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Metal Concentrations and Source Apportionment of PM_{2.5} in Chiang Rai and Bangkok, Thailand during a Biomass Burning Season

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ABSTRACT: One of the persistent environmental problems in the provinces of northern Thailand is severe air pollution during the dry season because of open vegetation burning by farmers for land clearance purpose. Aerosol optical depth and Ångström exponent data from MODIS-Terra satellite indicated that from mid-March to April, 2019, entire Thailand was covered with a high concentration of fine-sized aerosols. Trace metal concentrations of PM_{2.5} collected from Chiang Rai in northern Thailand and Bangkok in southern Thailand between January and April 2019 were analyzed. Average concentrations of crustal metals such as Al, Ca, and Fe are higher in Chiang Rai compared to that in Bangkok. The Fe/Al ratio in Chiang Rai decreases from 1.65 during the onset of haze to 0.87 during the peak haze approaching a crustal ratio of 0.48. In contrast, Bangkok has higher Na, Mg, and Zn with an average Na/Mg ratio of 6.07 indicative of a sea spray (Na/Mg ~ 8) origin. Principal component analysis identifies three possible sources in Chiang Rai: (1) crustal dust and biomass burning, (2) industrial source, and (3) refuse incineration mixed with road dust; and for Bangkok (1) natural background, industrial emissions, and coal combustion, (2) traffic emission, and (3) sea spray. The ranges of Pb isotope ratios in the bulk fraction of PM_{2.5} in Chiang Rai (²⁰⁶Pb/²⁰⁷Pb = 1.1445–1.1657 and ²⁰⁸Pb/²⁰⁷Pb = 2.4244–2.4468) and Bangkok (²⁰⁶Pb/²⁰⁷Pb = 1.1343–1.1685 and ²⁰⁸Pb/²⁰⁷Pb = 2.4138–2.4450) are not significantly different. However, in a time series plot, ²⁰⁶Pb/²⁰⁷Pb ratios in Chiang Rai follow PM_{2.5} during the peak burning season and correlate well with the Al/Pb ($r^2 = 0.61$) ratios, indicating that at least part of the Pb is derived from crustal dust during peak fire. Using a binary mixing model, the most radiogenic Pb isotopes in Chiang Rai during the peak haze can be explained by ~5 to 30% mixing of crustal dust with ~35–40% biomass burning generated aerosols with the background. From the trace metal systematics and Pb isotope ratios, it is evident that (1) during the biomass burning season, trace metals from Chiang Rai are not transported down south to Bangkok and (2) in addition to metals released from biomass burning, the raging fire remobilizes crustal dust that forms an important source of Pb and other trace metals in the Chiang Rai aerosol.

KEYWORDS: biomass burning season, PM_{2.5}, aerosol optical depth, angstrom exponent, trace element, Pb isotope ratios

INTRODUCTION

In Southeast Asia, countries such as Indonesia, Cambodia, Vietnam, Laos, Myanmar, and Thailand burn biomass for land clearing during the slash and burn agricultural waste creating severe air pollution.^{1,2} Particulate matter (PM) generated from biomass burning has complex physicochemical properties. They are mixtures of polycyclic aromatic hydrocarbons (PAHs), carbonaceous (black and organic carbon) and nitrogenous compounds, organic and inorganic ions, and metals to name a few.^{3–5} Metals bound to the breathable fraction of the PM (PM_{2.5}) are of particular concern as the metals get deposited in the lower airways of the lungs and eventually mixes with the blood stream.^{6,7} In the Upper Silesia in Poland, high levels of Cd and Pb emissions caused an increase of spontaneous abortion in women during the first 3 months of pregnancy who were living close to the emission sources.⁸ Once emitted, the trace metals

can get deposited on soils, fresh water, and marine ecosystems surrounding emission sources, as well as “en route” deposition during transport that can have far-reaching environmental impacts. Fe released from Indonesian wildfires stimulated a harmful algal bloom that caused extensive coral mortality off Sumatran coast.⁹ Fe-rich aerosols deposited over remote oceanic regions can augment photosynthesis, thus affecting marine biogeochemistry.¹⁰ Because of a long residence time (0.5–2 years) of elemental Hg in the atmosphere, industrial

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Figure 1. Aerosol sampling site and wind rose diagram to show the wind direction during January to April 2019 (A: wind rose at Chiang Rai and B: wind rose at Bangkok).

emissions in Asia were found to be a major source of Hg in rainwater that falls along the California coast.¹¹ Besides the essential nutrients (e.g., iron and nitrogen compounds), PM-bound micronutrients (Zn, Cu, Mn, Mo, B, Ni, Se, etc.) can be very important both in marine and terrestrial ecosystems.^{12,13}

Wildfires can lead to crustal dust entrainment by desiccating the soil and subsequently uplifting the dust by fire-related near-surface strong wind.^{14,15} Mineral dust can control the atmospheric radiation budget and affect climate changes.¹⁶

There have been several studies on source apportionment of metals in PM generated from biomass burning in Southeast Asia;^{3,5,17–19} however, none of the studies used isotope ratios as a “fingerprinting” tool. Lead (Pb) isotopes are an efficient tool for tracing the sources of Pb pollution^{20,21} as Pb isotopes do not fractionate during industrial and environmental processes and preserve the source signature even after degradation, processing, and transportation.²² Several previous studies from South and Southeast Asia used Pb isotopic composition of atmospheric aerosol to understand the sources of Pb.^{21,23–26} The identified Pb sources include industrial emission in Kanpur, India,²⁶ Middle Eastern dust storm over Delhi, India,²⁵ coal combustion and industrial emission in Kolkata, India,²⁴ natural Pb, historic/remnant leaded petrol and present-day industrial and incinerated waste in Singapore,²³ and industrial emission in Bangkok, Thailand.²¹ However, none of the studies investigated Pb sources using isotopes during biomass burning.

The fire season in northern Thailand generally occurs during the months of February to April. Biomass (agricultural wastes of sugarcane, rice straw, and other crops) is burnt prior to the harvest season to quickly clear land and prepare the fields for the next crop cycle.² Fire-related air pollution peaks in March and April in many provinces such as Lampang, Lamphun, Phrae, Nan, Mae Hong Son, Phayao, Uttaradit, Chiang Mai, and Chiang Rai in northern Thailand.²⁷ Chiang Rai is the northernmost province of Thailand sharing borders with Laos

and Myanmar. For 9–10 months in a year, Chiang Rai has a pristine atmosphere, which drastically changes during the burning season. Several studies on fire-related air pollution in northern Thailand primarily focused on quantifying PAHs, which are significantly higher during the haze season.^{28,29} Remote-sensing satellite data were used to monitor carbon monoxide (CO) and PM₁₀ that showed a significant correlation with the forest fire hotspot counts, especially in the rural areas.³⁰ Furthermore, several studies reported regional scale mapping of fire-related near-ground PM₁₀ concentrations.^{31,32}

To the best of our knowledge, none of the previous studies investigated metal emissions during the burning season and tracked the long-range transportation of released metals from northern Thailand. Here, we study trace element compositions of the PM_{2.5} generated during crop burning along with lead (Pb) isotope ratios to understand the sources (biomass vis a vis crustal dust) and the transportation pattern of the air pollution plume. MODIS-Terra aerosol optical (AOD) at 550 nm and Ångström exponent (AE) for 550–860 nm were used to investigate spatiotemporal patterns in regional aerosol loading over Thailand for January–April 2019. Monthly variations in air mass forward trajectories over Chiang Rai were examined to understand the dispersion pattern of the atmospheric aerosols. Backward trajectories over Bangkok were computed to identify the potential dust emission sources and to determine whether burning-related air pollution reached far down south to Bangkok.

