SECM/15/094

Heavy Metals in Atmospheric Deposition in Kandy City; Implications for Urban Water Resources

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Abstract: Atmospheric deposition is a serious issue in the context of biogeochemical cycling of heavy metals (HMs) and the resulting impacts on urban water resources. In this study, dry deposition (DD) and bulk deposition (BD) samples were collected from four sites located in heavy traffic areas in Kandy, Sri Lanka. Wet deposition (WD) was determined from the difference between DD and BD. Samples were analyzed for Al, Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb using inductively coupled plasma-mass spectrometry. Relatively high concentrations of Fe, Al and Zn were found in both DD and WD samples collected. In BD, percentage dissolved fraction of Ni, Cr, Cu, Cd, Al and Pb was 94, 86, 81, 78, 61, 46% respectively. Presence of high dissolved fraction of highly toxic HMs such as Cr and Pb can result in significant ecosystem health impacts due to their ready bioavailability. The presence of metals such as Al, Fe, Zn, Pb, Cr and Cd in WD was consistently more significant compared to DD. The presence of high concentrations of mobile forms of metals in WD will contribute to the pollution of urban stormwater, resulting in the degradation of urban receiving water environments and associated ecosystems.

Keywords: Atmospheric deposition, heavy metals, stormwater quality, urban water pollution

1. Introduction

Atmospheric deposition is a global issue since it leads to the degradation of terrestrial ecosystems. Among different pollutants in atmospheric deposition, heavy metals play an important role due to its availability to biogeochemical cycling. Heavy metals that are emitted from different sources into the atmosphere; natural and anthropogenic sources such as soil, sea water and volcanic eruptions, emissions from traffic, fossil fuel combustion, industrial activities and solid waste incineration, tend to deposit via dry and wet deposition processes [1]. Heavy metals can be toxic to humans at even trace levels, especially Cd, Cr, Hg and Pb like metals [1, 2]. Based on the WHO air quality guidelines the threshold levels Cd, Pb and Mn are 5 ng m^{-3} $year^{-1}$, 0.5 and 0.15 μg m^{-3} $year^{-1}$ respectively. As heavy metals are non-biodegradable and transport through biogeochemical cycling, they can be accumulated in fauna and flora, water bodies, soils and even in humans bodies [2, 3].

Either via wet or dry deposition, heavy metals will be transported to surface and groundwater [2]. Since wet deposition has a higher percentage of the dissolved fraction, the urban water resources can be directly affected [2]. Furthermore, heavy metals deposited as dry deposition on soil or impermeable surfaces will be transported by stormwater runoff to receiving waters [4]. Studies have shown that atmospheric deposition consists of a diverse range of heavy metals in high concentrations [5, 6]. Also, past research studies have provided detailed insights to urban water pollution by deposited heavy metals via stormwater runoff [7]. Therefore it is important to study about atmospheric deposition of heavy metals and its effects on urban water bodies.

Kandy is the second largest city in Sri Lanka, located at a valley in the hill country which shows typical characteristics of a mountainous city in the developing world. Although there have been very few studies on Kandy's atmospheric pollution, it is proven to be highly polluted by gases and hydrocarbons [8]. However, no studies have focused attention on the atmospheric deposition of heavy metals which can directly pollute the surface water bodies such as the Mahaweli River (the potable water source for the population of Kandy), via stormwater runoff. Hence, the objective of the study was to quantify the heavy metals loads, namely, Al, Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb in atmospheric deposition samples in Kandy in bulk, dry and wet deposition which will contribute to evaluating the effects on urban water bodies.

2. Material and methods

2.1 Sampling sites

For the preliminary study, four locations, Fire brigade site, Police station site, Railway station site and at National Institute of Fundamental Studies (NIFS), were selected within Kandy City area to collect deposition samples. Sampling sites were selected considering traffic volume and distance to major roads. The sampling station at NIFS was the control site since traffic volume is relatively low. Samples were collected during February 2015 based on rainfall events.

2.2 Sample collectors

Sample collectors were designed as a funnel bottle connected system [9]. Two polyethylene bottles connected to polyethylene funnels were used to collect deposition samples. Each bottle was placed inside a PVC column and two columns connected to a pole. The system was fixed at a height of 1.5m above ground. One bottle was used to collect dry deposition while other for bulk deposition.

