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Determination of trace elements in urban airborne particulates (PM_{10}) using energy dispersive X-ray fluorescence (EDXRF) spectroscopy

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ABSTRACT: assessment of the air quality in Newcastle upon Tyne, UK was performed by determining the trace element content in airborne particulates (PM_{10}). Samples were collected over a 12 month period (March 2011 to April 2012) using two high volume air sampler provided with a PM_{10} size selective inlet. The concentrations of 6 elements (Cr, Cu, Mn, Ni, Pb and Zn) were determined. The mean concentrations of these elements varied widely across the elements with Zn showing the highest concentration (41.3 ± 42.8 ng/m^3; ranging from 9.9 – 209.0 ng/m^3) and Cr the least concentration (1.7 ± 0.9 ng/m^3; ranging from 0.4 – 3.2 ng/m^3). The total elemental content obtained in this work was compared with regulatory limit values for 4 of the elements determined and it was discovered that none exceeded the limit values. © **JASEM**

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Introduction

Air quality is a key requirement for the functioning of the human respiratory system and our health. However, the air that we breathe can be contaminated with non-toxic and toxic elements associated with the PM_{10} fraction. One of the important aspects in any PM_{10} study is an understanding of the composition of this fraction. Airborne particulates are principally generated through a variety of physical and chemical mechanisms and are emitted into the atmosphere from numerous sources [1]. These sources are either natural or anthropogenic [2]. Human activities that pollute the air have been on the increase due to industrialization and man's consistent quest to improve the quality of life particularly in developing countries where typically there are no regulated air monitoring systems. An example of such activity is combustion; fossil fuel combustion (e.g. for energy generation, industrial processes and transportation) as well as the combustion of solid fuel, such as, coal and wood for domestic purposes particularly in developing countries [3]. Airborne particulates released into the atmosphere are involved in many atmospheric processes, and play an important role in reducing visibility, acid deposition, and the balance of radiation in the atmosphere, both directly and indirectly through cloud formation [2]. The concentration and composition of particulates may vary with size, time, and location, and depends strongly on the distance from point sources, rate of emission, convective and turbulent diffusive transfer rates, the efficiency of various removal mechanisms, and on metrological parameters which affect its distribution. The presence of toxic elements in airborne particulates has attracted a lot of attention due to potential adverse health impacts [4-5]. Human health risk from airborne contaminants is directly linked to inhalation; inhalation itself is an involuntary action in which human exposure cannot be avoided (especially for people who spend a long time in outdoor activities). Air pollution results in serious effects on people's health particularly those categorized as high-risk groups such as children, pregnant women and the elderly. Environmental and health effects of air pollution have been widely reported [6-7] to include; cardiovascular disease, asthma and reduced lung capacity. Air pollution is a global challenge and hence there is a need to constantly monitor its concentration because of environmental and health implications.

There is a daily monitoring of airborne particulates in Newcastle upon Tyne as part of a national UK monitoring programme; the monitoring station is located in the centre of the city close to major urban road networks. In this study, sampling took place on the campus of Northumbria University, Newcastle upon Tyne approximately 1 km from the monitoring station. It is expected that results from the study would contribute significantly to existing knowledge and also assess the human health risk from toxic elements. This study examined the concentration of 6 elements classified as being toxic [8] i.e. chromium (Cr), copper (Cu), manganese (Mn), nickel (Ni), lead (Pb) and zinc (Zn).

MATERIALS AND METHODS

Sample collection and preparation: airborne particulates (the PM_{10} fraction) was collected by using two high volume air samplers mounted within the campus (Ellison Yard) of Northumbria University, Newcastle upon Tyne, UK. The Tecora

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Echo samplers (Tecora, Rue la Fontaine, France) (Figure 1) are ultra-high volume particulate samplers equipped with an impactor cutoff of 10 µm with a flow rate of 200 L / min. Prior to every sampling, the Munktell quartz-microfibre filter papers with diameter of 102 mm were conditioned in a desiccator for 24 hours at a constant temperature (20 ^{0}C ± 1); samples were collected in pairs. Each sampling episode had a duration of 100 hours and constant air flow was maintained. After each run, the filter papers were removed and transported to the laboratory. Again, the filters were conditioned in a desiccator for 24 hours at constant temperature (20 ^{0}C ± 1). The filters were re-packaged ready for the determination of the total concentration of six elements. A total of 26 samples were collected over a period of one year (March 2011 to April 2012).

