to ICP-MS: A Tutorial for Beginners; CRC Press, 2013; pp 123–132.

(34) Thomas, R. *Chapter 14: Review of Interferences*, third edition ed.; Practical Guide to ICP-MS: A Tutorial for Beginners; CRC Press, 2013; pp 133–143.

(35) Draxler, R. R. HYSPLIT4 *User's Guide*; NOAA Tech Memo ERL ARL-230, 1999.

(36) Draxler, R. R.; Rolph, G. D. HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website. 2012.

(37) Rolph, G. D. Real-time Environmental Applications and Display sYstem (READY) Website. 2012.

(38) Draxler, R. R.; Hess, G. D. An overview of the HYSPLIT4 modeling system of trajectories, dispersion, and deposition. *Aust. Metor. Mag.* **1998**, *47*, 295–308.

(39) Draxler, R. R.; Hess, G. D. *Description of the* HYSPLIT4 *modeling system*; NOAA Tech. Memo ERL ARL-224, 1997.

(40) Wedepohl, K. H. The Composition of the Continental-Crust. *Geochimica et Cosmochimica Acta* **1995**, *59*, 1217–1232.

(41) Statistics Canada, Table 25-10-0020-01 - Electric power, annual generation by class of producer. Accessed February 2019 at https://www150.statcan.gc.ca/t1/tbl1/en/tv.action?pid=2510002001. **2017**,

(42) Energy Information Administration, *Monthly Energy Review, January 2019, accessed February 2019 at https://www.eia.gov/totalenergy/data/monthly/*; January 2019.

(43) Coutant, B.; Kelly, T.; Ma, J.; Scott, B.; Wood, B.; Main, H. *Source Apportionment Analysis of Air Quality Monitoring Data: Phase 1, Report for the Mid-Atlantic/Northeast Visibility Union and Midwest Regional Planning Organization*; 2002.

(44) Greenberg, R. R. A Study of Trace Elements Emitted on Particles from Municipal Incinerators. 1976.

(45) Reff, A.; Bhave, P. V.; Simon, H.; Pace, T. G.; Pouliot, G. A.; Mobley, J. D.; Houyoux, M. Emissions Inventory of PM(2.5) Trace Elements across the United States. *Environmental Science & Technology* **2009**, *43*, 5790–5796.

(46) EPA, SPECIATE Version 4.3. 2011.

(47) Hinkley, T. K.; Lecloarec, M. F.; Lambert, G. Fractionation of Families of Major, Minor, and Trace-Metals Across the Melt Vapor Interface in Volcanic Exhalations. *Geochimica et Cosmochimica Acta* **1994**, *58*, 3255–3263.

(48) Hinkley, T. K.; Lamothe, P. J.; Wilson, S. A.; Finnegan, D. L.; Gerlach, T. M. Metal emissions from Kilauea, and a suggested revision of the estimated worldwide metal output by quiescent degassing of volcanoes. *Earth and Planetary Science Letters* **1999**, *170*, 315–325.

(49) Hinkley, T. K.; Matsumoto, A. Atmospheric regime of dust and salt through 75,000 years of Taylor Dome ice core: Refinement by measurement of major, minor, and trace metal suites. *Journal of Geophysical Research-Atmospheres* **2001**, *106*, 18487–18493.

(50) Matsumoto, A.; Hinkley, T. K. Trace metal suites in Antarctic pre-industrial ice are consistent with emissions from quiescent degassing of volcanoes worldwide. *Earth and Planetary Science Letters* **2001**, *186*, 33–43.

(51) Drukenbrod, J. *1970 - 2011 Average annual emissions, all criteria pollutants in MS Excel - October 2011,*; 2012.

(52) Drukenbrod, J. *PM2.5 Filterable and PM10 Filterable emissions trends for Electric Generating Utilities for 1970 to 2005 - August 2008*; 2012.

(53) Environment Canada, National Pollutant Release Inventory, Available online: ec.gc.ca/inrp-npri/. 2012.

(54) US EPA, *2011 National Emissions Inventory (NEI) Data; accessed at https://www.epa.gov/air-emissions-inventories/2011-national-emissions-inventory-nei-data, February 2019.*; 2013.

(55) Linak, W. personal communication. 2008.

(56) Baskaran, M. Po-210 and Pb-210 as atmospheric tracers and global atmospheric Pb-210 fallout: A review. *Journal of environmental radioactivity* **2011**, *102*, 500–513.

(57) Turekian, K. K.; Benninger, L. K.; Dion, E. P. Be-7 and Pb-210 Total Deposition Fluxes at New-Haven, Connecticut and at Bermuda. *Journal of Geophysical Research-Oceans and Atmospheres* **1983**, *88*, 5411–5415.

(58) White, S. J. O.; Hussain, F. A.; Hemond, H. F.; Sacco, S. A.; Shine, J. P.; Runkel, R. L.; Walton-Day, K.; Kimball, B. A. The precipitation of indium at elevated pH in a stream influenced by acid mine drainage. *Science of The Total Environment* **2017**, *574*, 1484–1491.

(59) Wood, S. A.; Samson, I. M. The aqueous geochemistry of gallium, germanium, indium and scandium. *Ore Geology Reviews* **2006**, *28*, 57–102.

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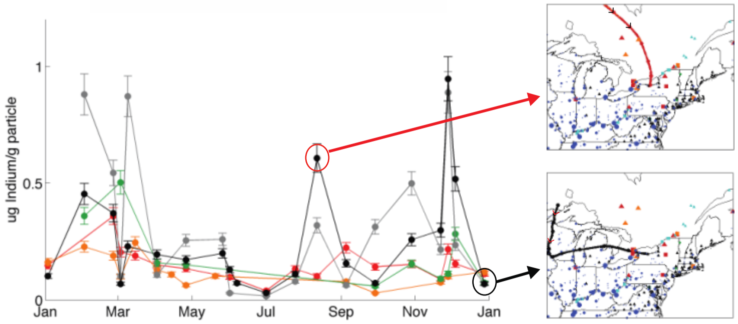

Atmospheric indium is dominated by human emissions, primarily from coal combustion and the smelting of lead, zinc, and other metal sulfides.