2.3 Sample collection

Same collection bottles were placed just after a rainfall event. Dry sample collection was done just before the next immediate rainfall event and the bulk deposition sample was collected just after the same rainfall event. After collection, the samples were transported to the laboratory as soon as possible (within maximum ½ hour) following standard quality control procedures.

2.4 Sample preservation and digestion

After sample bottles transferred to the laboratory, meniscus was marked in bulk deposition samples to determine the total volume of the sample. Funnels were rinsed with de-ionized water. For bulk deposition samples, pH was measured just after the samples received by the laboratory. Approximately 50 ml of sample was filtered using 45 μm membrane filter for analysis of dissolved elements and 50 ml of original sample separated for analysis of total recoverable elements. Remaining sample volume was measured using a measuring cylinder and added to a pre-weighed crucible to determine the weight of total solids. Finally, the bottles were filled with water to the meniscus and volume was measured as sample volume.

In dry deposition samples, funnels were rinsed with 100 ml of de-ionized water.

Samples separated for total recoverable elements and dissolved elements, were preserved until digestion. For preservation, samples were acidified to pH<2 with 1:1 HNO_3 solution. After 16 hours, samples were verified to be pH<2. Samples were kept in refrigerator until digestion.

Preserved samples were acid digested prior to analysis. 50 ml of sample transferred into a Griffin beaker and added 2 ml (1:1) HNO_3 acid and 1 ml (1:1) HCl acid was added. The temperature was maintained at no higher than 85 ^{o}C. The sample was evaporated until it approached 15 mL using gentle heating with avoided boiling. Then the solution contained in the beaker was allowed to cool and gravity settling of any solids. Samples were stored in 15 ml centrifuge tubes for further analysis.

2.5 Analysis

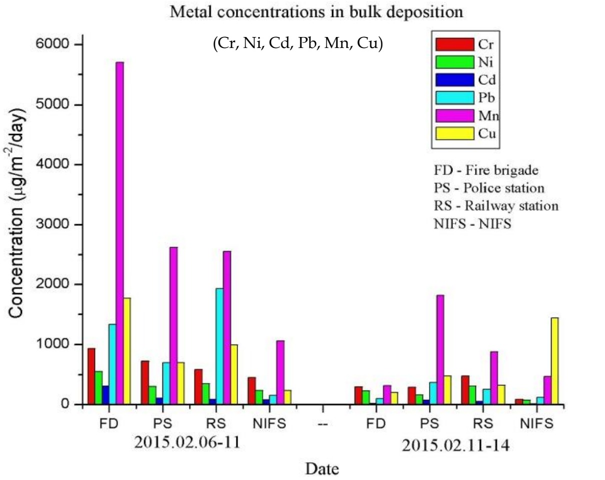
Digested samples were analysed for Al, Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb using Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) at Queensland University of Technology (QUT), Australia, laboratory which is a certified laboratory. For total solids, sample contained in the crucibles were placed in an oven at 105 ^{o}C until evaporation of all liquids. Total solids was measured by the weight difference between the oven dried and empty crucible.

3. Results and discussion

3.1 Bulk deposition

Heavy metal concentrations in bulk deposition are shown in Figure 1a and 1b. It shows the concentrations of heavy metals based on their loads. Al and Fe have been reported with relatively higher concentrations than the others. Both Al and Fe demonstrated significant difference from all other tested heavy metals. However, no significant difference was observed between them. At two consecutive rainfall events, the metal concentration change pattern in bulk deposition is Fe = Al >> Zn = Cu = Mn = Cr = Ni = Pb = Cd. There is no other significant difference between the two different time periods for heavy metals deposition in Kandy City. Accordingly, the deposition pattern of heavy metals was the same in Kandy City throughout the month of February 2015. For Al, Fe, Cu, Zn and Mn, no significant difference was observed for the four sites. However, Ni, Cr, Cd and Pb exhibited a significant difference among sample collection sites. The averages of metal concentrations among the sites varies as Railway station > Police station ~ Fire brigade > NIFS.

