Microwave assisted digestion followed by ICP-MS for determination of trace metals in atmospheric and lake ecosystem

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ABSTRACT

The study of trace metals in the atmosphere and lake water is important due to their critical effects on humans, aquatic animals and the geochemical balance of ecosystems. The objective of this study was to investigate the concentration of trace metals in atmospheric and lake water samples during the rainy season (before and after precipitation) between November and December 2015. Typical methods of sample preparation for trace metal determination such as cloud point extraction, solid phase extraction and dispersive liquid–liquid micro-extraction are time-consuming and difficult to perform; therefore, there is a crucial need for development of more effective sample preparation procedure. A convection microwave-assisted digestion procedure for extraction of trace metals was developed for use prior to inductively coupled plasma-mass spectrometric determination. The result showed that metals like zinc (133.50–419.30 μg/m³) and aluminum (53.58–378.93 μg/m³) had higher concentrations in atmospheric samples as compared to lake samples before precipitation. On the other hand, the concentrations of zinc, aluminum, chromium and arsenic were significantly higher in lake samples after precipitation and lower in atmospheric samples. The relationship between physicochemical parameters (pH and turbidity) and heavy metal concentrations was investigated as well. Furthermore, enrichment factor analysis indicated that anthropogenic sources such as soil dust, biomass burning and fuel combustion influenced the metal concentrations in the atmosphere.

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Introduction

The atmospheric environment contains numerous types of air pollutants from natural and/or anthropogenic sources. Trace metals, particularly heavy metals, are gradually being introduced into the environment as contaminants and pollutants, byproducts of industry and human civilization. A significant environmental compartment in the biochemical cycles of trace metals is the atmosphere (Hu and Balasubramanian, 2003). During the last decades, environmental pollution by toxic heavy metals at trace levels has dramatically increased. Atmospheric deposition is considered to be the major source of toxic metals such as Hg, Cd, Pb and others to ecosystems. These trace metals are present in various forms in the environment (water, soil and air). There is an increasing need to determine the natural background of trace metals...
(such as toxic heavy metals) to assess global environmental pollution. These trace metals are considered some of the most serious pollutants in the natural environment due to their toxicity, persistence and bioaccumulation, because they are being retained in plants, animals and nature in general (Gleyzes et al., 2002). The monitoring of trace metals in environmental samples is a key part of analytical chemistry due to their negative influence on human and environmental health (Najafi et al., 2010). Trace metal pollution not only affects the production of crops but also influences the quality of the atmosphere as well as water bodies, and threatens the health and life of animals, humans and microorganisms (Li et al., 2013). The environmental pollution caused by trace metals is a long-term, irreversible process and can be toxic even at low concentrations.

Trace metal pollution is a growing universal problem in the aquatic environment and currently it has reached an alarming level (Ogoyi et al., 2011). Many trace metals are regarded as serious pollutants of aquatic ecosystems because of their long environmental persistence, toxicity and ability to be incorporated into food chains. There are many sources of trace metals, however the most important sources of trace metals in aquatic ecosystems are anthropogenic activities. Conversely, trace metals also arise in minor amounts naturally and may enter into an aquatic system through leaching of rocks, airborne dust, vegetation and biomass burning (Fernandez and Olalla, 2000). Their concentration usually depends on both natural and anthropogenic sources, amount of suspended particulate matter and composition, salinity, pH and redox potential (Adiana et al., 2011). In aquatic environments, trace metal concentrations are usually monitored by measuring their concentrations in water and sediments such as those in lake ecosystems, and generally are present at low levels in water and contribute to contamination and pollution (Storelli et al., 2005).