METHODOLOGY

Sampling. Aerosol samples were collected from two different geographic locations in Thailand, Bangkok (13.83°N, 100.53°E) and Chiang Rai (19.85°N, 99.81°E) between January and April 2019 (Figure 1). Chiang Rai is the northernmost province of Thailand, approximately 800 km north of Bangkok. The atmospheric circulation of Thailand is characterized by the

monsoon system. Cool dry continental winds prevail during the northeast monsoon (October–February) season that transports air pollution from distant areas as opposed to the southwest monsoon (May–September), which is generally maritime and clean. Air pollution in northern Thailand due to burning of agriculture wastes, forest fire, and waste incineration has been recognized as smog crisis during the dry season from January to April every year since 2007.³³ In 2019, Thailand began to experience a haze from February that lasted until the end of April, peaking in March and April, which is the official crop burning season in Chiang Rai.³⁴ We collected nonhaze samples till 20th February, after which the hazy days commenced. Generally during January to April, wind blows from north–northeast thus transporting the pollution plume down south. However, the wind rose diagram shows southeast and southwest as the dominant wind directions in Chiang Rai though northerly winds were present for some days during the sampling period (Figure 1). In Bangkok, the dominant wind direction was from south between January and April 2019.

For the purpose, PM_{2.5} samples were collected on 47 mm PTFE filters with personal modular impactor PM_{2.5} (PMI, SKC Inc., USA) connected to a sampling pump (Gilian, AirCon-2) at a flow rate of 10 L/min. Samples were collected for 24 h from 6 AM, once every week. In Chiang Rai, the pump was placed on the roof top of a building at a height of ~9 m above ground level (AGL). In Bangkok, the pump was placed on 4th floor bridge connection of Khum-Watcharabol and Geology buildings, Chulalongkorn University, approximately ~22 m AGL. Before collecting the samples, the Teflon filters were cleaned with 1 N HCl at 140 °C for 2 h, washed in ultrapure water several times, and dried in an oven. The filter samples were stored in a desiccator before sampling. Post collection, the filters were immediately sealed in the Petri dishes and stored inside the desiccator. Field blanks were collected by placing the Teflon filter in the filter cartridge without turning on the pump and the filter was removed after ~5 min, approximately the time taken to change the sample filters. The blank filters were stored in the same way as the sample filters until further chemical analysis.

Satellite Data and Trajectory Modeling. MODIS-Terra Collection 6.1, Level-2 product (MOD04_L2) based on the Dark Target and Deep Blue algorithms³⁵ was downloaded at a spatial resolution of 10 km from <https://ladsweb.modaps.eosdis.nasa.gov/> for the period of January–April 2019 and a combined land and ocean AOD product centered at 550 nm was extracted. AOD centered at 550, 860, and 2100 nm over the ocean and AOD centered at 412, 470, and 650 nm over the land were used to derive combined AE over the spectral 550–860 nm range over land and ocean.

The potential location of the emission source for Bangkok was inferred by back-tracing hourly air-mass trajectories at 750 m height above mean sea-level for 72 h (3 days) using the hybrid single-particle Lagrangian integrated trajectory (HYSPLIT) model.³⁶ Similarly, hourly forward trajectories were computed for Chiang Rai to determine the dispersion of pollutants over a period of 120 h (5 days) using HYSPLIT at 750 m height above mean sea-level. Trajectory analysis was used to understand the atmospheric transport patterns and whether burning-related air pollution reached the capital city of Bangkok. Cluster analysis was then carried out to assemble the trajectories into three or four major groups based on the wind speed and direction to estimate the median trajectories for each month.

Metal Analysis. All chemical analyses were conducted in a class 1000 clean chemistry lab at the Earth Observatory of

Singapore, Nanyang Technological University. Pekney and Davidson (2004) used 0.5% HF (~0.30 M HF) to dissolve the silicate fraction in aerosols and calculated that less than 0.1% HF (~0.06 M HF) is enough to completely dissolve 180 µg of SiO₂ present as crustal dust on aerosol filters.³⁷ Other studies also used a dilute mixture of HF/HCl (4.5 M HF/1 M HCl) or HF/HNO₃ for complete extraction of trace elements from atmospheric aerosol.³⁸ Assuming a large fraction of PM_{2.5} can come from crustal dust in our samples, we decided to use ~10 times more concentrated HF as compared to Pekney and Davidson (2004). Hence, 50% (v/v) of 3:1 HNO₃/HF (3.6 M HF/6 M HNO₃) was used as the dissolution mixture. We tested our dissolution mixture on aerosol samples collected from Singapore. Half of the filter was leached in a concentrated 3:1 HNO₃/HF mixture and the other half in 50% (v/v) of 3:1 HNO₃/HF. No significant difference was observed in Pb isotope ratios between the two halves (Supporting Information, Table S1), indicating complete dissolution of natural Pb by the 3.6 M HF/6 M HNO₃ dissolution mixture. The PTFE filter samples (including SRM 2783 standard and blank filters) were leached with 5 mL of the dissolution mixture in Savillex beakers. The tightly capped Teflon beakers were sonicated at 60 °C for 1 h and heated at 150 °C for 12 h. PTFE filters were removed from the solution using a Teflon tweezer and washed with ultrapure water, and the solution was evaporated to dryness on a hot plate at 120 °C. The dried extracts were redissolved in 7 N HNO₃ and evaporated to dryness a couple of times to get rid of any traces of HF. Subsequently, the dried metal extracts were redissolved in 2 mL of 3% HNO₃ and separated into two parts. One aliquot was diluted for trace metal analysis and the other aliquot was stored for Pb isotope measurement. All acids used for analysis were of ultrapure grade from Seastar Chemicals and water used for dilution was ultrapure water with a 18.2 MΩ cm resistivity (Super-Q, Merck Millipore). The trace metal concentrations were measured on a sector-field inductively coupled plasma mass spectrometer (SF-ICP-MS, an Element 2 from Thermo Fisher Scientific)³⁹ at the Earth Observatory of Singapore. One ppb of indium was added into the solutions as the internal standard. Instrumental drift was corrected by a combination of the internal indium standard and external calibration from the bracketing standard (IV-ICPMS-71A from Inorganic Ventures). Typical instrument sensitivity was about 1.8 × 10⁶ cps/ppb for ¹¹⁵In. All samples were measured for 15 elements including Al, As, Ba, Ca, Cu, Cr, Fe, Mg, Mn, Na, Ni, Pb, Sr, V, and Zn. Different mass resolution modes were used to optimize the separation of measured isotopes from interfering polyatomic species (e.g., ⁷⁵As from ⁴⁰Ar³⁵Cl) and improve detection limits. The final concentrations were blank corrected using the average blank filter concentrations. Averages of the procedural filter blanks ranged from 1.3 to 3% of the average signal intensity of the samples. SRM 2783 of urban PM samples was used to validate the method. Recoveries for all metals including Pb were found to be >90%.⁴⁰ The detection limit (LOD) of all metal analytes was calculated based on three times of the standard deviation (SD) of blank. The value of LOD ranged from 0.0023 (Pb) to 2.2717 (Ca) ppb (*n* = 12).