The percentages of dissolved element fraction of heavy metals are illustrated in Figure 2a and 2b, respectively. Although, Cu and Zn have low total metal concentrations in bulk deposition compared to Al, Mn and Fe, they were high in the dissolved fraction. This is attributed to the higher solubility of Cu and Zn compared to the other elements. In the literature, the solubility change pattern is given as Zn > Cd > Cu > Ni > Pb > Cr [10]. However, in our study it was Ni > Cr = Al = Zn = Cd = Cu = Mn > Fe = Pb. This is attributed to the chemical characteristics of the heavy metal species present in the urban atmosphere in Kandy City. The presence of high soluble fraction indicates the studied metals are ready to impose eco-toxic impacts in the water-soil environment and on biota [11].



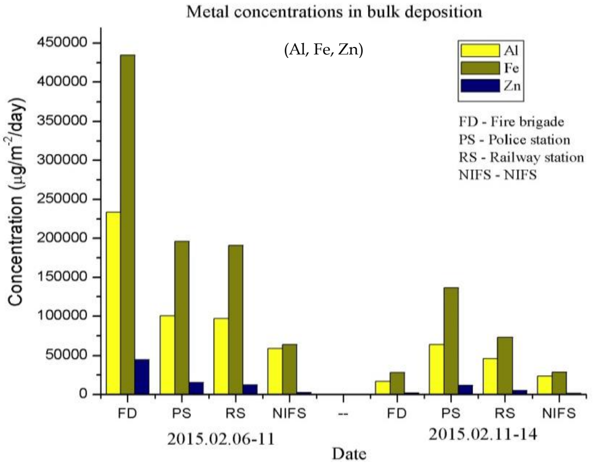
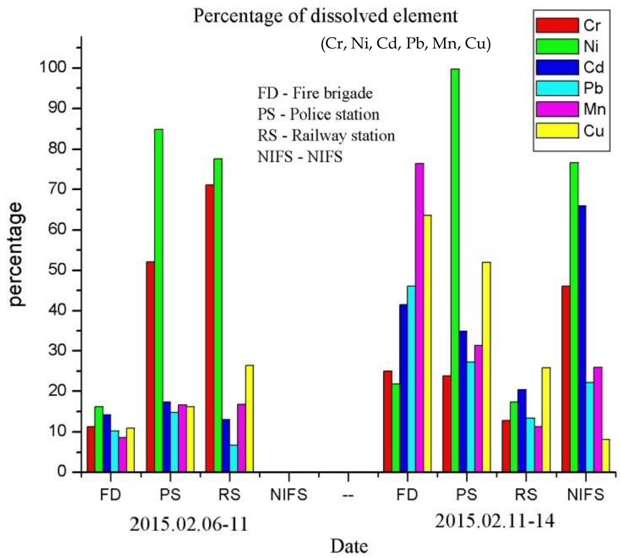


Figure 1a (top): Metal concentrations for Cr, Ni, Cd, Pb, Mn and Cu in bulk deposition in Kandy City during February 2015. 1b (bottom): Metal concentrations for Al, Fe and Zn in bulk deposition in Kandy City during February 2015

3.2 Dry deposition

Heavy metals in the dry deposition during February 2015 in Kandy City depicted in Figure 3a and 3b. Similar to the bulk deposition data, Al and Fe showed significantly high concentrations in dry deposition and there was no significant difference among rest of heavy metals.

Taking into consideration three different rainfall events, overall low heavy metal concentrations in dry deposition loads have been reported in Figure 3a and 3b for February 6th to 9th which was Friday to Monday, February 11th to 12th which was Wednesday to Thursday and February 14th to 16th which was Saturday to Monday.