Lakes are sensitive areas due to their potential exposure to pollutants from several sources. Lake ecosystems also provide an indication of climate variation, either directly or indirectly through their catchment. Pollutants enter the water body of a lake through the connecting rivers, runoff water and from atmospheric deposition. The limited water movement within lakes influences the degree of pollution, and high concentrations of pollutants can decrease the biodiversity, as well as the physical environment surrounding the lake ecosystems (Dudgeon et al., 2006). Atmospheric deposition is one of the major sources of pollutants in a lake ecosystem (Vuorenmaa et al., 2014). The emissions from industry, motor vehicles and agricultural activities (biomass burning) are released to the atmosphere, blown by the wind; they then interact with water and fall down to the ground through wet deposition. These pollutant particulates in air fall during rain as acid rain and as fine particles (particle size ≤ 2.5 μm) (Driscoll et al., 1995). These particles can bring nutrients and trace metals into aquatic ecosystems, such as lakes, during their settling down to the surface of earth. It has been noted that the deposition of sulfates and nitrates increases the acidity of a water body (Burton et al., 2013; Ding et al., 2014). Excessive amounts of trace metals from atmospheric deposition are toxic to aquatic organisms such as fish and microorganisms (Ashraf et al., 2011; Walraven et al., 2014). Trace metals deposited into lakes are usually sequestered in the layers of sediments on the bottom of the lake. Sediment quality is a good indicator of pollution in the water column, because it tends to concentrate the heavy metals and other organic pollutants, which can be recycled into the water body by any disturbance.

Determination of trace metals in atmospheric and lake ecosystems is important for monitoring environmental pollution. In general, direct estimation of very low levels of elements in environmental samples is often impossible due to the presence of interfering compounds or the concentration of analytes being below the detection limit of instrumentation. The most commonly used analytical method for trace metal determination is the atomic absorption spectroscopy (AAS) technique, which offers multi-elemental analysis but suffers from poor sensitivity in the determination of trace metals in environmental samples like lake water and atmospheric air samples, due to their low concentrations. Different pre-concentration techniques such as cloud point extraction, solid phase extraction and the use of chelating agents before samples that are analyzed by AAS have been developed and successfully applied in the determination of trace metals (Najafi et al., 2010; Soylak and Aydin, 2011; Gentscheva et al., 2012). However, these extraction techniques and methods of analysis are restricted for determination of trace metals in samples due to the usage of toxic organic solvents for extraction, and require extensive and complicated procedures. Inductively coupled plasma-mass spectrometry (ICP-MS) is considered attractive and one of the most sensitive techniques for the multi-elemental analysis of trace metals in various environmental samples. This technique usually requires a transformation (extraction) of the samples into solution before analysis. Using ICP-MS apparatus, the detection limits for trace metals can be down to sub-ppt or picomol/L levels in simple matrix solutions. Nowadays among the various pre-concentration procedures for trace metals, digestion procedures using closed-vessel microwave sample preparation systems are used for various environmental investigations of trace metals due to their excellent capabilities for multi-element concentration with minimum selectivity and sample manipulation.

The main objective of this investigation is to establish a simple and fast method of trace metals analysis in environmental samples, including atmospheric particulates and lake water. The trace metals from atmospheric deposition and lake samples were extracted using a combination of nitric acid (HNO₃) and hydrogen peroxide (H₂O₂) with the help of 650 W microwave energy, which is faster than other reported extraction methods. This study also quantifies the effect of trace metal concentration during rain fall in lake samples around the study area.

1. Materials and methods
1.1. Reagents and reference materials
For the preparation of reagents and standards, freshly prepared ultrapure water (18.2 MΩ cm) from a TKA smart2plus ultrapure water system (TKA, Germany) was used. Analytical grade reagent HNO₃ (Fluka, France) and H₂O₂ (Merck, Germany) were used for the digestion experiments. An ICP-MS multi-element standard was obtained from Perkin Elmer and used for calibration of the equipment. Polyethylene bottles for water
samples were obtained from Thermo scientific (Thermo scientific, Malaysia). All chemicals were of reagent grade and used without further purification.

1.2. Description of sampling site

The sampling site for the determination of trace metals is located around Kampar, within the state of Perak, which is on the north coast of peninsular Malaysia. Kampar is located at 4.3° North latitude, 101.15° East longitude and 63 m elevation above sea level (Fig. 1). This city has a humid tropical climate and great deal of rainfall even in the driest month. This climate is considered to be Af according to the Koppen-Geiger climate classification. The average temperature is 27.3°C and average annual rainfall of 3133 mm has been recorded. This area consists of a number of tin mine lakes and is at a great distance from local roads. The geographical location of this area is ideal to study the anthropogenic emissions from Sumatra, Indonesia and their chemical interactions.

