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A facile digestion protocol for metal analysis in ambient aerosols: Implications to mineral dust characteristics and human health impact

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ABSTRACT

Assessment of atmospheric metals produced from natural or anthropogenic sources is a major concern of many researchers worldwide for their source characterization and hazardous health impacts. Currently, many high tier labs, equipped with chemical (microwave digestion system), optical (X-ray fluorescence spectroscopy) or nuclear techniques (instrumental neutron activation analysis) can lead to or produce accurate data of metals rapidly. Owing to low concentration of several metals, large heterogeneity and matrix effect in atmospheric aerosol samples, many a times the chemical digestion followed by quantification approach is widely preferred. However, in South and South-east Asia, the major data set of atmospheric metals is relatively lacking, due to unavailability of rapid digestion technique in many labs. Towards this we report a new and facile analytical protocol for complete digestion of metals in atmospheric aerosols. Finalized protocol for metal digestion in ~ 12 h involves sample treatment with a mixture of HF+HNO₃+H₂O₂+H₂O in 1: 4: 1: 6 (v/v) at 150 °C. This protocol has been successfully applied for complete digestion and quantification of several metals (Al, As, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, V and Zn) in high-loading ambient PM_{2.5} (particulate matter of aerodynamic diameter ≤2.5 µm; 95□240 µg m⁻³). Mineral dust composition over IGP (Northern India) looks distinctly different than that over western India (reported previously). Several toxic metals (As, Cd, Cu, Pb, V and Zn) show enrichment factor more than 10, suggesting their significant inputs from anthropogenic sources. Thus, our analytical protocol could facilitate for accurate and rapid analysis of metals pertaining to environmental and toxicological research.

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1. Introduction

Depending on the receptor site location and also the season, atmospheric aerosols have been found with different fractions of mineral aerosols, total carbonaceous aerosols (organic matter and elemental carbon) and water-soluble ions (Gupta and Mandaria, 2013; Gustafsson et al., 2009; Mahowald et al., 2005; Rajput et al., 2013; Rajput et al., 2014a;b; Singh and Gupta, 2015; Venkataraman et al., 2006). Secondary aerosols formation further enhances the matrix and complexity in molecular characterization (Doezema et al., 2012; Rajeev et al., 2016; Rajput et al., 2016a; Rajput et al., 2011a). Consequently, achieving complete metal digestion and their quantification in various environmental samples have been a matter of concern to analytical chemists (Butler et al., 2016; Cuoco et al., 2013; Huang et al., 2010; Lamble and Steve, 1998; Lee and Park, 2010; Wu et al., 2010). Conventional approach adopting open-digestion technique is very time consuming (can take 3-4 days) and attentive (Mark et al., 1999). Also, the previous reported closed or open digestion protocols involved sample pre-treatment at ~ 400 °C in furnace to remove organic coating. This could lead to loss of soft metals like K and Na during sample pre-heating. With the advancement in technology, microwave digestion systems (MDS) came into utilization (Aldabe et al.,

2013; Butler et al., 2014; Lamble and Steve, 1998; Swami et al., 2001; Tursic et al., 2008). MDS can digest all metals in ~2-3 hours. As a consequence of which, labs equipped with MDS are able to process samples quickly and facilitates in determining easily accurate metals concentration in various environmental samples.

A recent study in GEOTRACES (An international study of the marine biogeochemical cycles of trace elements and their isotopes) from Southern Ocean (Cape Baseline Air Pollution Station: CGBAPS, Australia) achieves complete aerosol digestion at 95 °C in ~ 12 hours utilizing ultra-pure HNO₃ (1 mL) and HF (0.25 mL) in capped Teflon vials (Winton et al., 2016). The HF-HNO₃ based complete digestion approach has been used in many studies assessing aerosol trace metal dissolution in seawater e.g. (Mackey et al., 2015). Likewise the HF-HNO₃ based digestion method serves adequately in remote high-altitude locations (Marx et al., 2014). It is important to mention here that in remote areas (marine air-masses or high-altitude locations) the contribution of black particles is insignificant and therefore a complete digestion (closed) of particles on hot-plate could be achieved without oxidizing agents like H₂O₂. Metal analysis can also be carried out using X-ray fluorescence spectroscopy (XRF). The XRF spectroscopy is a non-destructive technique that provides multi-element information but could be less sensitive to replicate analysis as compared

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to inductively coupled plasma (ICP) based measurements. Recently, a study utilizes a nano micro-orifice uniform-deposit impactor (nano-MOUDI), to collect size segregated particles, and a field portable XRF (FP-XRF) to determine metal composition and concentration (Park et al., 2016). The other approach for measuring total concentration of metals is instrumental neutron activation analysis (INAA). The aspect related to low sensitivity for certain metals e.g. Cu, Cd and Ni poses a challenge to quantify their mass concentrations using INAA. However, the INAA technique for the determination of metals concentration is as accurate as acid-digestion approach (Chance et al., 2015). The other emerging technique for quantitative analysis of metals is LIBS (laser induced breakdown spectroscopy) (Butler, et al., 2014).