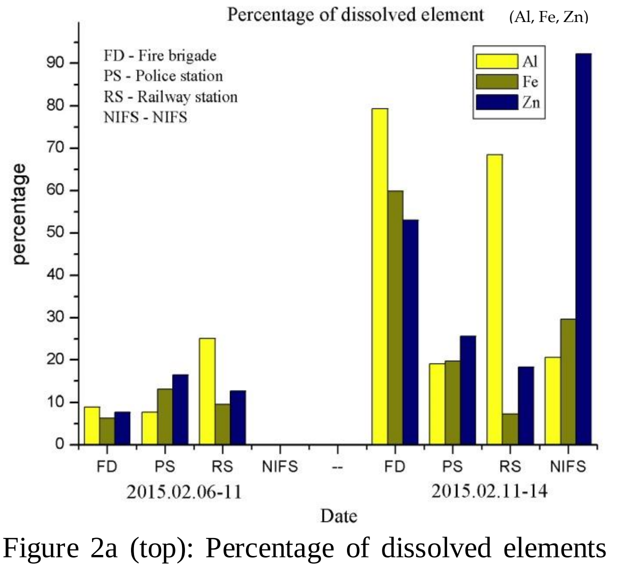
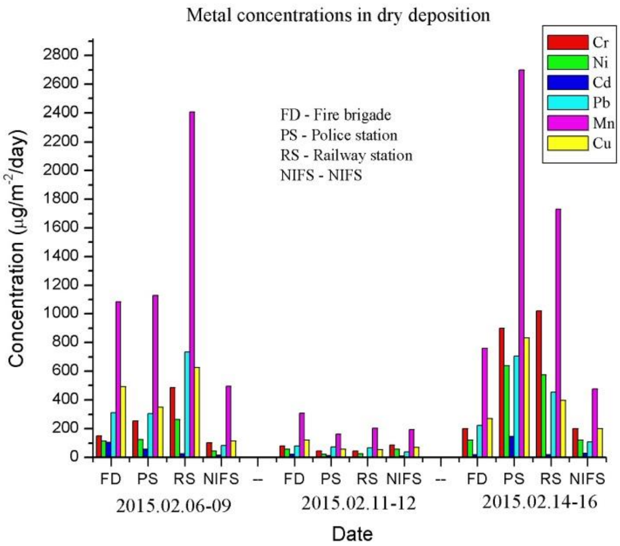


Figure 2a (top): Percentage of dissolved elements from total deposition during February, 2015 – for Cr, Ni, Cd, Pb, Mn and Cu. 2b (bottom): Percentage of dissolved elements from total deposition during February, 2015 – for Al, Fe and Zn.

Fridays and Mondays are the days where the highest traffic volumes are experienced due to the large number of vehicles entering and leaving Kandy City. The highest average metal concentrations in dry deposition have been reported for the period 14th to 16th February. As Kandy City has historical importance, even during the weekend, a high number of vehicles can be expected. The emissions from the large number of vehicles may be the reason for high heavy metal concentrations in dry deposition during February 6th to 9th and 14th to 16th. In the case of February 11th to 12th, which were Wednesday and Thursday, no significant difference was observed for Al, Fe, Zn, Mn, Cu, Cd and Ni among four sites whereas a significant difference among sites was observed for Cr and Pb. Similar data have been observed in Sha-Lu, Taiwan, during the year 2003 [12]. The average dry deposition fluxes reported for day time and night time as 54.1 and 26.2 g m^{-2} respectively. The higher day time dry deposition fluxes have been reported due to high traffic incidences. But in night time due to low traffic incidences the dry deposition fluxes are low [12].



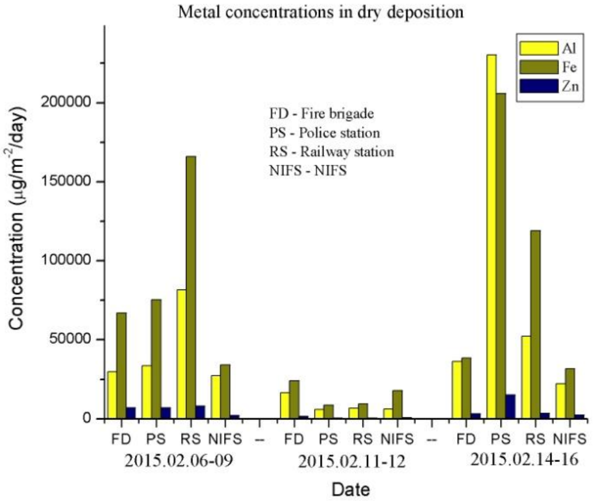
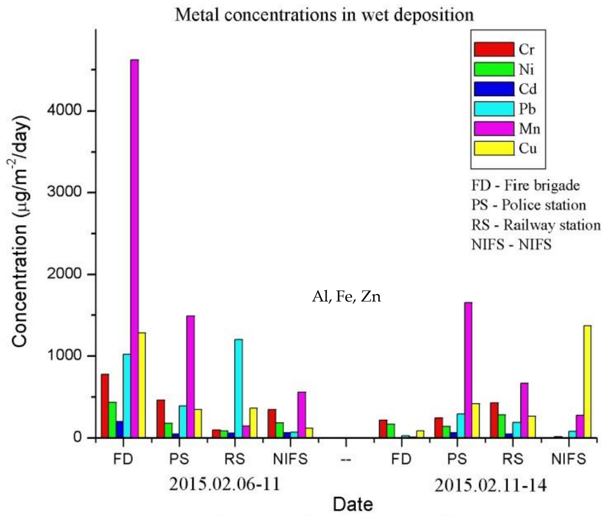