1.3. Sampling techniques

To ensure accurate determination of low amounts of trace metals, it is important to avoid contamination during all stages of sample collection and preparation. The sample collection from the lake was performed from four different sampling spots with fast moving water, at least 20–30 cm deep in 1000 mL polyethylene bottles. The bottles were soaked in 10% nitric acid solution and left for at least 24 hr, and then thoroughly cleaned with ultrapure water prior to sampling. These bottles were filled with acidified ultrapure water and transported to the lake. At the sampling site the acidified water was removed; all bottles were rinsed 3 times by the lake water prior to sample collection. Rinsing was conducted downstream of the sampling sites. After rinsing, the bottle was submerged below the water level approximately 15–20 cm from the surface to avoid contamination and allowed to fill completely to the top. The lids were then tightly screwed on to prevent leakage. The samples were refrigerated until analysis.

Atmospheric particulate samples were collected with a pre-calibrated Thermo scientific total suspended particulate (TSP) high volume air sampler (Thermo Scientific, USA) and Tisch environmental PM2.5 high volume air sampler (Tisch, USA). The samples were collected for 24 hr at flow rate of 1.132 m³/min in order to collect sufficient mass for chemical characterization. The accuracy of volume flow measurement was ±2%. The filters had been pre-heated at 120°C overnight before weighing. At least three blank samples were also taken by placing clean filters in the sampler for 24 hr with the sampling flow switched off. After sampling, the filters were packed in a clean aluminum foil until analysis.

1.4. Analytical methods

Sample pH values (Hanna Instrument, Romania) and turbidity (Lovibond, Germany) were measured immediately after collection. The samples were filtered through 0.45 μm, 47 mm glass microfiber filter paper using a vacuum pump in order to remove particulate matter. In filtered samples, a mixture of 4 mL concentrated nitric acid and 2 mL hydrogen peroxide was added and samples were digested in a microwave oven for 5 min at 650 W. After digestion the samples were allowed to cool and kept in the refrigerator at 4°C until further analysis, normally conducted within one month.

The air filter samples were cut into small pieces and placed in borosilicate glass vessels capped with Teflon. The samples were treated with 4 mL of concentrated nitric acid and 2 mL of hydrogen peroxide using the microwave oven for 15 min to ensure complete digestion of particles. The microwave process consisted of three steps with a power of up to 650 W. The first step was heating to 450 W for 5 min; the second step was holding at 650 W for 10 min and the last cooling down to room temperature. The digested solution was diluted to 50 mL with ultrapure water and carefully filtered using Membrane solution
Polytetrafluoroethylene (PTFE) synergy filters (25 mm, 0.45 μm) prior to analysis, and stored at 4°C until further analysis.

1.5. Instrumentation

Determination of trace metal concentrations in the samples was performed with a Perkin Elmer NexION 300Q ICP-MS (Perkin-Elmer Inc., USA) equipped with a Perkin Elmer integrated auto-sampler, cross-flow nebulizer and a Quartz torch. The instrumental operating parameters for sample analysis are listed as follows: nebulizer gas flow rate 0.90 L/min, auxiliary gas flow rate 1.20 L/min, plasma gas flow rate 16 L/min, deflector voltage –12 V, Inductive coupled plasma radio-frequency (ICP RF) power 1150 W, analog stage voltage –1750 V, pulse stage voltage 1100 V, discriminator threshold 26, Alternating current (AC) rod offset –4, trace metals m/z measurement 27Al, 52Cr, 65Zn, 75As, 111Cd, 115Sn, 202Hg and 208Pb, replicates 3, and rinse time 30 sec. The ICP-MS NexION instrument software was used to control all instrument operation including tuning, data acquisition and data analysis. Argon was used as the reaction gas in the collision cell to reduce the polyatomic interference. ICP-MS calibration solutions were prepared by dilution of a commercially available 100 ppm multi-element standard (Perkin-Elmer) in ultrapure water. The ICP-MS NexION instrument software was used to perform all instrument operation including tuning, data acquisition and data analysis. Argon was used as the reaction gas in the collision cell to reduce the polyatomic interference. ICP-MS calibration solutions were prepared by dilution of a commercially available 100 ppm multi-element standard (Perkin-Elmer) in ultrapure water.