Pb Isotope Analysis. The remaining aliquot of the sample solutions was passed through an ion exchange column (Eichrom AG-1X8 chloride form, 200–400 mesh) for separation of Pb. Sample solutions were dried and dissolved in 1.1 N HBr before loading into the columns. For column blanks, 1.1 N HBr was loaded instead of the sample. 1.1 N HBr and 2 N HCl were used as the mobile phase. Pb was eluted with 6 N HCl and collected in

Table 1. Metal Concentrations in ng/m³ and PM_{2.5} in μg/m³ (Source: Pollution Control Department) from Chiang Rai (CR 1–CR 11) and Bangkok (BKK 1–BKK 10)

	date	Al	As	Ba	Ca	Cu	Cr	Fe	Mg	Mn	Na	Ni	Pb	Sr	V	Zn	PM _{2.5}
CR1	29/01/2019	59	0.58	2.3	72	2.0	1.2	136	20	2.7	72	0.97	6.2	0.36	0.35	8.3	111
CR3	12/02/2019	91	0.35	2.3	93	2.7	19	193	26	16	73	7.3	2.9	0.42	0.52	7.3	101
CR4	19/02/2019	90	0.30	2.2	151	6.6	1.3	148	50	5.1	121	0.81	8.8	0.94	0.36	28	97
CR5	26/02/2019	147	0.65	3.6	122	2.1	1.1	155	43	8.5	67	0.56	9.1	1.2	0.64	21	151
CR6	05/03/2019	162	0.33	2.5	126	2.1	2.8	147	60	4.4	86	0.53	4.0	1.3	0.57	11	147
CR7	12/03/2019	230	0.76	3.4	191	2.8	1.0	213	85	13	75	1.3	17	3.4	0.76	31	203
CR8	19/03/2019	84	0.88	2.0	90	2.3	1.4	92	31	4.1	79	0.79	4.2	0.63	0.63	13	195
CR9	26/03/2019	62	0.40	1.3	60	1.3	0.55	63	26	2.5	65	0.39	2.4	0.39	0.53	6.9	281
CR10	02/04/2019	128	0.62	2.3	107	1.8	0.59	112	36	4.2	57	0.47	3.6	0.67	0.54	11	206
CR11	09/04/2019	159	0.55	2.6	117	1.8	0.93	158	58	5.4	50	0.55	5.3	1.1	0.46	11	206
mean		121	0.54	2.45	113	2.6	3.0	142	44	6.6	75	1.4	6.4	1.0	0.54	15	170
median		110	0.57	2.3	112	2.1	1.2	148	40	4.8	73	0.68	4.8	0.81	0.54	11	173
min		59	0.30	1.3	60	1.3	0.55	63	20	2.5	50	0.39	2.4	0.36	0.35	6.9	97
max		230	0.88	3.6	191	6.6	19	213	85	16	121	7.3	17	3.4	0.76	31	281
SD		54	0.19	0.66	38	1.5	5.7	44	20	4.5	19	2.1	4.4	0.90	0.13	8.7	59

	date	Al	As	Ba	Ca	Cu	Cr	Fe	Mg	Mn	Na	Ni	Pb	Sr	V	Zn	PM _{2.5}
BKK1	29/01/2019	103	3.8	17	173	14	2.5	274	58	15	353	2.1	43	1.5	2.4	61	157
BKK2	05/02/2019	30	0.53	2.3	98	2.3	1.6	83	56	6.0	389	1.4	2.2	0.53	2.6	11	99
BKK3	12/02/2019	51	1.0	6.7	90	7.0	1.9	168	42	12	302	2.2	15	0.76	4.0	79	87
BKK4	19/02/2019	15	0.33	1.4	35	1.5	0.90	79	35	2.9	234	0.80	1.5	0.30	2.1	9.1	66
BKK5	05/03/2019	38	1.0	2.0	86	2.9	0.89	76	39	3.7	226	1.0	5.4	0.69	1.8	26	80
BKK6	12/03/2019	113	1.4	4.4	122	6.0	1.6	195	74	13	255	1.7	12	1.7	2.5	66	75
BKK7	19/03/2019	39	0.80	1.8	49	2.2	0.64	79	67	4.6	454	1.3	5.2	0.72	2.6	26	109
BKK8	26/03/2019	19	0.56	1.9	41	2.5	5.3	99	38	7.2	247	1.4	2.3	0.52	2.2	14	83
BKK9	02/04/2019	75	1.4	2.5	54	3.4	1.2	107	39	4.5	196	3.1	7.2	0.49	3.7	25	79
BKK10	09/04/2019	26	1.3	1.9	42	2.6	1.1	71	37	3.7	232	1.1	3.2	0.34	2.4	19	75
mean		51	1.2	4.2	79	4.4	1.8	123	49	7.3	289	1.6	9.7	0.76	2.6	34	91
median		39	1.0	2.2	70	2.8	1.4	91	41	5.3	251	1.4	5.3	0.61	2.5	26	82
min		15	0.33	1.4	35	1.5	0.64	71	35	2.9	196	0.80	1.5	0.30	1.8	9.1	66
max		113	3.8	17	173	14	5.3	274	74	15	454	3.1	43	1.7	4.0	79	157
SD		35	1.0	4.8	44	3.8	1.4	68	14	4.4	84	0.69	13	0.47	0.69	25	26