Figure 3a (top): Metal concentrations for Cr, Ni, Cd, Pb, Mn and Cu in dry deposition in Kandy City during February 2015. 3b (bottom): Metal concentrations for Al, Fe and Zn in dry deposition in Kandy City during February 2015

The average heavy metals in dry deposition was distributed as Railway station > Police station ~ Fire brigade > NIFS.

3.3 Wet deposition

Wet deposition concentrations are shown in Figure 4a and 4b. Wet deposition has been calculated on the basis of the difference between bulk and dry deposition for a particular rainfall event. Similar to the dry and bulk deposition, wet deposition showed comparatively higher concentrations for Al and Fe than the other metals. In Izmir, Turkey during year 2004 the HM changing pattern in wet deposition is same as present study [11]. For both of studies it was as Zn > Pb > Ni > Cd [11]. The highest average wet depos (Cr, Ni, Cd, Pb, Mn, Cu) ported at the Railway station and lowest at the NIFS. The wet deposition is more critical than dry deposition in terms of urban water pollution. Also the wet deposition is higher than dry deposition for studied HMs. Similar data was shown in Izmir, Turkey [11].



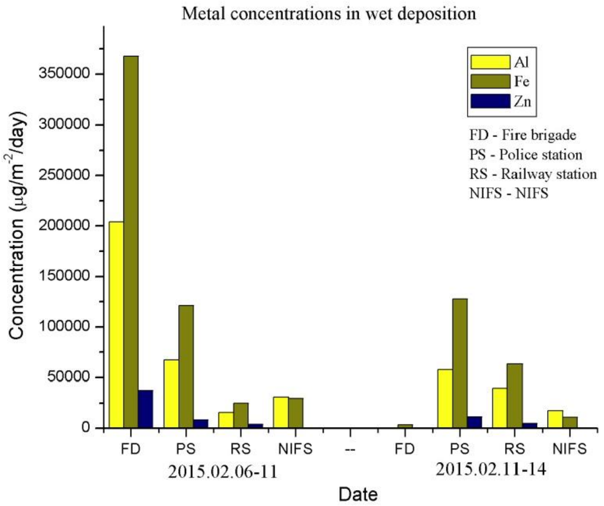


Figure 3a (top): Metal concentrations for Cr, Ni, Cd, Pb, Mn and Cu in wet deposition in Kandy City during February 2015. 4b (bottom): Metal concentrations for Al, Fe and Zn in wet deposition in Kandy City during February 2015.

4. Conclusions

The bulk and dry deposition were collected in Kandy City during February 2015 encompassing two consecutive rainfall events. Al and Fe were reported in significantly higher concentrations in deposition loads than other heavy metals that were tested. For Fe, the reported highest values are 434.86 g/m^2/day for bulk deposition during February 6^{th} to 11^{th} at Fire brigade and 205.53 g/m^2/day for dry deposition during February 14^{th} to 16^{th} at Police station. The lowest Fe values are 28.122 g/m^2/day for bulk deposition during 11^{th} to 14^{th} at Fire brigade whereas it was 8.845 g/m^2/day for dry deposition during 11^{th} to 14^{th} February at Police station. Other heavy metals, Mn, Cu, Zn, Ni, Cr, Cd and Pb did not show a significant difference among each other for bulk, dry and wet deposition. The Railway station showed a significant difference among other sampling sites exhibiting highest average heavy metal concentrations.

The dissolved fraction represents the bioavailable form that is contained in atmospheric deposition. Even though Cu and Zn showed lower total metal concentrations in bulk deposition, percentage of dissolved fractions is higher at 64% and 53%, respectively. This indicates that high percentages of deposition are already available in bioavailable form.

Acknowledgement

The Authors wish to offer a special acknowledgement to the National Science Foundation, Sri Lanka for providing funding for undertaking this research study (Grant number RG/2014/EB/03).

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