Protocol for total elemental content determination via XRF Air-bornedust samples were analysed *in situ* on filter paper using energy dispersive X-ray fluorescence (EDXRF) spectroscopy on a Spectro Analytical X-Lab 2000 instrument fitted with a Gresham Si(Li) detector. Samples were prepared for analysis by cutting 2.6 cm diameter circles from the collection filter, then sandwiched between two layers of prolene film; this was then assembled to make a standard cuvette (including lid), with the filter held tight between the prolene layers. Blank quartz-microfibre filter samples were also prepared for analysis. Each sample and blank was analysed using a 'filters' method of the EDXRF, with concentrations output as ng/cm^2. The EDXRF was operated according to the following programme of targets: Compton/secondary molybdenum, 40 keV tube voltage, 200 s measurement time; Barkla scatter, aluminium oxide, 50 keV, 200 s; and, Barkla scatter, HOPG, 15 keV, 200 s. Calibration of the elemental concentrations on the filter papers, after blank correction, was carried out using a SRM 2783 filter standard. The standard was supplied as a polycarbonate filter membrane filter with an average mass loading of 48.7 µg/cm^2 (i.e. 485 µg per filter on a deposit area of 9.96 cm^2 per filter) which had been deposited on the filter as a PM_{10} fraction of airborne particulate matter; a blank polycarbonate filter was also supplied for the blank correction. This allowed a series of calibration factors to be determined for sampled particulates collected on the micro-quartz filters: Cr, 0.574; Cu, 1.016; Mn, 0.753; Ni, 0.279; Pb, 1.022; and, Zn, 0.788.

*SEM analysis***:** EM micrographs of the quartz-microfibre filters before and after sampling were obtained using an FEI Quanta 200 instrument.

RESULTS AND DISCUSSION

Calculation of concentrations;The EDXRF 'filters' method outputs concentrations in units of ng/cm^2 which, after blank correction for the quartz-microfibre filter and the application of the calibration factors listed in Section 2.2, then need to be converted to ng/m^3, based on the volume of air sampled and the total filter area on which the particulates were sampled. These concentrations can then be compared with airborne metal concentrations from other studies and with regulatory guideline values or limits.

The collection area of the micro-quartz filters was 63.62 cm^2 (r = 4.5 cm) and the total volume of air sampled was 1200 m^3 during the 100 hour sampling period (at 200 L / min), hence each concentration in ng/cm^2 was multiplied by 63.62, and divided by 1200, to convert to ng/m^3.

*SEM analysis***.:** Sscanning electron microscopy (SEM) has been used to capture the quartz filter paper before and after sample collection. Figure 2 shows the configuration of the fibres on the filter before sample collection. The image of one of the filters after sample collection (Figure 3) shows the distribution of PM_{10} on the filter. It can be seen that the configuration of the fibres of the filter allowed small air-borne particulates to be trapped below the surface of the filter. It is observed that these fine particles collected often formed clumps and are unevenly distributed on the fibres of the filters [Note: this is a subjective observation based on viewing multiple SEM images]. The concentrations of the elements in the PM_{10} collected on the filters were measured using EDXRF.

Total elemental concentrations : Statistical parameter: arithmetic mean, medians and concentration ranges for the six elements are displayed in Table 1. Among these trace elements, Zn showed the highest concentration (41.3 ± 42.8 ng/m^3; ranging from 9.9 – 209.0 ng/m^3) and Cr the least concentration (1.7 ± 0.9 ng/m^3; ranging from 0.4 – 3.2 ng/m^3). Overall, the decreasing trend of average element in the airborne particulates reveals the following order: Zn > Mn > Pb > Cu > Cr > Ni (Table 1). Most of the trace elements showed a random distribution pattern manifested by higher standard deviation (SD) values on one hand and considerable skewness values on the other hand. Maximum dispersion was observed for Zn, Mn and Pb, thus supporting their variable distribution in the urban airborne particulates. All the atmospheric particulate elements were found to spread over an order of 10 x as shown by their respective ranges (Table 1).

The mean concentrations of the trace elements in the atmospheric particulate matter were compared with data from different worldwide urban areas (Table 2). The results from this study, in general terms, indicated that the PM_{10} concentrations of the 6

elements determined in the air particulates in Newcastle upon Tyne were considerably lower than other reported concentrations in urban cities worldwide (Table 2). The exception to this general statement was Metropolis (India) which had lower concentrations of the 6 trace elements in all cases determined i.e. for Mn, Cu, Zn and Pb.