a Savillex beaker.⁴¹ The collected solutions were evaporated at 90 °C to dryness and redissolved in 2% ultrapure HNO₃ and analyzed for Pb isotopes using a Multicollector ICP–MS (Neptune Plus from Thermo Fisher Scientific) at the Earth Observatory of Singapore.²⁴ Thallium (Tl) was added as an internal standard and a ²⁰³Tl/²⁰⁵Tl ratio of 0.418911 was used to correct for instrumental mass fractionation.^{26,42} The samples were measured at similar Pb/Tl ratios to the standards to avoid any analytical bias. The ²⁰²Hg signal was used to correct the isobaric interference of ²⁰⁴Pb by ²⁰⁴Hg. The isotope ratios of the NBS-981 Pb standard were measured during the analytical sessions, indicating ²⁰⁶Pb/²⁰⁴Pb = 16.92599 ± 0.002, ²⁰⁷Pb/²⁰⁴Pb = 15.47794 ± 0.0027, ²⁰⁸Pb/²⁰⁴Pb = 36.6591 ± 0.0086, ²⁰⁶Pb/²⁰⁷Pb = 1.0935 ± 0.0001, and ²⁰⁸Pb/²⁰⁷Pb = 2.3684 ± 0.0002 (2 standard deviations, *n* = 22). The ratio averaged between the measured NBS 981 Pb isotope composition during an analytical session and the true ratios as reported by Baker et al. (2004)⁴³ were used to normalize the Pb isotope ratios of the measured samples.²⁴ The procedural blanks were measured and ranged from 0.05 to 0.77% of the sample concentration and were corrected for the reported concentration.

RESULTS AND DISCUSSION

Particulate Matter (PM_{2.5}). The average PM_{2.5} concentrations in Chiang Rai and Bangkok provided by Division of Air Quality Data, Air Quality and Noise Management Bureau, and

Pollution Control Department are 170 μg/m³ (range: 97–281 μg/m³) and 91 μg/m³ (range: 66–157 μg/m³), respectively (Table 1). Average PM_{2.5} concentrations at Chiang Rai are higher than those at Bangkok during the sampling period (January to April 2019). The first four samples (CR 1 to CR 4) were collected during the nonhaze period between January and mid-February. The onset of haze is evident from the increase in PM_{2.5} concentrations in Chiang Rai from the end of February (26th February) to April (CR 5 to CR 11) from biomass burning.⁴⁴ The PM_{2.5} concentrations during haze (average: 198 μg/m³) are significantly higher than those during nonhaze (average: 103 μg/m³) at Chiang Rai. In contrast, average Bangkok PM_{2.5} in January–February was 102 μg/m³ (BKK 1 to BKK 4), which decreased to 83.5 μg/m³ (BKK 5 to BKK 10) after burning in Chiang Rai commenced. The higher concentrations of PM_{2.5} in January–February in Bangkok are possibly because of thermal inversion in winter.^{45,46} After the onset of haze in Chiang Rai, PM_{2.5} concentrations in Bangkok do not show any increase, which indicates a minimal effect of biomass burning in the northern provinces on fine particle concentrations in Bangkok.

Aerosol Optical Depth and Ångström Exponent. Satellites routinely measure the spatial distribution of AOD, which represents the integrated extinction of electromagnetic radiation due to the amount of total column aerosol of all sizes. AE represents the spectral slope of AOD, indicating a systematic size distribution of the scattering particles.^{47,48} AOD acquired

Figure 2. Spatial variation of AOD during the prehaze and haze periods for Chiang Rai and Bangkok. Each panel is 24 h average during the sampling period. The black dots represent the sampling locations (Chiang Rai and Bangkok).

from satellite measurements has demonstrated to have a linear regression relationship with near ground $\text{PM}_{2.5}$.^{49,50} A good correlation has not only encouraged the use of AOD as a surrogate for $\text{PM}_{2.5}$ but has also been used for monitoring and nowcasting air quality.^{51–54} Several different models have been proposed for studying the AOD– $\text{PM}_{2.5}$ relationship based on simple linear regression,⁵⁵ multivariate regression including meteorological parameters,^{56–59} chemical transport models,⁶⁰ and temporally structured models.⁶¹ MODIS-derived spatial distribution of AOD (550 nm) displays relatively clean marine areas (South China Sea) and a high concentration of fine particles prevalent over land areas (Figure 2). This can be attributed to various natural and anthropogenic sources influencing the Thailand environment. The spatial gradients of AE (550–860 nm) (Figure 3) indicate the abundance of fine particles (AE > 1) over the terrestrial region mainly from anthropogenic sources and biomass burning⁶² and the dominance of coarse particles such as sea salt (AE < 1) over the marine environment.⁶³

A high AOD from the spatial distribution map (Figure 2) indicates a substantial amount of fine-sized (AE > 1) aerosol concentration around Bangkok during January and February, which is consistent with our high $\text{PM}_{2.5}$ in situ measurements. Chiang Rai depicts reduced aerosol load with relatively lower AOD and relatively coarser particles ($\sim \text{AE} = 1$) in coherence with lower $\text{PM}_{2.5}$ values in January and February. Mid-March onwards to April, entire Thailand including Chiang Rai is

covered with a high concentration (high AOD) of fine-sized (AE > 1.5) aerosols (Figure 2) in coherence with high $\text{PM}_{2.5}$ measurements.

HYSPLIT Trajectory. Trajectory analysis is helpful for ascertaining the origins of air masses (back-trajectory) and identifying the transports of air mass from a location to determine the dispersion of pollutants (forward trajectory). Monthly variability of median air-mass trajectories (Figure 4) over Bangkok was carried out based on backward analysis to identify the potential source bringing the pollutants to Bangkok. In January, 72% of the cluster originated from the South China Sea and the rest came from Vietnam. All the clusters traveled long distances over land (Cambodia, Laos, Vietnam, and parts of Thailand) before reaching Bangkok. In February, the largest cluster (57%) originated in southern Vietnam and traveled over the Gulf of Thailand before reaching Bangkok. The remaining cluster came from the South China Sea, Cambodia, and Laos. Overall, the majority of the wind trajectories travel long distances over landmass in January and February before reaching Bangkok. In March, most of the air mass originates over sea such as Andaman Sea (55%), Gulf of Thailand (19%), and South China Sea (26%). In April, 33% of the cluster blows from Andaman Sea and the remaining from the Gulf of Thailand. Overall, wind clusters in March and April make minimal land travel before reaching Bangkok.

The forward trajectory (all the clusters) analysis showed that the atmospheric aerosols originating from northern Thailand are

Figure 3. Spatial variation of AE during the pre haze and haze periods for Chiang Rai and Bangkok. Each panel is 24 h average during the sampling period. The black dots represent the sampling locations (Chiang Rai and Bangkok).

