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Seasonal Evaluation of Trace Metal Concentrations in Airborne Particulate Matter in Kanyakumari District

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ABSTRACT

Airborne particulate matter (APM) was collected non-simultaneously ten sampling sites in Kanyakumari District during summer and winter season using a high volume sampling method. The sampling sites are characterized by different contributions of vehicular traffic intensity, mountain and paddy field areas in and around of Kanyakumari district. The concentration of several trace elements (TEs): Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni and Zn in particulate matter collected on whatman filters were determined by means of Atomic Absorption Spectrometer (AAS).

KEYWORDS: air particulate matter; trace elements, vehicle emissions,AAS.

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INTRODUCTION

Atmospheric particulate matter (PM) has significant impact on human health, climate change, visibility reduction, agriculture and atmospheric chemistry. Aerosol particles may include a range of chemical species, ranging from metals to organic and inorganic compounds. Among the inorganic compounds, most important ones are the trace metals, which are emitted by various natural and anthropogenic sources such as crustal materials, road dust, construction activities, motor vehicles, coal and oil combustion, incineration and other industrial activities. Health impacts associated with particulate matters are linked to respiratory, cardiovascular problems, premature mortality, lung cancer, heart diseases and also damage to other organs[1].Heavy metals present in the atmosphere in trace amounts may pose a serious risk to human health in rural populations. The potential hazard of several toxic elements such as Cd, Cr and Pb is well known. Therefore, World Health organization (WHO) gives guidelines for some trace metals[2] that can be present in air well above natural background levels as the result of anthropogenic process.

The measurements of metal concentration in total suspended particles (TSP), PM_{10} or $PM_{2.5}$ give some indication of the general levels of pollution, but provide no information on size distribution of the pollutants. From a toxicological point of view, the most important particles are those with a diameter <10 µm (PM_{10}), so called reparable fraction, which penetrate the human respiratory system deeply. It is well established that fine particles (smaller than 2.5 µm) penetrate the pulmonary region and tend to deposit in alveoli [2]causing adverse health effects leading to pulmonary and respiratory diseases.

Trace elements (TEs) are released into the atmosphere both from natural and anthropogenic sources, namely: resuspended surface dust, combustion of fossil fuels and traffic. Combustion of fossil fuels and emissions from gasoline fueled road vehicles are the principal anthropogenic source of Cu, Ni and Zn in the urban air particulate matter[3]. In some cities industry (e.g. smelters, foundries) produces high trace element emissions. Long range transport of pollutants is also of great importance. For these reasons the examination of heavy metals and trace elements concentration size distribution is a useful tool for the characterization and apportionment of the sources of rural and urban airborne particulate matter[4,5,6].

The KanyaKumari district is recognized as the area with the highest level of air pollution. This is a result of the fact that in a relatively small area of 1684 km^2 with a dense population (over 1.8 cores inhabitants). Indian rare earths (IRE), Cashew nut factories, Tiles and brick factories are the industrial sources in KanyaKumari District. Present research focused on size distribution of trace metals in ambient particulate matter. The comparison of the results obtained for ten sites in the district in diverse periods of the year allows appraisal of the input of different pollution sources in the district.

METHODS

The samples were taken in diverse periods in the years 2013–2016 non-simultaneously at ten measuring points to analyze the influence of traffic intensity and other sources on ambient air pollution. The six sampling points from the urban areas of KanyaKumari district are discussed below:The first measurement place taken as Kaliyakkavilai town and is characterized by dense buildings, narrow streets and heavy traffic. Also, many of the old apartment houses are not connected to the town central heating system and is available in between the border and of Tamilnadu and Kerala. The high volume air sampler was situated 2m above ground level, 5m from the nearest busy street intersection, with intense car, bus and train traffic.

The second sampling point, at Martha dam located from Kaliyakkavilai at the distance of 6.2 km. This area is exposed to heavy traffic and local combustion and the sampler was placed at the ground level, 30 m from nearest busy street (car, bus, and heavy duty vehicle and tram traffic).

The third point, Thuckalay situated at 14km near to mar thandam which is highly immense with dense population and vehicular traffic area. The APM sampler was placed 2m above ground level, 5m from local street with car and bus traffic, 3m from small local road.

The Fourth sampling point taken as Villukuri,a mountain area located covered with a distance of 8kms from thuckalay, exposed to vehicular traffic, but with elevated smoke area during winter period. The APM sampler was placed 1 m above ground level, 50 m from local street with car and bus traffic area.