With this background information, we initiated to establish an analytical protocol for complete digestion of metals in ambient aerosol samples (without pre-combustion of sample in furnace) utilizing a facile closed digestion approach. We initially started digestion with HF+HNO₃ and then based on our observations of undigested black particles in the solution, the HF+HNO₃+H₂O₂ mixture in a stoichiometric proportion has been used for complete digestion of metals. The established protocol provides a complete digestion of metals in high loading ambient aerosols (up to 240 µg m⁻³), evidenced from this study. Analytical method reported herein looks very promising in terms of the cost effective metals digestion without compromising on the precision and accuracy of their determination.

2. Materials and method

PM_{2.5} samples (n = 22) assessed in this study have been collected from a highly polluted urban location at Kanpur in the Indo-Gangetic Plain (IGP) (26.30°N; 80.14°E; 142 m above mean sea level) (Rajput, et al., 2016a; Rajput et al., 2016b). These samples were collected using a high-volume air-sampler (calibrated flow rate: 0.95 m³/min) (Kumar and Gupta, 2015) during December 2014–February 2015 (wintertime). It is important to mention here that during wintertime, prevailing NE-winds favor the transport of air-pollutants from source-region of biomass burning emissions upwind in the IGP (Rajput, et al., 2016 b; Rajput et al., 2011b). Soon after the sampling onto pre-combusted quartz micro-fiber filters (Whatman™, ~ 20 x 25 sq. cm), samples were stored at ~ -19°C until analysis. PM mass concentrations have been ascertained gravimetrically on an analytical balance after equilibrating the filters at 37 ± 3% RH and 24 ± 2 °C temperature for ~8-10 h. Concentrations of metals have been measured using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES; iCAP 6300, Thermo Scientific) (Chakraborty and Gupta, 2010; Rajput, et al., 2016 a; Rajput, et al., 2016 b), post to complete chemical digestion. High purity chemicals (Seastar Chemicals, Fisher) viz. HF (47-51%, Suprapure), HNO₃ (67-69%, Suprapure) and H₂O₂ (> 30%, Trace analysis) are used for the digestion and sample preparation. Milli-Q water of resistivity 18.2 MΩ cm has been used in sample preparation. Clean metal digestion in aerosols has been achieved in Teflon vials (Savillex) on a hot plate (Graphite coated with PFA; perfluoroalkoxy, Analab Scientific Instruments) with 24 positions. The hot plate was operated inside a fume-hood (Envair Electrodyne) in a clean lab.

3. Results and discussion

3.1. Optimization of closed digestion protocol

From sampled filters, 6 punches (3.14 sq. cm each) are taken and subjected to digestion. Initially we started with HF+HNO₃+H₂O for aerosol samples digestion. But then we observed that some black particles are not at all getting digested with this combination. So, we decided after a series of preliminary experiments to test in different stoichiometry with a combination of HF, HNO₃, H₂O₂ and H₂O at different temperatures (on hot plate) for complete digestion of all particles. Finally, mixture of HF+HNO₃+H₂O₂+H₂O in stoichiometric proportion of 1:4:1:6 (v/v) at 150°C is accepted ensuring complete digestion of ~19 sq. cm area of quartz filter with maximum loading of 6 mg of aerosols in this study (Table 1). Basically we have added for the aforementioned sample area (and loading) these chemicals (in stoichiometry as detailed above) and capped the Teflon vials. Subsequently, vials were kept on hot plate (Graphite coated) maintained at 150 °C. We have observed that in ~ 12 hours all particles in PM_{2.5} are getting digested completely. After digestion, hot-plate temperature was reduced to 100 °C and the solution is allowed to evaporate till near dryness. Subsequently, we have added 1 mL of 8N HNO₃ and the final volume was made to 31 mL for metal analysis.

3.2. Analytical accuracy of the measurements

We show here the analytical accuracy with measured concentration of refractory metals (Fe, Al, Ca and Mg) in PM_{2.5} samples (Figure 1).

Table 1. Standardization of temperature protocol for aerosol sample digestion with HF + HNO₃ + H₂O₂ + H₂O (1: 4: 1: 6; by volume)

Temperature (°C)	Observed time (h)	Particles left
130	12	Yes
140	12	Yes
150	12	No
160	11	No
170	11	No
180*	11	No

*slight softening of Teflon vial was noticed, so we avoided to test at higher temperature

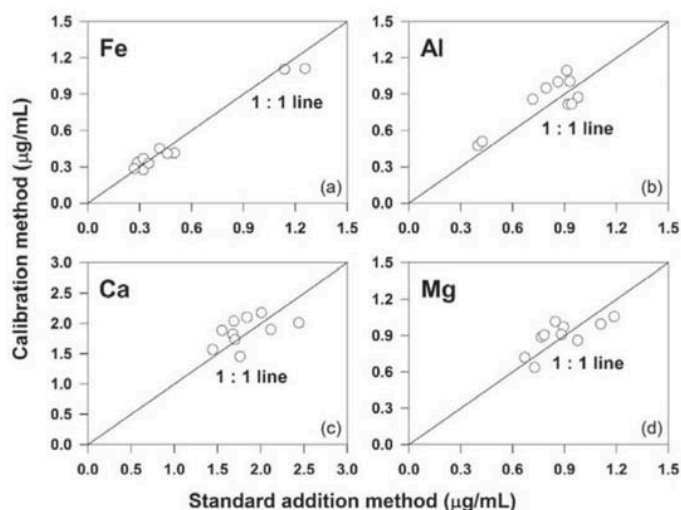


Figure 1: Scatter plot (n = 10) showing a good agreement (within ± 15%) for refractory metals determined using two independent methods