Figure 4. Median forward air-mass trajectories of the major clusters initiating at Chiang Rai forward-traced for 120 h and median backward air-mass trajectories of major clusters terminating at Bangkok backtraced for 72 h at 750 m above mean sea-level using the HYSPLIT model through January–April. Red arrows show the flow direction at a 24 h interval.

transported toward the north–east direction across from the Chiang Rai Province predominantly toward mainland China and some part of northern Laos, and northern Vietnam throughout January–April. This observation is consistent with the general pattern of air mass movement observed in the northern Thailand province of Chiang Mai during the burning season.⁶⁴

Metal Concentrations. Concentrations of fifteen metals and metalloid (collectively referred to as metals in this study) are determined in the PM_{2.5} fraction collected from Bangkok and Chiang Rai. The metal concentrations of PM_{2.5} along with their mean, median, and concentration ranges are given in Table 1. Box plots of the metal concentrations are given in Figure 5. Average concentrations of typically crustal metals such as Al, Ca, Fe, and Sr are higher in Chiang Rai, and many of the industrial, traffic, high-temperature combustion, and sea spray-related metals such as Ba, Cu, Cr, Mg, Mn, Ni, V, Zn, Na, and As are higher in Bangkok. We use elemental ratios, Pearson's correlation coefficient, crustal enrichment factor (EF), and principal component analysis (PCA) to understand the sources of the metals in the two locations.

For mitigation efforts to be successful, source apportionment of metals in atmospheric chemistry is of utmost importance. Often the absolute concentrations are inadequate to pinpoint sources and elemental ratios are more useful. However, the range of emission factor of metals can vary within a factor of 2–

Figure 5. Box plot of metal concentrations in Bangkok and Chiang Rai.

10 and result in a large variation of the metal ratios.⁶⁵ We use the ratios Zn/Al and Fe/Al as a qualitative marker to infer the relative importance of possible sources such as biomass burning and remobilized crustal dust^{14,15} by the raging fire. Al and Fe are the 3rd and 4th most abundant elements in the Earth's crust after oxygen and silicon, and the Fe/Al ratio⁶⁶ in the crust is typically ~0.48. Zn can come from a variety of sources including coal combustion, nonferrous metal production, and industrial emissions.⁶⁵ In the case of plants, Fe and Zn are micronutrients that are preferentially taken up from soil while Al is considered as a toxin for plants as it inhibits root elongation.¹⁸ Metals emitted from combustion experiments of vegetation from Indonesia¹⁸ have an Fe/Al ratio (0.20–2.73) and a Zn/Al ratio (0.06–1.70), which are higher than the values of haze-related PM_{2.5} from Chiang Rai (Figure 6). The Fe/Al ratio of PM_{2.5} in Chiang Rai

Figure 6. Relationship between Fe/Al and Zn/Al in Chiang Rai and Bangkok aerosols. Average UCC⁶⁶ ratio and aerosol generated by biomass burning from Indonesia¹⁸ are plotted for reference.

ranges from 0.87 to 2.30 and shows a moderately strong negative correlation ($r^2 = -0.72$) with PM_{2.5}. This indicates that with increasing haze, the Fe/Al ratio decreases. Figure 6 shows that the nonhaze PM_{2.5} has Fe/Al > 2, which decreases to 1.65 during the onset of haze and finally below 1 during the haze period approaching the crustal Fe/Al ratio of 0.48. In contrast, the Fe/Al ratio of Bangkok samples ranges between 1.42 and 5.14, indicating the anthropogenic input of Fe over the crustal background. The Zn/Al ratio of Chiang Rai PM during clear days ranges from 0.08 to 0.31, which decreases during the hazy days to 0.07 to 0.15. Sites with dominant crustal sources show a Zn/Al ratio of 0.05 ± 0.02 in Sagar Island in Bay of Bengal, India²⁴ and 0.14 from rural sites near Delhi,⁶⁷ which are in the range measured during hazy days in Chiang Rai. In contrast, the Zn/Al ratio of Bangkok PM is higher (0.34–1.54), indicating the anthropogenic input for Zn in Bangkok aerosols. Previous

studies from Bangkok reported Zn/Al ratios of 0.13 and 0.20 from two residential sites⁶⁸ and attributed the Zn source to automobile exhaust. The Zn/Al values measured in Bangkok are common in urban settings with anthropogenic Zn sources and are similar to California, USA (1.15), Kashima, Japan (0.50), Ghent, Belgium (1.64), and Brisbane, Australia (0.9).^{68,69}

Bangkok is situated 30 km north of the Gulf of Thailand and is characterized by the presence of sea salt aerosol (Na = 289 ng/m³). The Na/Mg ratio observed in Bangkok aerosol (range 3.43–7.17, average 6.07) is close to the typical Na/Mg ratio of sea spray aerosol (approximately 8). Na and Mg in Bangkok aerosol correlate well ($r^2 = 0.64$), indicating their similar source. Combustion in residential, commercial, and industrial applications can be a major source of Ni and V in PM. Bangkok is notorious for heavy road traffic, which might be the primary source of Ni and V ($r^2 = 0.82$). The average V/Ni ratio of Bangkok aerosol is 1.76, which is within the range (1.49–2.4) from road traffic.⁷⁰ Pb and Zn can have a variety of anthropogenic sources including coal combustion, traffic emissions, and nonferrous metal smelting to name a few. Pb and Zn correlate well in both Chiang Rai ($r^2 = 0.90$) and Bangkok ($r^2 = 0.68$), indicating similar sources (Supporting Information, Tables S2 and S3). The concentrations of other trace metals such as Ba, Cu, Cr, Mn, and As in Bangkok are higher than those in Chiang Rai probably because Bangkok is located near the industrial estate of Samut Prakan, Chachoengsao, Rayong, and Samut Sakhon⁷¹ and is exposed to industrial emission sources.

Enrichment Factors. We use crustal EF to understand which of the elements in the aerosol have crustal dust as the primary source. The crustal EF can indicate natural emissions and anthropogenic activities. Calculations are generally based on the average upper continental crustal (UCC) composition given by Rudnick and Gao.⁶⁶ The EF of an element in a PM sample is defined as

$$\text{Enrichment factor} = \frac{(\text{metal}/\text{ref. metal})_{\text{aerosol}}}{(\text{metal}/\text{ref. metal})_{\text{crust}}}$$

Al and Fe are commonly used as reference elements although there are no strict requirements for which reference element to use. Bangkok has a high traffic congestion and has numerous industries nearby, both of which can be potential sources of Fe. Hence, Al was chosen as reference element. EF values <5 suggest elements have crustal sources and EF between 5 and 10 is likely to have a minor anthropogenic input over the natural background. Elements with EF between 10 and 100 are likely to be moderately enriched by anthropogenic sources. EF values greater than 100 are most probably related to industrial, high-temperature combustion, and vehicular emissions.^{72,73} In

Figure 7. Enrichment factor of Chiang Rai and Bangkok aerosol.