1.6. Enrichment factor (EF)

The EF is a way to characterize the chemical composition of airborne particulate matter. The concept of EF was originally introduced by Menard and Chesselet (1979), and was used to calculate the ratio of the concentration of metals in a sample with that of a selected reference (such as aluminum) which is almost entirely crustal in origin, compared with the corresponding ratio in the average composition of the earth crust. The EF value was calculated by Eq. (1):

$$EF = \frac{(X/Al)_{sample}}{(X/Al)_{crust}}$$

where $(X/Al)_{sample}$ is the ratio of metal and Al concentration of the sample; $(X/Al)_{crust}$ is the ratio of metal and Al concentration in the earth crust.

2. Results and discussion

2.1. Physicochemical parameters

The physicochemical parameters such as pH and turbidity of water samples were determined in the laboratory from the collected lake samples.

2.1.1. pH

The basic physicochemical parameters of lakes including pH are given in Table 1. A lake pH fluctuates somewhat each day and from season to season in response to photosynthesis by algae, watershed runoff and other factors. Each sampling site exhibited different pH values ranging between 7.63 and 7.88, which is slightly basic, and shifted to slightly acidic conditions between 6.81 and 6.89 after precipitation. From the pH measurements, it was noticed that the pH of lake water was acidic after precipitation when compared to that before precipitation. This may be due to the possible reaction of rainwater with atmospheric carbon dioxide to produce acidic runoff water, which ultimately saturated the lake water, hence lowering the pH of water samples. It is suggested that the area under study is influenced by biomass burning that emits particulate matter in the atmosphere, as well as great quantities of acidity generating gases such as CO, NOx and SO2, which contribute to the development of acid rain.

2.1.2. Turbidity

Turbidity is produced due to suspended soil particles and organic matter along with planktonic growth. The present study result shows that the turbidity of lake samples ranged from a minimum of 17.3 Nephelometric Turbidity Units (NTU) (before precipitation) to 31.5 NTU (after precipitation). The highest turbidity levels were observed after precipitation in all sampling sites and the lowest before precipitation; the corresponding data are shown in Table 1. Therefore, high turbidity may be attributed to the soil particles, inflow of silt, wood ashes, undesirable insoluble inorganic substances, and other particles in the atmosphere mixing during precipitation and subsequent runoff water. The study of Offem et al. (2011) reached a similar conclusion for Ikwori Lake in Nigeria. They reported that high turbidity due to flooding occurred during the wet season due to the rainfall and runoff from nutrient-rich agricultural lands, which increased the level of some particles and debris in Ikwori Lake.

Turbidity can be used to detect the occurrence of pollutants such as trace metals because it is strongly influenced by the properties of transported suspended solids, such as shape, size and mineral composition (Landers and Sturm, 2013). It has been reported that heavy metals are particle-bound pollutants in water, with suspended solids associated with 60%–97% of total metals (Nguyen et al., 2005). During this study it was also noticed that the concentration of trace metals depended on the turbidity, and the relationship between the turbidity and trace metal concentrations is shown in Fig. 2. From the relationship it can be seen that the concentration of toxic metals increases with increase in the turbidity, leading to the conclusion that the trace metal concentrations are directly related to the suspended solids, which could be supported by the relationship to particulate matter.