In order to accurately assess the human health risk of the measured trace elements present in the inhalable particle size fraction (PM_{10}), it was considered necessary to compare the results from this study with regulatory limit values. Though a complete list of regulatory limit values for all the elements investigated is not available, some are however, and are shown in Table 3. It can be seen that the mean concentration of Cr, Mn, Ni and Pb in the PM_{10} fraction in Newcastle upon Tyne is considerably lower that the values published by regulatory bodies i.e. European Commission, Agency for Toxic Substances and Disease Registry and the World Health Organisation.

Conclusion: This study highlights the need for vigilance in the regular monitoring of the element concentration of airborne particulates (PM_{10}) in the urban environment. of the determined mean element concentrations of the 4 elements determined with known regulatory guidelines mean values all were acceptable (i.e. considerably below regulatory guideline values).

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Table 1. Statistical summary of trace element levels (ng/m^3) in the airborne particulate matter (n = 26)

Statistical parameters	Cr	Mn	Ni	Cu	Zn	Pb
Minimum	0.4	2.4	0.1	4.1	9.9	1.5
Median	1.5	6.2	0.4	8.5	30.6	8.4
Maximum	3.2	63.3	4.5	23.2	209.0	37.1
Mean	1.7	13.5	1.0	9.9	41.3	12.2
SD	0.9	19.4	1.4	4.9	42.8	10.6
Skewness	0.3	2.1	1.9	1.3	3.2	1.2

SD = standard deviation
NA = not applicable

Table 2. Mean concentration of toxic elements in PM_{10} from other studies (ng/m^3)

City (country) / No. of samples / [Reference]	Cr	Mn	Ni	Cu	Zn	Pb
This study (UK) / 12 / [NA]	1.7 ± 0.9	13.5 ± 19.4	1.0 ± 1.4	9.9 ± 4.9	41.3 ± 42.8	12.2 ± 10.6
Metropolis (India) / 32 / [2]	NA	0.26 ± 0.1	NA	9.65 ± 6	2.08 ± 1	3.56 ± 4
Santa Cruz (Brazil) / 43 / [9]	421	1216	0.5	335	2126	1011
Thessaloniki (Greece) /30 / [10]	NA	33 ± 23	6.8 ± 5.3	118 ± 100	127 ± 119	77 ± 25
Athens (Greece) / 59 / [11]	16.0	18.1	13.8	141.2	NA	48.3
Islamabad (Pakistan) / 153 / [12]	7.18	38.8	NA	38.1	3325	63.5
Paris (France) / 21 / [13]	4.12	6.95	NA	18.4	45.8	15.4

NA = Not available

Table 3. Regulatory guideline mean values for airborne particulates (PM_{10}) (ng/m^3)

Regulatory body [reference]	Cr	Mn	Ni	Pb
European Commission [14]	NA	NA	5	NA
ATSDR [15]	100	500	NA	1500
WHO [16]	1100	150	NA	500

NA = Not available

Fig 1. Tecora Echo high volume PM_{10} sampler.

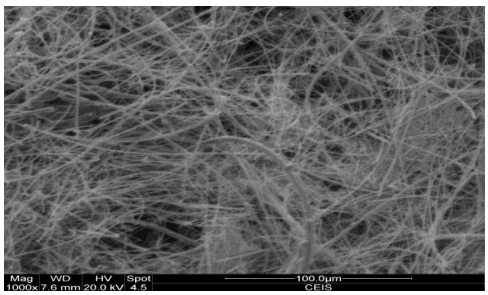

Fig 2. SEM image of quartz filter paper before sample collection

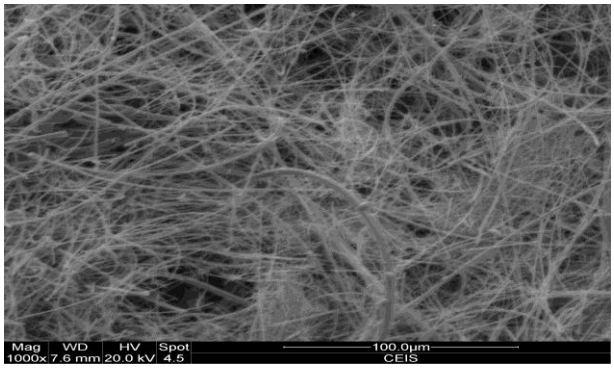

Fig 3. SEM image of quartz filter paper showing collected air-borne dust

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