Analytical accuracy of the measurements has been ascertained by a 1-to-1 comparison of the data set (n = 10; Figure 1a, b, c, d) derived from calibration method and those from standard addition method. Basically, in standard addition method we add known amounts of standard and make the final volume of each sample aliquot to same level. Standard addition method is a well-established approach to assess the influence of matrix effect on low-level analyte concentration. Concentration of analytes reported herein (Fe, Al, Ca and Mg), obtained from calibration versus standard addition method show agreement within ± 15%. Thus, our study shows a reasonably good agreement between the two set of independent measurements of Fe, Al, Ca and Mg on ICP-OES.

3.3. Ambient concentrations of PM_{2.5} and associated metals

In this study, we report ambient concentrations of 14 metals in PM_{2.5} during a study conducted in wintertime (December 2014–February 2015) at Kanpur location in IGP. PM_{2.5} mass concentrations varies from 95–240 (Avg ± SD: 157 ± 37) µg m⁻³. Average concentration (± SD) of metals assessed in this study is listed in Table 2. It is evident from table 2 that concentrations of refractory metals (Fe, Al, Ca and Mg) at Kanpur are in µg m⁻³ (~ 3-10). Whereas, the other metals are reported in ng m⁻³, exception being the ambient concentrations of V at Kanpur location (Avg: 1.09 µg m⁻³). Also, in table 2 we have given literature-based hazardous health effects associated with these metals (www3.epa.gov/ttnemc01/prelim/otm31appC.pdf). Besides several acute health effects of metals, it is important to mention here that the generation of reactive oxygen species (ROS) by Fe, Cu and Mg is one of the major concerns of several researchers (Demokritou et al., 2002;2003). Thus, ambient aerosol records of metals are very much important to understand their source characteristics and impact on human health (Gupta et al., 2004; Gupta et al., 2011; Gupta et al., 2010; Moreno et al., 2010; Rajput et al., 2015; Rajput et al., 2014c; Singh et al., 2014).

Now we discuss temporal co-variability of mineral dust, using Al as a proxy, along with PM_{2.5} mass concentration. The variability in mass concentrations of associated Al is recorded from 1.1-7.4 µg m⁻³. The mineral dust contribution in PM_{2.5} varies from 14-93 (Avg ± SD: 52 ± 20) µg m⁻³. Thus, mineral dust contributes to 34 ± 11% of PM_{2.5} over IGP (Kanpur) during the wintertime (December 2014–February 2015). In

Table 2: Ambient concentrations of metals in PM_{2.5} (this study) and literature based their potential health impacts on inhalation

Parameters	Concentration ($\mu\text{g m}^{-3}$)	Hazardous health effects
Al	4.2 \pm 1.6	Very reactive element
As	0.012 \pm 0.009	ATP disruption, inhibits PO ₄ ³⁻ binding with enzymes
Ca	9.8 \pm 2.0	Relatively harmless
Cd	0.005 \pm 0.003	Bronchial and pulmonary irritation, high acute toxicity, cadmium build-up in kidneys, effects on the liver, lung, bone, immune system, blood and nervous system
Co	0.002 \pm 0.001	Respiratory irritation, wheezing, asthma, pneumonia, fibrosis, cardiac effects, congestion of the liver, kidneys
Cr	0.012 \pm 0.017	Carcinogenic, perforations and ulcerations of the septum, bronchitis, decreased pulmonary function, pneumonia, shortness of breath
Cu	0.012 \pm 0.009	Irritation of nasal mucous membranes, eye irritation, upper respiratory tract irritation, metallic taste, nausea, metal fume fever, nausea, dizziness, vomiting and diarrhea, generation of reactive oxygen species
Fe	3.4 \pm 1.2	Induce oxidative stress and DNA damage, cause severe rickets in infants, nausea, stomach pain or cramping, vomiting, generation of reactive oxygen species
Mg	4.4 \pm 1.1	Generation of reactive oxygen species
Mn	0.055 \pm 0.054	Effects on the central nervous system (CNS), including slowed visual reaction time, hand steadiness and eye-hand coordination
Ni	0.013 \pm 0.006	Cancer risk, respiratory effects, risk of lung and nasal cancers
Pb	0.236 \pm 0.431	Endocrine disruption (inappropriately turn off and on genes)
V	1.09 \pm 1.03	Lung cancer, kidney damage
Zn	0.27 \pm 0.15	Cause anemia and decrease the levels of good cholesterol

this study, we have estimated the contribution of mineral dust in atmospheric aerosols considering Al content to be 8% of mineral dust (McLennan, 2001). Total carbonaceous aerosols (TCA = 1.6*OC + EC) contributes to ~ 18% to PM_{2.5} in this study (Rajput and Sarin, 2014; Turpin and Lim, 2001). Temporal variability records in the mass concentrations of PM_{2.5} and associated mineral dust abundance is shown in Figure 2. It is obvious from figure 2 that variability pattern of mineral dust is quite similar to that of PM_{2.5} mass concentration. This is attributable to significant contribution of mineral dust to PM_{2.5}. In subsequent section, we have made attempts to understand natural (crustal dust) versus anthropogenic inputs of all metals assessed in this study.