<table>
<thead>
<tr>
<th>Table 1 – pH and turbidity Nephelometric Turbidity Units (NTU) of the lake samples before and after precipitation.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sampling site</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>pH</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
</tr>
</tbody>
</table>
2.2. Detection limits

The concentration of trace metals in the filter and water blanks was measured to establish a baseline. For the quantitative analysis no blank correction was necessary, as standards and samples were treated exactly the same way, adding the same amount of extraction solution. The detection limits were estimated by using the equivalent concentrations corresponding to three times the standard deviation of measurement of analytes in a series of blanks treated the same way as the samples. The detection limits were evaluated on different dates to obtain their range. Overall the blank values and trace metal detection limits generally ranged from 0.01-0.5 μg/L, except for Zn and Al, and were sufficient to determine the metal concentrations in samples. The detection limits are shown in Table 2.

2.3. Trace metals in lake water

In order to assess the water quality of Kampar lakes, 4 samples on a bimonthly basis before and after precipitation were collected from November to December 2015, from four sites around the study area as shown in Fig. 1, and analyzed for total dissolved trace metals. Analysis of lake samples was performed by the procedure described above and the results are shown in Table 3. Among the trace metals, the highest concentrations were recorded for Zn (19.777–43.289 μg/L) after precipitation, followed by Al, Cr, As, Hg, Pb, Sn and Cd. The only trace metal that showed no significant difference between seasons was Cd. A very interesting observation occurred in sampling site 1, where all trace metals had their highest concentrations during the whole study. In our present investigation, it was noted that the levels of trace metals such as zinc and aluminum in the lake samples during precipitation were within allowable limits. Other than these trace metals, others such as arsenic, chromium, tin, cadmium, lead and mercury were not within allowable limits recommended by the Malaysian standard (NAHRIM, 2016). A study of Ismaniza and Saleh (2012) showed almost the same results that the concentrations of some heavy metals in water samples were beyond the detection limits of the Malaysian standard.

The high concentrations of Zn and Al in lake samples from the study area are expected to originate from soil dust. The major ongoing land reclamation and construction activity around the study area potentially contribute to the amount of wind-blown dust, and appear to have contributed to the increased concentration and deposition of the trace metals associated with soil dust, which contains a high amount of zinc and aluminum. According to the agency responsible for the toxic substance and disease registry, zinc and aluminum are naturally occurring elements found in the earth. Forest-clearing activities using slash and burn methods could also have contributed to the amount of zinc- and aluminum-containing dust, since the emission of biomass burning pollutants from the upwind source from Sumatra, Indonesia was prominent. The study of Latif et al. (2015) found that the concentration of Zn was enriched when there is contribution from biomass burning or wood combustion. Meanwhile, the concentrations of anthropogenic Pb and Cd likely originated from vehicle emissions, such as from the trucks and cars moving around the lake.

<table>
<thead>
<tr>
<th>Metals</th>
<th>Limit of Detection (LOD) of blank atmospheric samples (μg/m³)</th>
<th>Limit of Detection (LOD) of blank lake water samples (μg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>2.801</td>
<td>2.187</td>
</tr>
<tr>
<td>Cr</td>
<td>0.006</td>
<td>0.001</td>
</tr>
<tr>
<td>Zn</td>
<td>1.519</td>
<td>1.876</td>
</tr>
<tr>
<td>As</td>
<td>0.002</td>
<td>0.001</td>
</tr>
<tr>
<td>Cd</td>
<td>0.001</td>
<td>0.002</td>
</tr>
<tr>
<td>Sn</td>
<td>0.003</td>
<td>0.015</td>
</tr>
<tr>
<td>Pb</td>
<td>0.550</td>
<td>0.002</td>
</tr>
<tr>
<td>Hg</td>
<td>0.088</td>
<td>0.001</td>
</tr>
</tbody>
</table>