The Fifth sampling point taken as District Collect orate junction in Nagercoil located in a urban area covered with a distance of 12kms from villukuri, exposed to vehicular traffic, but with elevated smoke and dust affected area during all seasons. The APM sampler was placed 1 m above ground level.The Sixth sampling point taken as KanyaKumari located in a distance of 20kms from Nagercoil, exposed to vehicular traffic and highly populated areas during summer season. The high volume air sampler was placed 1m above ground level and 15m from traffic signal.

The four sampling points from rural are considered in KanyaKumaridistrict is discussed below:The first measurement place taken as Colachel Municipality known to be dense populated area and is characterized by high wind and sea shore with dense buildings, narrow streets and heavy traffic. The high volume air sampler was situated 2m above ground level, 5m from the nearest busy street intersection, with intense car, bus and train traffic.

The second sampling point, taken to measure the metal concentration is at manavalakurichi.

This area is exposed to heavy vehicular traffic and factories like cashew nut factory, ore refining factory and the sampler was placed at 4m from the ground level in the buildings nearest to factories.

The third point, Monday Market situated at 10km near to manavalakurichi which is highly immense with dense population and vehicular traffic area. The high volume airsampler was placed 2m above ground level, 5m from local road with car and bus traffic and 3m from small local road.

The Fourth sampling point taken as Kurunthencode an area is specialized for agriculture located with a distance of 7kms from Monday Market. The high volume air sampler was placed 1 m above ground level, 5 m from local street.

Each sampling lasted to minimize the influence of short-term weather condition changes. A high volume air sampler running on electrical energy has been purchased to collect air sample contaminated with automobile exhaust at the above mentioned sampling sites. The extent of absorption of heavy metals in each sample is calculated and correlated with the results obtained earlier. The suspended particles of air are retained on the filter. The duration of sampling is measured in an elapsed time meter which is placed in series with the blower. The sampler was placed 2m above the ground level. For the determination of heavy metals in the samples, exposed filter paper was punched in to 8 circle of 2.5cm diameter. The circle of filter paper was treated with acid digestion process. A blank filter paper was similarly digested and same procedure was carried out. The metals were determined using an Atomic Absorption Spectrometer. The concentration was calculated comparing the absorbance of sample solution with the standard metals solution.

RESULTS AND DISCUSSION

In the six sampling sites of urban area, the concentration of air particulate matter in the fine particles region (< 2μm) were higher during the winter period, which indicated higher contribution of the fuel combustion sources. The increased input of the coarse fraction during the summer months can be explained by lower contribution of surface soil resuspension to total AMP concentration.

Table: 1Concentration of Metals [ppm] - Winter Season

Urban Area- Winter Season									
Area	**Cd**	**Cr**	**Co**	**Cu**	**Fe**	**Pb**	**Mn**	**Ni**	**Zn**
Kaliyakkavilai	0.1902	0.2481	0.0989	0.1779	1.17	0.2432	0.0898	0.1286	1.7223
Marthandam	0.1921	0.2396	0.0952	0.1698	1.2397	0.2365	0.0856	0.1234	1.6032
Thuckalay	0.1898	0.2368	0.0964	0.1765	1.3198	0.2576	0.0942	0.1275	1.7389
Villukuri	0.1856	0.2365	0.0997	0.1756	1.2492	0.2398	0.0798	0.1198	1.7021
Nagercoil	0.1802	0.2471	0.0889	0.1759	1.2154	0.2332	0.0887	0.1265	1.7095
Kanyakumari	0.1912	0.2451	0.0959	0.1749	1.2394	0.2356	0.0851	0.1221	1.6943
Min	0.1802	0.2365	0.0889	0.1698	1.17	0.2332	0.0798	0.1198	1.6032
Max	0.1921	0.2481	0.0997	0.1779	1.3198	0.2576	0.0942	0.1286	1.7389
Average	0.188183	0.2422	0.095833	0.1751	1.238917	0.240983	0.0872	0.12465	1.69505

Table 1&2 show the values of weight concentration [ppm] of 9 TEs in fly ashes escaping from power plants and originating from other traffic sources (low emissions) compared with their concentration in relevant ambient aerosol fractions: PM_3 and PM_{10}, respectively, for both sampling seasons in urban area.