3.4. Enrichment of metals in aerosols compared to upper continental crust

Enrichment factors (EF) of metals with respect to Al are shown in Figure 3. Basically, excess amount of metals with respect to crustal composition is expressed in terms of EF using a mathematical expression given below:

$$EF_X = \frac{X_{aerosol}/Al_{aerosol}}{X_{UCC}/Al_{UCC}} \quad (1)$$

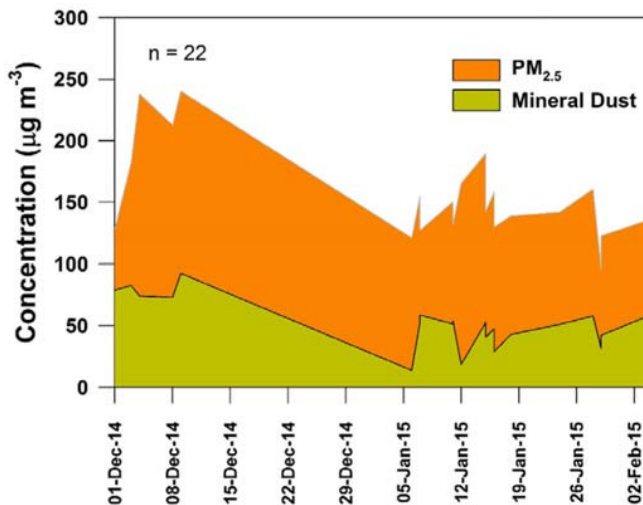
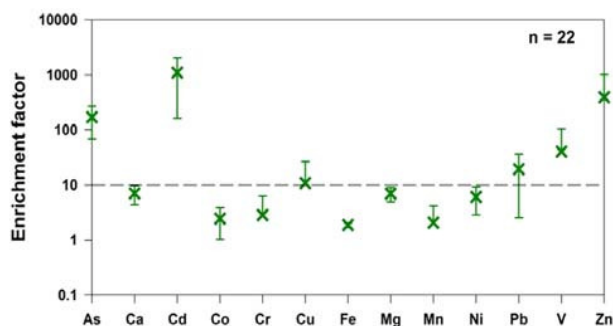


Figure 2: Temporal variability of PM_{2.5} mass concentration and associated mineral dust at Kanpur location (IGP)



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Figure3: Enrichment factors of several metals assessed in this study at Kanpur location (IGP) with respect to Al

Where, EF_x represents enrichment factor of a particular element (X).

In general, Al is considered to be of the crustal origin. A literature reports upper continental crust (UCC) composition: As/Al ratio of 0.00002, Ca/Al ratio of 0.375, Cd/Al ratio of 0.000001, Co/Al ratio of 0.00021, Cr/Al ratio of 0.001045, Cu/Al ratio of 0.00031, Fe/Al ratio of 0.4375, Mg/Al ratio of 0.16625, Mn/Al ratio of 0.0075, Ni/Al ratio of 0.00055, Pb/Al ratio of 0.00021, V/Al ratio of 0.00134 and Zn/Al ratio of 0.00089 (McLennan, 2001). In this study, we have found As/Al ratio of 0.003 ± 0.002 , Ca/Al ratio of 2.64 ± 1.01 , Cd/Al ratio of 0.001 ± 0.001 , Co/Al ratio of 0.001 ± 0.000 , Cr/Al ratio of 0.003 ± 0.004 , Cu/Al ratio of 0.003 ± 0.005 , Fe/Al ratio of 0.82 ± 0.07 , Mg/Al ratio of 1.16 ± 0.34 , Mn/Al ratio of 0.015 ± 0.016 , Ni/Al ratio of 0.003 ± 0.002 , Pb/Al ratio of 0.053 ± 0.085 , V/Al ratio of 0.347 ± 0.546 and Zn/Al ratio of 0.071 ± 0.037 . Using the aforementioned equation, we have found that EF for As is 170 ± 101 , Ca is 7 ± 3 , Cd is 1101 ± 940 , Co is 2 ± 1 , Cr is 3 ± 3 , Cu is 11 ± 16 , Fe is 2 ± 0.2 , Mg is 7 ± 2 , Mn is 2 ± 2 , Ni is 6 ± 3 , Pb is 19 ± 17 , V is 40 ± 63 and Zn is 394 ± 614 . Thus, it can be summarized that some toxic metals viz. As, Cd, Cu, Pb, V and Zn show significant (c.a. 10) EF with respect to the upper continental crust (UCC). Thus, these metals have high inputs from anthropogenic emission sources. Toxic effects of these metals are listed in Table 2. In this context, it is very important to mitigate the pollution level of these metals. However, metals exhibiting $EF < 10$ is widely considered to be primarily derived from the crust (Chakraborty and Gupta, 2010; Gupta and Mandaria, 2013).