Chiang Rai, eight of fifteen measured metals (Ba, Ca, Na, Fe, Mg, Mn, Sr, and V) have EF less than 6 indicating crustal sources. In Bangkok, Ba, Ca, Fe, Mg, and Sr have EF between 4 and 10 indicating moderate enrichment from anthropogenic sources. In Chiang Rai, Ni, Cr, Cu, and As have EF between 10 and 100 and Pb and Zn have EF > 100. In Bangkok Na, Mn, V, Ni, and Cr have EF between 10 and 100 and Cu, As, Pb, and Zn have EF > 100 indicating a strong anthropogenic influence (Figure 7). In both the locations, Pb and Zn have the highest EF. A high EF of Zn (153–240) has been reported from Bangkok and the source was attributed to automobile exhaust and refuse incineration.⁶⁸ EF of Pb > 100 has been observed in many previous studies and the sources were identified to be coal-based power stations and industrial and vehicular emissions.^{73,74} The common anthropogenic sources of the moderately enriched metals could be vehicular exhaust for Cu, coal combustion, and vehicular exhaust for Cr, coal combustion for As, and oil combustion for V and Ni.^{8,75} However, solely based on EF and elemental characteristics, source identification of PM cannot be achieved with a reasonable accuracy.

Statistical Analysis. We use PCA of the Statistical Package for the Social Sciences (SPSS) version 22 to analyze sources of metals during the burning season in the two different locations. PCA is a statistical technique based on variations in the sequencing data and brings out strong patterns in a dataset. It is often used in environmental studies. Only the factors with eigenvalues higher than 1 were selected. The Varimax rotated Kaiser-normalized component matrix results indicate three possible factors representing three different contributing sources in both the locations. The loadings of variables on factors, communalities, eigenvalues, percentage variance, and percentage cumulative variance are given in Supporting Information, Table S4.

In Chiang Rai, 86.14% of the variation can be explained by three factors. The first factor explains 46.59% variance of the data and shows high loading for Al, Ba, Ca, Fe, Mg, Pb, Sr, V, and Zn (0.608–0.959). Most of these metals (except Pb and Zn) have EF < 6 indicating the crustal origin. Hence, the first factor possibly denotes metals with crustal dust⁷⁶ and biomass burning (Pb and Zn) as the primary source.⁷⁷ The second factor explains 20.96% of the variance and shows a high loading for Cr, Ni, and Mn (0.852–0.974). These metals indicate emission from the industrial source.⁷⁸ The third factor shows a high loading of Cu (0.937) and Na (0.914) explaining 18.59% of the variance. Strong correlation between Cu and Na (0.889) (see the Supporting Information, Table S2) suggests that the two metals have similar emission sources such as refuse incineration mixed with road dust.^{79,80}

In Bangkok, 54.97% of the variance is observed in factor 1 that shows a high loading of Al, Ba, Ca, Cu, Fe, Mn, Pb, Sr, Zn, and As (0.704–0.973). These metals represent a mixture of natural and anthropogenic sources. Cu, Pb, and Zn have EF > 100 and can originate from industrial emissions and coal combustion.⁸¹ Factor 2 explains 14.78% variance and has a high loading of Ni (0.855) and V (0.947). Strong correlation of Ni and V coupled with a V/Ni ratio in the range of road traffic emission (see the Supporting Information, Table S3) suggests that the two metals are sourced from fossil fuel combustion.⁷⁰ Factor 3 shows a high loading of Mg (0.864) and Na (0.700) and has 12.98% variance of the data. Mg and Na show good correlation with the Na/Mg ratio close to that of marine aerosol.^{82–84} During the biomass burning season in the northern provinces, entire Thailand is covered by fine PM. However, the disparity in trace metal systematics between Chiang Rai and Bangkok indicates that the metals are possibly not transported down south to Bangkok.

Pb Isotopic Composition. Atmospheric Pb can be emitted by anthropogenic processes such as vehicle exhausts, coal combustion, and high-temperature industrial processes. Pb isotopes provide a powerful tool to investigate Pb pollution and identify the origin of the metal. The amount of Pb isotopes presented in a system is determined by the relative proportion of initial U–Th–Pb, which varies with the origin or geological conditions. The Pb isotope ratios, Pb, and PM_{2.5} concentrations are given in Table 2. The Pb isotope ratios of the NBS 981 standard and procedural blank are also given in Table 2.

Pb concentrations in the PM_{2.5} in Chiang Rai and Bangkok range from 2.43 to 16.50 (6.29 ± 4.25, 1SD) and 1.53 to 42.91 (9.69 ± 12.47, 1SD) ng/m³, respectively. However, if only the burning season is considered, average Pb in Bangkok (5.95 ± 3.64, 1SD) is lower than that in Chiang Rai (6.44 ± 4.91, 1SD). Pb concentrations in both Bangkok and Chiang Rai do not correlate with PM_{2.5}. However, in Bangkok, only BKK 1 shows very high Pb (42.91 ng/m³) and PM_{2.5} (157 μg/m³) concentrations. The ²⁰⁶Pb/²⁰⁷Pb ratios in Chiang Rai range from 1.1445 to 1.1657 (1.1523 ± 0.0056, 1SD) and the ²⁰⁸Pb/²⁰⁷Pb ratios range from 2.4244 to 2.4468 (2.4324 ± 0.0063, 1SD), and the ²⁰⁶Pb/²⁰⁷Pb ratios in Bangkok show a larger variation, 1.1343–1.1685 (1.1495 ± 0.0085, 1SD) and the ²⁰⁸Pb/²⁰⁷Pb ratios range between 2.4138 and 2.4450 (2.4282 ± 0.0081, 1SD).

A time series plot of the ²⁰⁶Pb/²⁰⁷Pb ratio and PM_{2.5} in Chiang Rai and Bangkok shows that the ²⁰⁶Pb/²⁰⁷Pb ratio in Chiang Rai follows the PM_{2.5} during the burning season and the ratio increases with PM_{2.5} (Figure 8), indicating that at least a part of the Pb is burning related. Normally, Bangkok records high PM_{2.5} concentrations during December and January due to thermal