Fig. 2 – Relationship between turbidity and concentration of trace metals in lake samples before and after precipitation.
However, the detected arsenic concentrations were also higher in this study than those in most of the previous reports (Taweel et al., 2013; Salim et al., 2008). The high concentration of arsenic in lake water might be due to biomass burning and volcano activity from the southern air mass and transferred to the water bodies by wet deposition. Most toxic heavy metals in trace amounts released into the environment find their way into the aquatic system as a result of direct input, atmospheric deposition and erosion due to rain water. In general, wet and dry atmospheric depositions are the major pathways of accumulation of heavy metals in lake ecosystems (Öztürk et al., 2009). It has been determined that approximately 80% of the atmospheric removal of toxic metals such as Pb, Cd, Zn, As and others to the aquatic medium takes place by wet deposition, while 40% of removal for Al and Hg is related to dry deposition (Kvietkus et al., 2011). Thus, the low concentrations that were obtained for other metals may be attributed to domestic and agricultural effluents. These pollutants can change the natural conditions of an aquatic medium and cause behavioral changes as well as morphological imbalance in aquatic organisms.

### 2.3.1. Comparison of trace metal concentrations before and after precipitation

Many studies in the literature have been reported on the seasonal variation of concentrations of trace metals during wet deposition (Takeda et al., 2000; Kim et al., 2000; Pike and Moran, 2001). These studies have confirmed that different trace metals show different seasonal variation in wet deposition fluxes depending on the nature and strength of their contamination source, major wind direction, mixing depth, hours of dry weather and monthly precipitation amount. In this study, there was no clear seasonal trend noticed in the metal deposition except that the highest deposition rates occurred after precipitation. Statistical analyses were conducted to test significant differences in the concentrations of trace metals in lake samples as a function of the sampling time before and after precipitation (Table 3). It is clear that concentrations of all the metals detected after precipitation were highest, while low concentrations were measured before precipitation. The variation in the concentration of trace metals before and after precipitation is likely due to the difference in the size distribution of atmospheric particles, and could be related to the source of pollutant emissions. This result can also be explained by the fact that the heavy metals which arise from anthropogenic sources (high temperature combustion-generated aerosols) containing trace metals could be transported, collected and concentrated during the no-rain time period, and then washed out of the air with the rain runoff and leached into the ground-water through the soil and lake sediment.

### 2.4. Trace metals in atmospheric samples

The contents of the eight trace metals Zn, Al, As, Cd, Pb, Sn, Cr and Hg in the ambient air samples collected over a period of 2 months are shown in Fig. 3. The total number of ambient air samples was 8, collected using two types of high volume air sampler (TSP and particulate matter smaller than 2.5 μm aerodynamic sizes (PM$_{2.5}$)) before and after wet precipitation. The heavy metal concentrations of atmospheric samples were analyzed both before and after precipitation using ICP-MS. The result indicates that the recorded concentrations of heavy metals in the air samples before precipitation were high in both types of samples (TSP and PM$_{2.5}$), and were found to be higher than the World Health Organization guidelines (WHO, 2000). The contents of heavy metals were as follows: Zn ranged from 133.50–419.30 μg/m$^3$; Al: 53.58–378.93 μg/m$^3$; As: 2.83–5.43 μg/m$^3$; Sn: 3.88–8.27 μg/m$^3$; Cr: 5.15–17.32 μg/m$^3$; Pb: 7.15–37.41 μg/m$^3$; Cd: 0.21–0.39 μg/m$^3$ and Hg: 0.23–3.82 μg/m$^3$.

The occurrence of heavy metals in the atmosphere and their distribution pattern in the study area suggest that some of the emitted metals were transported via wind as aerosols to this site from the city. The prevailing southwest wind in this region favors the transport of metals from Sumatra to the study area. As mentioned by a number of studies, metals bound to aerosols can be transported over long distances, even over thousands of kilometers, before they return to the ground surface (Barbante et al., 2001). For instance, the average

### Table 3 - Trace metal concentrations in different sampling sites before and after precipitation in the months of November and December (unit: μg/L).