3.5. Characteristic ratios of mineral aerosols in the IGP

As discussed above that EF of Fe, Ca and Mg with respect to Al is less than 10. This suggests that Fe, Ca and Mg are derived from upper continental crust. In other words, they are constituent of mineral aerosols. It is well known that mineral dust is a perennial constituent of the lower atmosphere (Hatch and Grassian, 2008). In this study at Kanpur location, one of our major interests was to assess geochemistry of mineral aerosols over the Indo-Gangetic Plain. In this context, it is important to mention here that IGP extends from north-west to north-east and is the most populated and polluted region with a large agricultural-land cover area in India. Despite of this fact, there is a scarcity of metals data over the IGP. Linear regression analysis has been performed (Figure 4a, b, c) to assess the characteristic ratios of Fe/Al, Ca/Al and Mg/Al in atmospheric $PM_{2.5}$ samples. We have found that in IGP (Kanpur; $n = 22$): Fe/Al ratio is 0.80 ± 0.03 , Ca/Al ratio is 2.19 ± 0.14 and Mg/Al ratio is 1.00 ± 0.07 . It is important to mention here that couple of studies have highlighted the role of Fe(III) in heterogeneous formation of secondary aerosol species and photo-chemistry (Al-Abadleh, 2015; Rajput, et al., 2016a). However, total Fe content in aerosols does not alter due to such reactions. Thus, these ratios represent the characteristics quite well even under long-range transport.

3.6. Geochemistry (chemical fingerprinting) of mineral aerosols

Ternary diagram is one of the well-established approaches to characterize environmental samples (rock, sediments and water samples and aerosols). In this study, we have made a ternary diagram with three characteristic ratios: Fe/Al, Ca/Al and Mg/Al (Figure 5). Our purpose herein, is to assess differences in mineral aerosol characteristics over the IGP (this study) and those over semi-arid high dust regions in western India: Mt Abu (a high-altitude site; $24.6^\circ N$, $72.7^\circ E$, 1680 m amsl) (Kumar and Sarin, 2009) and Ahmedabad (an urban region; $23.0^\circ N$, $72.6^\circ E$) (Rastogi and Sarin, 2009). It is evident from figure 5 that chemical

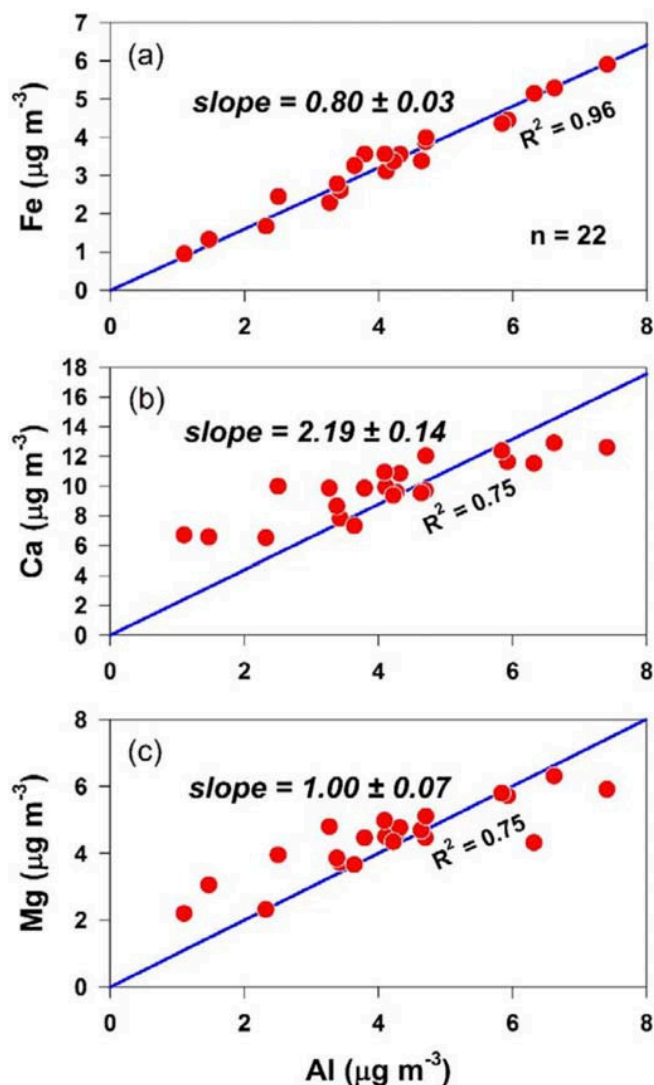


Figure4: Linear regression analysis of crustal elements: (a) Fe, (b) Ca and (c) Mg with Al over IGP (Kanpur)