Table 2. Pb Concentration and Pb Isotope Composition of the PM_{2.5} Aerosol Sample

sample	²⁰⁶ Pb/ ²⁰⁴ Pb	2se	²⁰⁷ Pb/ ²⁰⁴ Pb	2se	²⁰⁸ Pb/ ²⁰⁴ Pb	2se	²⁰⁶ Pb/ ²⁰⁷ Pb	2se	²⁰⁸ Pb/ ²⁰⁷ Pb	2se	Pb conc. (ng/m ³)	PM _{2.5} (μg/m ³)
CR1	17.9666	0.0017	15.5871	0.0022	37.9279	0.0074	1.1523	0.00005	2.4353	0.00021	6.2	111
CR2	18.1441	0.0091	15.7091	0.0085	38.2184	0.0227	1.1552	0.00012	2.4350	0.00027	4.1	68
CR3	18.0356	0.0029	15.6134	0.0037	38.0025	0.0123	1.1548	0.00007	2.4361	0.00028	2.9	101
CR4	17.8541	0.0029	15.5945	0.0032	37.7718	0.0103	1.1445	0.00007	2.4244	0.00030	8.8	97
CR5	17.9380	0.0027	15.6123	0.0030	37.8613	0.0103	1.1487	0.00007	2.4270	0.00027	9.1	151
CR6	17.9587	0.0026	15.6046	0.0030	37.8546	0.0103	1.1505	0.00006	2.4280	0.00026	4.0	147
CR7	17.8834	0.0019	15.5975	0.0023	37.8015	0.0079	1.1463	0.00005	2.4256	0.00022	17	203
CR8	17.9602	0.0019	15.6068	0.0022	37.9082	0.0075	1.1505	0.00005	2.4310	0.00021	4.2	195
CR9	18.0325	0.0018	15.6138	0.0021	37.9754	0.0074	1.1546	0.00004	2.4341	0.00022	2.4	281
CR10	18.2426	0.0033	15.6453	0.0042	38.2504	0.0139	1.1657	0.00010	2.4468	0.00038	3.6	206
CR11	17.9960	0.0025	15.6105	0.0029	37.9512	0.0098	1.1525	0.00006	2.4331	0.00026	5.3	206
BKK1	17.9800	0.0033	15.6013	0.0044	37.9077	0.0149	1.1522	0.00010	2.4319	0.00041	43	157
BKK2	18.2626	0.0018	15.6254	0.0022	38.1744	0.0077	1.1685	0.00005	2.4450	0.00023	2.2	99
BKK3	17.8754	0.0018	15.5758	0.0022	37.7331	0.0075	1.1473	0.00005	2.4245	0.00021	15	87
BKK4	17.8993	0.0043	15.5842	0.0048	37.8153	0.0157	1.1484	0.00009	2.4285	0.00041	1.5	66
BKK5	17.8964	0.0023	15.5924	0.0028	37.7893	0.0097	1.1474	0.00006	2.4256	0.00028	5.4	80
BKK6	17.8990	0.0018	15.5925	0.0021	37.7910	0.0073	1.1476	0.00005	2.4258	0.00020	12	75
BKK7	17.9914	0.0018	15.6025	0.0021	37.9378	0.0072	1.1529	0.00004	2.4337	0.00020	5.2	109
BKK8	17.9641	0.0019	15.5940	0.0023	37.8689	0.0077	1.1517	0.00006	2.4305	0.00023	2.3	83
BKK9	17.8279	0.0019	15.5759	0.0024	37.7055	0.0081	1.1443	0.00005	2.4228	0.00023	7.2	79
BKK10	17.6562	0.0029	15.5617	0.0034	37.5332	0.0111	1.1343	0.00007	2.4138	0.00028	3.2	75
	²⁰⁶ Pb/ ²⁰⁴ Pb	2SD	²⁰⁷ Pb/ ²⁰⁴ Pb	2SD	²⁰⁸ Pb/ ²⁰⁴ Pb	2SD	²⁰⁶ Pb/ ²⁰⁷ Pb	2SD	²⁰⁸ Pb/ ²⁰⁷ Pb	2SD		
NBS 981 (true value)	16.93736						1.0933	0.0004	2.3704	0.0012		
NIST 981 (<i>n</i> = 22)	16.9259	0.0022	15.4779	0.0027	36.6591	0.0086	1.0935	0.0001	2.3684	0.0002		
procedural blank (<i>n</i> = 3)	18.9395	0.3205	17.1765	0.2892	40.4743	0.6835	1.1051	0.0030	2.3632	0.0023		

^aNBS 981 true value is taken from Baker et al., 2004.⁴³

Figure 8. Time series plot of the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio and $\text{PM}_{2.5}$ during January to April 2019 in Bangkok and Chiang Rai. The shaded area shows the burning season.

inversion. For the remaining ten months, average Bangkok $\text{PM}_{2.5}$ remains lower⁸⁵ than $100\text{ }\mu\text{g}/\text{m}^3$. During the haze, the $\text{PM}_{2.5}$ concentration and the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in Bangkok do not show much variation. The Pb isotopic composition of atmospheric aerosol results from mixing of many different sources. We present an overview of the Pb isotopic compositions (mainly $^{206}\text{Pb}/^{207}\text{Pb}$) of different possible anthropogenic sources from the region as published in the literature to understand the source(s).

Figure 9a presents the range of $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of Chiang Rai and Bangkok aerosols along with the plausible end members of anthropogenic Pb. Atmospheric Pb emission from vehicular exhaust has significantly reduced in Thailand⁸⁶ after 1991 when leaded gasoline was phased out. However, even considering the very low Pb concentrations in fuels, the heavy road traffic, particularly in Bangkok, must magnify Pb emissions to the atmosphere.⁸⁷ $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of the unleaded petroleum fuel from the region (Vietnam, Shanghai, Guiyang, Hong Kong, and Taiwan)^{70,88–91} range from 1.1415 to 1.1577. Most of the aerosols collected from Bangkok (except BKK 2 and BKK 10) and Chiang Rai (except CR 10) plots in this range. Hence, the gasoline exhaust can be a potential source of Pb, at least in Bangkok aerosols.

The second plausible Pb source can be high-temperature industries such as roasting and smelting of ores in nonferrous metal smelters. Pb–Zn ores from different geochemical provinces in the region (north and northeast China, Yangtze Province, and Indo-china geochemical Province) have a wide range⁹² of $^{206}\text{Pb}/^{207}\text{Pb}$ (1.091–1.194). However, in a Pb triple isotope plot ($^{206}\text{Pb}/^{207}\text{Pb}$ vs $^{208}\text{Pb}/^{207}\text{Pb}$) (Figure 9b), the Pb–Zn ores do not plot on a linear mixing trend with the aerosol samples implying they are less likely to be a major contributor to the aerosol Pb.

Post phasing out of leaded gasoline, Pb emissions from coal combustion have increased by an order of magnitude.⁹³ Thailand imports coals from Indonesia and Australia (Energy Policy and Planning Office Ministry of Energy, www.eppo.ac.th). The $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of Indonesian coal⁹⁴ range from 1.1804 to 1.1881, whereas those of Australian coal⁹⁴ range between 1.2053 and 1.2057. Though all the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in the Bangkok and Chiang Rai aerosols are lower than those in Australian and Indonesian coal, the coal combustion emissions can be a mixing end member. The residence time of Pb aerosols in the atmosphere is around $\sim 5\text{--}10$ days.⁹⁵ Hence, trans-boundary pollution remains an important source of atmospheric