<table>
<thead>
<tr>
<th>Sampling site 1 Before</th>
<th>Sampling site 1 After</th>
<th>Sampling site 2 Before</th>
<th>Sampling site 2 After</th>
<th>Sampling site 3 Before</th>
<th>Sampling site 3 After</th>
<th>Sampling site 4 Before</th>
<th>Sampling site 4 After</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd 0.502 0.259 0.112 0.741</td>
<td>0.057 0.264 0.048 0.807</td>
<td>0.048 0.807</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Sn 1.440 2.191 4.371 5.073</td>
<td>2.221 1.163 1.419 0.637</td>
<td>1.419 0.637</td>
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<td></td>
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</tr>
<tr>
<td>Hg 2.256 3.869 2.772 3.173</td>
<td>1.802 2.185 1.332 2.133</td>
<td>1.332 2.133</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Pb 1.651 3.593 1.805 6.032</td>
<td>1.115 3.646 0.748 8.675</td>
<td>0.748 8.675</td>
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</tr>
<tr>
<td>Zn 15.137 23.27 18.126 19.777</td>
<td>19.593 43.289 11.964 34.067</td>
<td>11.964 34.067</td>
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<tr>
<td>As 1.421 2.428 3.635 3.877</td>
<td>2.165 4.304 2.598 5.855</td>
<td>2.598 5.855</td>
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<tr>
<td>Cd 0.394 0.479 0.088 0.307</td>
<td>0.061 0.264 0.054 1.244</td>
<td>0.054 1.244</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn 1.204 1.734 0.9928 1.095</td>
<td>1.833 1.094 1.175 0.819</td>
<td>1.175 0.819</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg 2.441 3.547 1.947 3.567</td>
<td>1.364 2.083 1.154 3.178</td>
<td>1.154 3.178</td>
<td></td>
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</tr>
<tr>
<td>Pb 4.068 5.281 1.410 4.379</td>
<td>0.971 3.857 0.694 5.672</td>
<td>0.694 5.672</td>
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</tr>
</tbody>
</table>
The atmospheric residence time of particles is 3 to 7 days (Pleßow and Heinrichs, 2001).

In this study it is noted that the concentrations of trace metals in TSP were higher than in PM2.5. The discrepancy between TSP and PM2.5 is normal because TSP would include particles larger than PM2.5. In particular, Southeast Asia biomass burning episodes greatly affect and increase the mass concentration of coarse particles (Lee and Hieu, 2011).

Of all the trace metals examined, Zn and Al showed higher concentrations in both types of samples collected during the period under study, followed by Pb, Cr, As, Cd, Sn and Hg. The high concentrations of Zn and Al in dry deposition indicate sources such as peat soil dust and strong emissions from anthropogenic sources (fossil fuel and biomass burning) and also attributed to elevated concentrations of these metals in the atmosphere around the study area. The characteristics of peat soil, which is acidic with a high specific surface area, influence its capability to be a natural adsorbent (Kyziol, 2002). According to the study of Shah et al. (2012) Zn, Cd and Pb are produced during biomass burning and anthropogenic activities. Another study reported that the presence of Zn in ambient air is due to the traffic emission originating from engine oils, brake and exhaust systems (Bender and Lange, 2011). The concentration of As in the atmosphere is usually low, but as noted above, it was higher in this study. Arsenic enters the atmosphere through volcanic emission, wind erosion, and low temperature volatilization from soil. The most important anthropogenic source of arsenic is fossil fuel and biomass combustion, and As is present in the atmosphere as As(III)2O3 dust particles. The Pacyna and Pacyna (2001) study estimated that anthropogenic sources of atmospheric As contribute 30% of the global atmospheric As flux. However, it is accepted that these anthropogenic sources have an important impact on airborne arsenic composition.

From the experimental results it can be clearly stated that the concentrations of the studied heavy metals were higher during dry deposition. However, during wet deposition the values were in general low and fell within standard levels. This discrepancy might have occurred because of rainfall and dilution, which suggests that the amount or intensity of rainfall may affect the dynamics of air quality (André et al., 2007). For Cd and Pb only, the concentration levels were almost the same during dry and wet deposition. This might be due to the high percentage of motor vehicles passing through the study area. The study of Othman and Latif (2013) supported the above conclusion that traffic emission and biomass burning are the major sources of heavy metals and major contributors to the particulate matter in urban air.