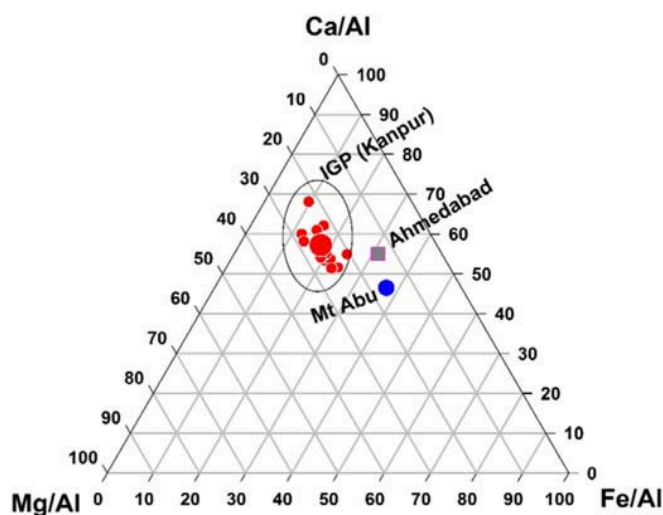


Figure5: Chemical fingerprinting of mineral aerosols over Indo-Gangetic Plain (at Kanpur, this study) shows distinct differences from semi-arid high dust regions (Ahmedabad and Mt. Abu) in western India. The average data at Kanpur location (this study) is shown by a bigger circle

characteristics of mineral dust over IGP (Northern India) are distinctly different than those over western India. Thus, it can be summarized that complete metal digestion in conjunction with an accurate and precise quantification of crustal metals viz. Fe, Al, Ca and Mg has led to a better understanding on mineral aerosol characterization from different geographical locations. Summing up, this study could serve rapid and accurate analysis of metals for environmental and toxicology assays (Lee and Park, 2010; Singh and Gupta, 2016).

4. Conclusions

The established analytical protocol involves a mixture of HF: HNO₃: H₂O₂ in 1: 4: 1: 6 (by volume), followed by heating (closed digestion) at 150 °C in Teflon vials on hot-plate (Graphite-coated). Complete digestion could be achieved in ~ 12 h. Several toxic metals (As, Cd, Cu, Pb, V and Zn) exhibit their significant input from anthropogenic emission sources. Mineral dust and total carbonaceous aerosols contribute to ~35% and 18%, respectively in this study. Ternary diagram utilizing Fe/Al, Ca/Al and Mg/Al ratios exhibits distinct difference between the mineral aerosol chemical characteristics over IGP (Northern India) and high dust semi-arid locations in western India (Mt Abu and Ahmedabad). Thus, complete digestion of metals and accurate analysis has revealed diagnostic information on mineral dust characteristics and anthropogenic emission of several toxic metals. This study has implications to facilitate processing and analysis of metals for environmental and toxicology assays.