Table : 2Concentration of Metals [ppm]-Summer Season

Urban Area-Summer Season									
Area	**Cd**	**Cr**	**Co**	**Cu**	**Fe**	**Pb**	**Mn**	**Ni**	**Zn**
Kaliyakkavilai	0.1501	0.2033	0.0677	0.1368	1.2404	0.2015	0.0576	0.0942	1.6023
Marthandam	0.1432	0.1954	0.0532	0.1345	1.1756	0.1954	0.0476	0.0843	1.2312
Thuckalay	0.1434	0.1998	0.0578	0.1334	1.1854	0.1956	0.0645	0.0867	1.7756
Villukuri	0.1545	0.1987	0.0598	0.1336	1.1978	0.2056	0.0534	0.0846	1.6874
Nagercoil	0.1598	0.2289	0.0536	0.1389	1.2089	0.2112	0.0557	0.1056	1.6554
Kanyakumari	0.1343	0.1983	0.0587	0.1388	1.2974	0.1975	0.0686	0.0842	1.7533
Min	0.1343	0.1954	0.0532	0.1334	1.1756	0.1954	0.0476	0.0842	1.2312
Max	0.1598	0.2289	0.0677	0.1389	1.2974	0.2112	0.0686	0.1056	1.7756
Average	0.14755	0.204067	0.058467	0.136	1.217583	0.201133	0.0579	0.089933	1.617533

For this group of elements the weight concentrations are within the range of values observed for $PM_{2.5}$ collected at a site strongly influenced by vehicular traffic. Besides, the winter-to-summer ratios of C_{PM} (both for PM_3 and PM_{10}) for those elements at Nagercoil and Martha dam sites (i.e. sites with constant, relatively heavy traffic, including passenger cars, buses and heavy duty trucks) are below 1. This fact can indicate both a generally higher, in percentage terms, influence of vehicular traffic on particulate matter emission (due to lower emissions from small factory sources), or better air mixing and transport of traffic-related particles in dry, summer weather.

Table :3 Concentration of Metals [ppm]in Rural Area- Winter Season

Rural Area- Winter Season									
Area	**Cd**	**Cr**	**Co**	**Cu**	**Fe**	**Pb**	**Mn**	**Ni**	**Zn**
Colachel	0.1102	0.1981	0.0342	0.1279	1.1451	0.1832	0.0298	0.0616	1.8623
Manavalakurichi	0.1121	0.1796	0.0492	0.1045	1.1045	0.1765	0.0256	0.0434	1.1432
Monday Market	0.1498	0.1268	0.0264	0.1165	1.1231	0.1976	0.0342	0.0275	1.5889
Kurunthencode	0.1656	0.1265	0.0397	0.1198	1.1092	0.1738	0.0198	0.0498	1.6221
Min	0.1102	0.1265	0.0264	0.1045	1.1045	0.1738	0.0198	0.0275	1.1432
Max	0.1656	0.1981	0.0492	0.1279	1.1451	0.1976	0.0342	0.0616	1.8623
Average	0.1344	0.1577	0.0373	0.1171	1.1204	0.1827	0.0273	0.0455	1.5541

Table 3&4 show the values of weight concentration [ppm] of 9 TEs in fly ashes escaping from power plants and originating from other traffic sources (low emissions) compared with their concentration in relevant ambient aerosol fractions: PM_3 and PM_{10}, respectively, for both sampling seasons in rural area.

Table :4 Weight concentration [ppm] of 9 TEs in Rural Area-Summer Season

Rural Area-Summer Season									
Area	**Cd**	**Cr**	**Co**	**Cu**	**Fe**	**Pb**	**Mn**	**Ni**	**Zn**
Colachel	0.1001	0.1887	0.0241	0.1087	0.9784	0.1738	0.0176	0.0516	1.7823
Manavalakurichi	0.1012	0.1733	0.0343	0.0945	1.0116	0.1656	0.0145	0.0298	1.0812
Monday Market	0.1158	0.1031	0.0251	0.1034	1.1094	0.1526	0.0245	0.0176	1.4456
Kurunthencode	0.1297	0.1257	0.0368	0.1136	1.1028	0.1586	0.0134	0.0346	1.3574
Min	0.1001	0.1031	0.0241	0.0945	0.9784	0.1526	0.0134	0.0176	1.0812
Max	0.1297	0.1887	0.0368	0.1136	1.1094	0.1738	0.0245	0.0516	1.7823
Average	0.1117	0.1477	0.0301	0.1051	1.0506	0.1627	0.0175	0.0334	1.4166