2.5. Comparison between atmospheric and lake samples

The trace metal concentrations of lake and atmospheric samples in ambient air were compared during the observation period. It was noted that the overall heavy metal concentrations in the lake samples in this study were much lower than the concentrations observed for the ambient air samples. According to the obtained results, it was also noted that the lake sample concentration increased with decreases in the concentration of atmospheric samples during precipitation, and the results are shown in Fig. 4. This study supports other reported observations (Kozak et al., 2015; Pan and Wang, 2015; Lynam et al., 2015; Melaku et al., 2008) that precipitation actions can strongly influence the variability in concentration of both atmospheric and lake samples.

2.6. EF analysis

In order to assess the origins of the trace metals accumulated in atmospheric particulates, the results are often analyzed using EFs. Measuring EF is an essential part of geochemical studies and is usually used to differentiate between metals originating from anthropogenic (non-crustal) and geogenic (crustal) sources, and to assess the degree of metal contamination (Yongming et al., 2006). Fig. 5 shows EF values of Cr, Zn, As, Cd, Sn, Pb and Hg for the two sampling time periods (before and after precipitation). According to Zhang and Liu (2002), an EF value approaching 1 suggests that the element originated from a crustal source, whereas the EF values in the 10 range (1-10) indicates that it mainly comes from a naturally occurring source and is not enriched. Moreover, a value of (10–100) suggests that the element was moderately enriched, while an EF value >100 suggests that the element was highly enriched, with anthropogenic activities as the main sources, and hence termed as an enriched element.
However, the types of crustal materials are unique in different areas and not much is known about the uncertainties concerning fractionation during weathering (Kaya and Tuncel, 1997). Duan et al. (2002) stated that the reference element must have the characteristics of being the most abundant element in the earth’s crust, very stable and not affected by pollution; and according to Al-Momani (2003), Al is derived almost exclusively from crustal material, so this is the element most often used for normalization.

Fig. 5 indicates that Cr, Zn, As, Cd, Sn, Pb and Hg have very high EF values in both TSP and PM$_{2.5}$, suggesting contributions from various anthropogenic sources like fossil fuel combustion and industrial emissions (Kang et al., 2011; Gangwar et al., 2012). High EF values of metals indicate their contribution from emissions of non-crustal origin. The high values for Zn and Cd obtained in this study are similar to results in the studies by Latif et al. (2015). Another study demonstrated that Zn is one of the indicators of biomass burning, and had a high EF value from peat soil combustion during a haze episode in Southeast Asia (See et al., 2007). From the statistical results it was also noticed that Cr had EF values greater than 10, suggesting that this element was moderately enriched, and might have originated from airborne dust and also have significant contributions from both natural and anthropogenic sources. The EF value recorded for Hg was the highest (more than 14,000) among all the elements, and may have originated from non-crustal sources such as a forest fire near the sampling site. The results of the present study show that all the elements were significantly enriched at the study locations since their EF values were greater than 100.

### 3. Conclusions

We have reported the measurement of 8 trace metals in lake water and atmospheric ambient air samples before and after precipitation events, collected around Kampar, Perak during the period of November to December 2015. The trace metal concentrations in lake water samples showed the following trend, Zn > Al > Cr > As > Hg > Pb > Sn > Cd, while those in atmospheric samples showed the trend Zn > Al > Pb > Cr > As > Sn > Hg > Cd. Higher values of the trace metals were observed before precipitation in atmospheric samples, except for cadmium and lead, which showed almost the same concentrations before and after precipitation periods. It appears that the main reasons for the high concentration levels of the studied heavy metals in Kampar city are various emission sources such as fossil fuel combustion, biomass burning and soil dust around the study area. A similar situation can be observed when the data are expressed in terms of the crustal enrichment, which refers to the composition of the earth’s crust. When the trace metal data were compared with lake water samples after precipitation events, it should be mentioned that the concentrations of metals decreased in the atmospheric samples because of washing by the rainwater, while the concentrations in the lake water increased. The results of this study also showed that an increase in turbidity of lake water samples accompanied increases in the concentrations of metals.

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