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References

- Gupta, T, Mandaria, A, 2013, Sources of Submicron Aerosol during Fog Dominated Wintertime at Kanpur, Environmental Science and Pollution Research, DOI: 10.1007/s11356-11013-11580-11356.
- Gustafsson, Ö, Kruså, M, Zencak, Z, Sheesley, RJ, Granat, L, Engström, E, Praveen, PS, Rao, PSP, Leck, C, Rodhe, H, 2009, Brown Clouds over South Asia: Biomass or Fossil Fuel Combustion?, Science, 323, 495-498.
- Mahowald, NM, Baker, AR, Bergametti, G, Brooks, N, Duce, RA, Jickells, TD, Kubilay, N, Prospero, JM, Tegen, ICGB, 2005, Atmospheric global dust cycle and iron inputs to the ocean, Global Biogeochemical Cycles, 19, GB4025, doi:10.1029/2004GB002402.
- Rajput, P, Sarin, MM, Kundu, SS, 2013, Atmospheric particulate matter (PM_{2.5}), EC, OC, WSOC and PAHs from NE-Himalaya: abundances and chemical characteristics, Atmospheric Pollution Research, 4, 214-221.
- Rajput, P, Sarin, MM, Sharma, D, Singh, D, 2014a, Atmospheric polycyclic aromatic hydrocarbons and isomer ratios as tracers of biomass burning emissions in Northern India, Environmental Science and Pollution Research, 21, 5724-5729.
- Rajput, P, Sarin, MM, Sharma, D, Singh, D, 2014b, Organic aerosols and inorganic species from post-harvest agricultural-waste burning emissions over northern India: impact on mass absorption efficiency of elemental carbon, Environmental Science: Processes & Impacts, 16, 2371-2379.
- Singh, DK, Gupta, T, 2015, Speciation of atmospheric polycyclic aromatic hydrocarbons (PAHs) present during fog time collected submicron particles, Environmental Science and Pollution Research, DOI: 10.1007/s11356-11015-14413-y.
- Venkataraman, C, Habib, G, Kadamba, D, Shrivastava, M, Leon, JF, Crouzille, B, Boucher, O, Streets, DG, 2006, Emissions from open biomass burning in India: Integrating the inventory approach with high-resolution Moderate Resolution Imaging Spectroradiometer (MODIS) active-fire and land cover data, Global Biogeochemical Cycles, 20, GB2013.
- Doezema, LA, Longin, T, Cody, W, Perraud, V, Dawson, ML, Ezell, MJ, Greaves, J, Johnson, KR, Finlayson-Pitts, BJ, 2012, Analysis of secondary organic aerosols in air using extractive electrospray ionization mass spectrometry (EESI-MS), RSC Advances, 2, 2930-2938.
- Rajeev, P, Rajput, P, Gupta, T, 2016, Chemical characteristics of aerosol and rain water during an El-Niño and PDO influenced Indian summer monsoon, Atmospheric Environment, 145, 192-200.
- Rajput, P, Gupta, T, Kumar, A, 2016a, Diurnal variability of sulfate and nitrate aerosols during wintertime in the Indo-Gangetic Plain: Implications to heterogeneous phase chemistry, RSC Advances, DOI: 10.1039/C6RA19595D.
- Rajput, P, Sarin, MM, Rengarajan, R, 2011a, High-precision GC-MS analysis of atmospheric polycyclic aromatic hydrocarbons (PAHs) and isomer ratios from biomass burning emissions, Journal of Environmental Protection, 2, 445-453.
- Butler, OT, Cairns, WRL, Cook, JM, Davidson, CM, 2016, Atomic spectrometry update - a review of advances in environmental analysis, Journal of Analytical Atomic Spectrometry, 31, 35-89.
- Cuoco, E, Tedesco, D, Poredda, RJ, Williams, JC, De Francesco, S, Balagizi, C, Darrah, TH, 2013, Impact of volcanic plume emissions on rain water chemistry during the January 2010 Nyamuragira eruptive event: Implications for essential potable water resources, Journal of Hazardous Materials, 244-245, 570-581.
- Huang, SL, Yin, C-Y, Yap, SY, 2010, Particle size and metals concentrations of dust from a paint manufacturing plant, Journal of Hazardous Materials, 174, 839-842.
- Lamble, KJ, Steve, JH, 1998, Microwave digestion procedures for environmental matrices. Critical Review, Analyst, 123, 103R-133R.
- Lee, B-K, Park, G-H, 2010, Characteristics of heavy metals in airborne particulate matter on misty and clear days, Journal of Hazardous Materials, 184, 406-416.
- Wu, S, Xia, X, Lin, C, Chen, X, Zhou, C, 2010, Levels of arsenic and heavy metals in the rural soils of Beijing and their changes over the last two decades (1985-2008), Journal of Hazardous Materials, 179, 860-868.
- Mark, RC, Owen, B, Jennifer, MC, Malcolm, SC, Louise, MG, Alexis, JH, Douglas, LM, 1999, Environmental Analysis, Journal of Analytical Atomic Spectrometry, 14, 279-352.
- Aldabe, J, Santamaria, C, Elustondo, D, Lasheras, E, Santamaria, JM, 2013, Application of microwave digestion and ICP-MS to simultaneous analysis of major and trace elements in aerosol samples collected on quartz filters, Analytical Methods, 5, 554-559.
- Butler, OT, Cairns, WRL, Cook, JM, Davidson, CM, 2014, 2013 Atomic spectrometry update-A review of advances in environmental analysis, Journal of Analytical Atomic Spectrometry, 29, 17-50.
- Swami, K, Judd, CD, Orsini, J, Yang, KX, Husain, L, 2001, Microwave assisted digestion of atmospheric aerosol samples followed by inductively coupled plasma mass spectrometry determination of trace elements, Fresenius J Anal Chem, 369, 63-70.
- Tursic, J, Radic, H, Kovacevic, M, Veber, M, 2008, Determination of selected trace elements in airborne aerosol particles using different sample preparation, Arh Hig Rada Toksikol, 59, 111-116.
- Winton, H, Bowie, A, Keywood, M, van der Merwe, P, Edwards, R, 2016, Suitability of high-volume aerosol samplers for ultra-trace aerosol iron measurements in pristine air masses: blanks, recoveries and bugs, Atmos. Meas. Tech. Discuss., 2016, 1-32.
- Mackey, KRM, Chien, C-T, Post, AF, Saito, MA, Paytan, A, 2015, Rapid and gradual modes of aerosol trace metal dissolution in seawater, Frontiers in Microbiology, 5.
- Marx, SK, Lavin, KS, Hageman, KJ, Kamber, BS, O'Loingsigh, T, McTainsh, GH, 2014, Trace elements and metal pollution in aerosols at an alpine site, New Zealand: Sources, concentrations and implications, Atmospheric Environment, 82, 206-217.
- Park, JH, Mudunkotuwa, IA, Crawford, KJ, Anthony, TR, Grassian, VH, Peters, TM, 2016, Rapid analysis of the size distribution of metal-containing aerosol, Aerosol Science and Technology, 1-8.
- Chance, R, Jickells, TD, Baker, AR, 2015, Atmospheric trace metal concentrations, solubility and deposition fluxes in remote marine air over the south-east Atlantic, Marine Chemistry, 177, Part 1, 45-56.
- Rajput, P, Mandaria, A, Kachawa, L, Singh, DK, Singh, AK, Gupta, T, 2016b, Chemical characterization and source-apportionment of PM₁₀ during massive loading at an urban location in Indo-Gangetic Plain: Impact of local sources and long-range transport, Tellus-B, 68, 30659.
- Kumar, A, Gupta, T, 2015, Development and Field Evaluation of a Multiple Slit Nozzle-Based High Volume PM_{2.5} Inertial Impactor Assembly (HVIA) Aerosol and Air Quality Research, 15, 1188-1200.
- Rajput, P, Sarin, MM, Rengarajan, R, Singh, D, 2011b, Atmospheric polycyclic aromatic hydrocarbons (PAHs) from post-harvest biomass burning emissions in the Indo-Gangetic Plain: Isomer ratios and temporal trends, Atmospheric Environment, 45, 6732-6740.
- Chakraborty, A, Gupta, T, 2010, Chemical Characterization and Source Apportionment of Submicron (PM₁₀) Aerosol in Kanpur Region, Aerosol and Air Quality Research, 10, 433-445.
- Demokritou, P, Gupta, T, Ferguson, S, Koutrakis, P, 2002, Development and laboratory characterization of a prototype coarse particle concentrator for inhalation toxicological studies, Journal of Aerosol Science, 33, 1111-1123.
- Demokritou, P, Gupta, T, Ferguson, S, Koutrakis, P, 2003, Development of a High-Volume Concentrated Ambient Particles System (CAPS) for Human and Animal Inhalation Toxicological Studies, Inhal. Toxicol., 15, 111-129.
- Gupta, T, Demokritou, P, Koutrakis, P, 2004, Development and Performance Evaluation of a High-Volume Ultrafine Particle Concentrator for Inhalation Toxicological Studies, Inhal. Toxicol., 16, 851-862.
- Gupta, T, Jaiprakash, Dubey, S, 2011, Field Performance Evaluation of a newly Developed PM_{2.5} Sampler at IIT Kanpur, Science of the Total Environment, 409, 3500-3507.
- Gupta, T, Kothari, A, Srivastava, DK, Agarwal, AK, 2010, Measurement of number and size distribution of particles emitted from a mid-sized transportation multipoint port fuel injection gasoline engine, Fuel, 89, 2230-2233.
- Moreno, T, Querol, X, Alastuey, As, Amato, F, Pey, J, Pandolfi, M, Kuenzli, N, Bouso, L, Rivera, M, Gibbons, W, 2010, Effect of fireworks events on urban background trace metal aerosol concentrations: Is the cocktail worth the show?, Journal of Hazardous Materials, 183, 945-949.
- Rajput, P, Mandaria, A, Kachawa, L, Singh, DK, Singh, AK, Gupta, T, 2015, Wintertime source-apportionment of PM₁₀ from Kanpur in the Indo-Gangetic plain, Climate Change, 1, 503-507.
- Rajput, P, Sarin, MM, Sharma, D, Singh, D, 2014c, Characteristics and emission budget of carbonaceous species from post-harvest agricultural-waste burning in source region of the Indo-Gangetic Plain, Tellus-B, doi.org/10.3402/tellusb.v66.21026.