According to the data presented in Tables, there is a group of elements (Cd, Cr, Ni, Pb, Cu, Co and Mn) for which the ratios C_{PM3}/C_{EFA} and C_{PM10}/C_{TFA} are <<1, which suggests that those TEs originate also from other sources. The elements Fe and Zn shows the concentration values >>1 in airborne particulate matter. Sinceburning coal and certain wastes can release zinc into the environment and iron is released to air from natural deposits, industrial wastes, refining of iron ores, corrosion of iron containing metals and abrasion of iron in vehicles.

The long-term air sampling period (10–14 days) necessary for fractioned ambient particulate matter collection allows for the weather influenced fluctuations of trace metal concentrations in the urban atmosphere. This is important for a reliable appraisal of the inhabitant's exposure to the inhalation of toxic elements with suspended fine particles. TheKanyaKumari district is still contingent upon most important source: vehicular traffic influences mainly the aerosol composition in the centre of the city, predominantly in the fine particulate matter range. According to environmental monitoring and modeling data, the mean 24-hr concentration of PM_{10} resulting from vehicular traffic ranges from 1 µg for most of the city area up to 2 µg in the centre of the city and around main highway junctions.

Table: 5 Average Metal Concentration on Summer Season

SUMMER SEASON									
Area	Cd	Cr	Co	Cu	Fe	Pb	Mn	Ni	Zn
Rural	0.1117	0.1477	0.0301	0.1051	1.0506	0.1627	0.0175	0.0334	1.4166
Urban	0.14755	0.204067	0.058467	0.136	1.217583	0.201133	0.0579	0.089933	1.617533

Table 5 & 6 show the values of average weight concentration [ppm] of 9 TEs in fly ashes escaping from various anthropogenic sources in both rural and urban area during summer season and winter season.

Table 6: Average Metal Concentration on Winter Season

WINTER SEASON

Area	Cd	Cr	Co	Cu	Fe	Pb	Mn	Ni	Zn
Rural	0.1344	0.1577	0.0373	0.1171	1.1204	0.1827	0.0273	0.0455	1.5541
Urban	0.188183	0.2422	0.095833	0.1751	1.238917	0.240983	0.0872	0.12465	1.69505

Figure 1 shows the graphical representation of weight concentration [ppm] of 9 Trace Elements in urban and rural area during winter Season. Due to seasonal variation trace metal concentration in the atmospheric aerosol vary significantly. The values of weight concentration [ppm] of 9 TEs in fly ashes during winter season from both rural and urban areas were compared with their average concentration values.

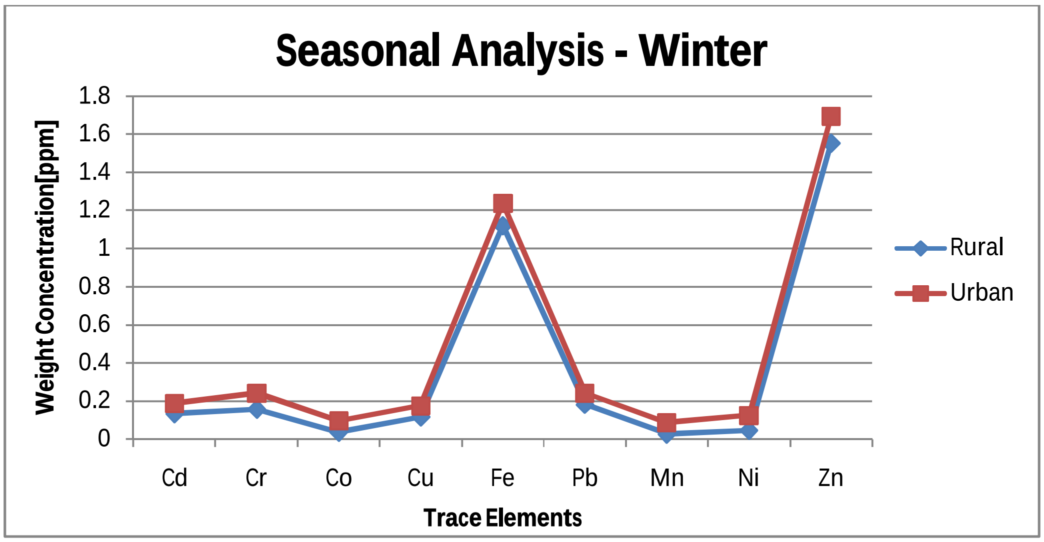

Figure1: Concentration of Metals [ppm] - Winter Season

Figure 2 shows the graphical representation of weight concentration [ppm] of 9 Trace Elements in urban and rural area during Summer Season.According to the data presented in Table 1 – 4, generally there are three types of weight distribution in rural and urban areas during both sampling seasons.