Figure 9. (a) Box plot of the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in this study (Bangkok and Chiang Rai), in comparison with petroleum fuels^{70,88–91} from southeast Asia, Pb–Zn ore deposits from China (CN) and Indonesia (ID),⁹² coal^{70,88,91,94,96,97} from China (CN), Vietnam (VN), Australia (AU), and Indonesia (ID), river sediment in Asia,⁹⁹ Indonesian plant (Das et al., 2019-Goldschmidt abstract), South China Sea sediment,⁷⁰ and average UCC.⁶⁶ (b) Pb triple isotope Plot of Chiang Rai and Bangkok aerosols, in comparison with different possible anthropogenic end members. (c) Plot of $^{206}\text{Pb}/^{207}\text{Pb}$ ratio vs Al/Pb of Chiang Rai and Bangkok aerosols from this study, in comparison with average UCC^{66,99} and river sediments in Asia⁹⁹ as representative of crust soil in the region and Indonesian plant¹⁸ as representative of biomass burning aerosol from northern Thailand.

aerosols. Long-range transport of coal combustion Pb is also a possibility from Southeast Asian countries. Pb isotopes of coal from Vietnam^{70,96} ($^{206}\text{Pb}/^{207}\text{Pb}$ ranges between 1.1494 and 1.1950) and China^{88,91,94,97} ($^{206}\text{Pb}/^{207}\text{Pb}$ ranges between 1.1546 and 1.2438) are plotted for reference in Figure 9a,b.

Apart from the above-mentioned anthropogenic sources, Pb can come from biomass burning in Chiang Rai. Remobilized mineral dust from the desiccated soil^{15,98} during wildfire could be a significant source of atmospheric Pb. $^{206}\text{Pb}/^{207}\text{Pb}$ of average UCC⁹⁹ is 1.1924, river sediments in Asia⁹⁹ are 1.1672–1.2325 and biomass from the region is 1.1410–1.1613 (Das et al., 2019-Goldschmidt abstract).

In summary, the Pb isotope ratios of the PM alone are unable to differentiate between the possible end member sources because their isotopic compositions have overlapping ranges (Figure 9a) and several of the plausible end members plot on linear mixing trend (Figure 9b). In order to understand the source(s) of atmospheric Pb, we combined Pb isotope ratios and trace metal systematics because natural and anthropogenic end members should have distinct trace metal signatures. From trace metal systematics, it is evident that during haze, dominance of crustal metals such as Al increases in Chiang Rai. Hence, we select Al to ratio with Pb. In Figure 9c, the Al/Pb ratio of the Chiang Rai samples ranges from 9.61 to 40.63 and correlates well with $^{206}\text{Pb}/^{207}\text{Pb}$ ($r^2 = 0.61$). The Bangkok aerosols have a much lower Al/Pb ratio (2.39–13.52) and do not show any significant correlation with the Pb isotopes ($r^2 = 0.33$). However, it is to be noted that sample BKK 2 has the highest $^{206}\text{Pb}/^{207}\text{Pb}$ ratio among all the Bangkok aerosols and also the highest Al/Pb ratio (13.52). This indicates that crustal dust can play an important role during the fire and contribute significantly toward atmospheric Pb. For comparison, the Al/Pb ratios of biomass from Indonesia and average UCC⁶⁶ and river sediments in Asia⁹⁹ are plotted in Figure 9c.

From the trace metals and Pb isotopes, it is evident that during haze, there is some degree of mixing of PM from biomass burning and crustal dust with the background. The average Pb isotope ratios ($^{206}\text{Pb}/^{207}\text{Pb} = 1.1517 \pm 0.0050$, 1SD and $^{208}\text{Pb}/^{207}\text{Pb} = 2.4327 \pm 0.0056$, 1SD) during clear day is considered to be the background. Biomass and mineral soil composition from northern Thailand were not measured in this study, and hence, we had to rely on the existing literature for these plausible end member Pb isotopic compositions. We use the average of the Indonesian plants (Das et al., 2019-Goldschmidt abstract) for biomass composition. For regional crustal sediment composition, average of the large river sediments from South and Southeast Asia⁹⁹ (India, Bangladesh, Myanmar, and Vietnam) is used. Sediment samples from large river deltas are large-scale integrated samples of the weathering products of the present-day UCC. To obtain an isotope-mixing model, iterative percentages of each component's abundance were used. The most radiogenic Pb isotopes (CR 9 and CR 10) during peak haze can be explained by ~5 and 30% mixing of crustal dust with ~35 and 40% biomass burning generated aerosols with the background.

A decade-long study on wildfires in western United States demonstrated that crustal dust is significantly enhanced in wildfire plume identified based on enrichments of typical crustal metals such as Si, Ca, Al, Fe, and Ti in fine aerosol.¹⁴ High-resolution large-eddy simulation, conducted with the all scale atmospheric model demonstrated that the energy released by the fires controls the near-surface wind patterns and mobilize dust particles.¹⁵ However, to what extent mineral dust will be

mobilized depends primarily on fire properties such as fire size, intensity, and shape, in addition to the ambient wind velocities.

CONCLUSIONS

Air pollutants released from forest fires and stubble burning in northern Thailand are of major concern to human health, ecosystem, and climate. Images of size-resolved aerosols from MODIS-Terra satellite show that entire Thailand is covered with high concentrations of fine-sized aerosol during the peak fire from mid-March to April. However, forward air mass trajectories from northern Thailand provinces show winds mostly flow toward north and northeast toward mainland China, whereas Bangkok in southern Thailand receives air mass from the South China Sea and Bay of Bengal. Metal composition of PM_{2.5} from Chiang Rai during haze shows high concentrations of crustal metals and may have three primary sources: 1, crustal dust and biomass burning, 2, industrial source, and 3, refuse incineration mixed with road dust. Bangkok PM_{2.5} metals are influenced by 1, natural background mixed with industrial emissions and coal combustion, 2, traffic emission, and 3, sea spray. The Pb isotope ratio ($^{206}\text{Pb}/^{207}\text{Pb}$) in Chiang Rai aerosol increases with increasing haze (and PM_{2.5}) and correlates well with the crustal metal to Pb ratio (Al/Pb), indicating that at least part of the Pb is derived from crustal dust during increasing fire. However, no such pattern is observed in Bangkok. From the PM_{2.5} concentrations, wind trajectories, AOD and AE observations, and trace metal and Pb isotope analysis, it is concluded that during peak fires, crustal dust can form a significant source of Pb and other metals in the aerosol. Though entire Thailand is covered with fine aerosols during the peak fire in northern provinces, it is not evident that long-range atmospheric metal transport occurs from fire hotspots to southern Thailand. Local sources and sea spray remain the primary sources of metals in PM_{2.5} in Bangkok.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsearthspace-chem.0c00140>.

Pb isotope ratios of Singapore clear day (SIN A12) and hazy day (SIN A13) aerosol samples (PM_{2.5}) collected in 2015 extracted with dilute (50% v/v) and concentrated acid mixture; metal correlation in Chiang Rai; metal correlation in Bangkok; and PCA of metal composition in PM_{2.5} at Chiang Rai and Bangkok (PDF)

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733 Notes

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