41. Singh, A, Rajput, P, Sharma, D, Sarin, MM, Singh, D, 2014, Black Carbon and Elemental Carbon from Postharvest Agricultural-Waste Burning Emissions in the Indo-Gangetic Plain, *Advances in Meteorology*, 2014, 10.
42. McLennan, SMC, 2001, Relationships between the trace element composition of sedimentary rocks and upper continental crust, *Geochemistry, Geophysics, Geosystems*, 2, doi: 2000GC000109.
43. Rajput, P, Sarin, MM, 2014, Polar and non-polar organic aerosols from large-scale agricultural-waste burning emissions in Northern India: Implications to organic mass-to-organic carbon ratio, *Chemosphere*, 103, 74-79.
44. Turpin, BJ, Lim, H-J, 2001, Species contribution to $PM_{2.5}$ Mass concentrations: Revisiting common Assumptions for Estimating Organic Mass, *Aerosol Science and Technology*, 35, 602-610.
45. Hatch, CD, Grassian, VH, 2008, 10th Anniversary Review: Applications of analytical techniques in laboratory studies of the chemical and climatic impacts of mineral dust aerosol in the Earth's atmosphere, *Journal of Environmental Monitoring*, 10, 919-934.
46. Al-Abadleh, HA, 2015, Review of the bulk and surface chemistry of iron in atmospherically relevant systems containing humic-like substances, *RSC Advances*, 5, 45785-45811.
47. Kumar, A, Sarin, MM, 2009, Mineral aerosols from western India: Temporal variability of coarse and fine atmospheric dust and elemental characteristics, *Atmospheric Environment*, 43, 4005-4013.
48. Rastogi, N, Sarin, MM, 2009, Quantitative chemical composition and characteristics of aerosols over western India: One-year record of temporal variability, *Atmospheric Environment*, 43, 3481-3488.
49. Singh, DK, Gupta, T, 2016, Effect through inhalation on human health of PM_{10} bound polycyclic aromatic hydrocarbons collected from foggy days in northern part of India, *Journal of Hazardous Materials*, 306, 257-268.