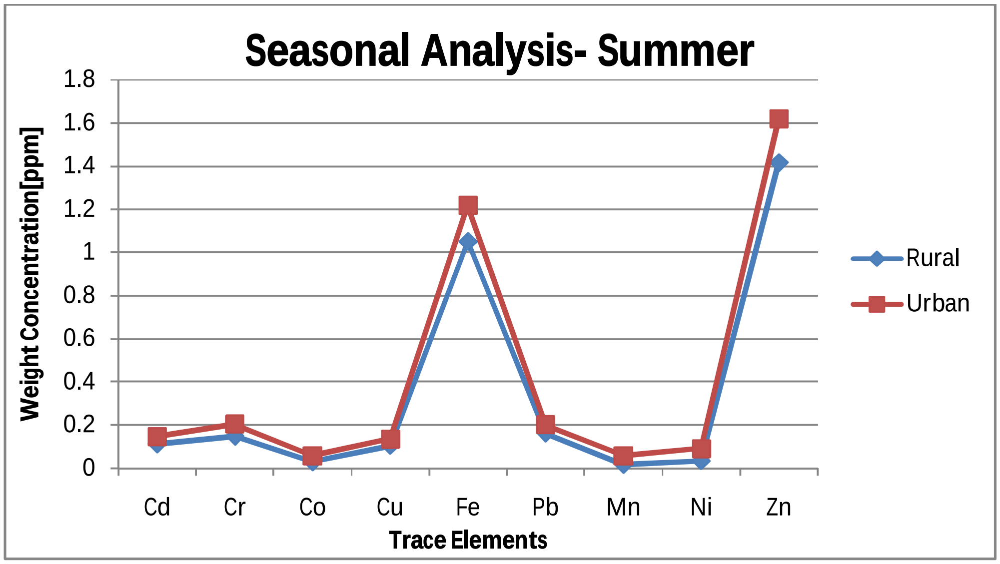

Figure2: Concentration of Metals [ppm]-Summer Season

First, there is a group of elements whose weight concentrations are greater than 1ppm during both summer and winter season but the abundant amount of Fe and Zn is present comparatively greater in above locations during winter. These locations are strongly influenced by vehicular traffic and ores refining factories in KanyaKumari District. The airborne particulate matters indicate higher concentration of heavy metals in air due to the lack of air flow during winter season.

Second, there is another group of elements such as Pb, Cd, Cu and Cr whose weight concentrations are marked as below 1ppm at above sites. Since those sites are strongly influenced by constant heavy traffic including passenger cars, buses and heavy duty trucks, the particulate matter indicates lower concentrations due to lower emissions from small factory sources and transport of traffic-related particles in dry, summer weather when compared with winter season.Third, rest of the group of elements such as Co, Mn and Ni shows the less level of trace elements present in atmosphere while compared to other elements considered during both seasons.

CONCLUSION

High concentrations of trace metals in atmospheric particulate matters are a great threat for the public health in KanyaKumari District. The long-term air sampling period (10–14 days) necessary for fractioned ambient particulate matter collection allows for the weather influenced fluctuations of trace metal concentrations in the rural atmosphere. This is important for a reliable appraisal of the inhabitant’s exposure to the inhalation of toxic elements with suspended fine particles. The KanyaKumari district is still contingent upon most important source: vehicular traffic influences mainly the aerosol composition in the centre of the district, predominantly in the fine particulate matter range. According to environmental monitoring and modeling data, the mean 24-hr concentration of PM_{10} resulting from vehicular traffic ranges from 1 µg for most of the district area up to 2 µg in the centre of the district and around main highway junctions. The airborne particulate matters indicate higher concentration of heavy metals in air due to the lack of air flow during winter season.

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