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Investigation of Arsenic Airborne in Particulate Matter around Caterers' Wood Fires in the Cape Town Region

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ABSTRACT

Smoke from wood fires has long been recognized as a significant health hazard. Our recent work has reported on the occurrence of waste timber previously treated by chromated copper arsenate (CCA) insecticide in the fuel supplies of informally operating caterers in the Cape Town region. The main objective of this paper is to report evidence that the burning of CCA-treated wood by informal caterers does lead to arsenic enrichment of the smoke.

Atmospheric particulate matter with aerodynamic diameter ≤ 10 μm (PM_{10}) was collected using an Air Metrics MiniVol portable aerosol sampler onto quartz filters for durations varying from 1 h to 4 h, at 5 L/min. Smoke was first sampled under controlled conditions, in which CCA-treated samples (of hazard classes H5 and H2) and two untreated wood samples were burned. 18 field samples were collected, from Nyanga, Langa and Khayelitsha (Cape Town) and Kayamandi (Stellenbosch). The PM_{10} concentrations were calculated and the smoke samples were microwave-digested using nitric acid for metals analysis by ICP-AES.

Under controlled conditions, the concentrations of arsenic volatilised from (H2 and H5) were 19 and 52 μg/m^3, and the As:Cu and As:Cr ratios strongly increased compared the ratios found in the timber. The lowest concentration of PM_{10} was found around the Nyanga taxi rank at a distance of ± 100 m from caterers, at 33 μg/m^3, while the highest concentration was 8139 μg/m^3 for a 1-hour sample representing occupational exposure close to wood burning fires. Arsenic was detected in 15 smoke samples. The average arsenic level of positive samples was 1.3 μg/m^3. The arsenic levels measured exceed normal background levels, which have been reported by the WHO to be 0.02–4 ng/m^3 in rural air and up to 30 ng/m^3 in urban air.

Keywords: Arsenic exposure; CCA-treated wood; PM_{10}; Smoke; Wood burning.

INTRODUCTION

Particulate matter is one of the criteria air pollutants regulated in many jurisdictions, generally in the size range of < 10 μm (PM_{10}) or < 2.5 μm ($PM_{2.5}$). Fuel wood burning has been widely recognized as a significant contributor to ill-health through inhalation of such particulate matter in many developing countries (WHO, 2005). Our recent work has reported evidence that waste timber, previously treated with the insecticide CCA (chromated copper arsenate) is being used by informally operating street caterers in urban and peri-urban settings in the Cape Town region (Niyobuhungiro *et al.*, 2012). The combustion of such wood, which may contain each of the elements Cr, Cu and As in the range of 500–6000 mg/kg, has previously been shown to lead to preferential volatilization of arsenic (Rogers *et al.*, 2007).

Arsenic in the atmosphere exists as particulate matter, mostly as particles less than 2 μm in diameter. These particles are transported by wind and air currents until they return to the ground by wet or dry deposition. Re-suspension may contribute to the concentration of arsenic in air (EHC 224, 2001; Kapaj *et al.*, 2006).

It was reported by WHO (2000) that normal background levels of arsenic in the air are 0.02–4 ng/m^3 for rural, and up to 30 ng/m^3 for urban settings. Maas *et al.* (2004) reported that small arsenic exposure cause existing human cancer tumours to grow more rapidly and aggressively.

In the Cape Town context, Benson (2007) reported that metal compounds including those of Arsenic, Chromium and Copper are found in particulate matter.

Tobacco smoke is another source of As emissions into the environment. Cigarette smoke contains 0.04 to 0.12 μg As per cigarette (Kapaj *et al.*, 2006). It is already known that cigarette smoking is a main risk factor for lung cancer; Kapaj *et al.* (2006) found that cigarette smoking plus ingestion of As from drinking water had a synergistic effect, thus increasing the risk of lung cancer. They suggested that

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reduction in As exposure should reduce the lung cancer risk in cigarette smokers.

The South African PM_{10} ambient air quality standard was set by the national Department of Environmental Affairs to be 120 μg/m^3 as the average for 24 hour exposure (25°C and 101.3 kPa), while the City of Cape Town uses the UK daily average standard of 50 μg/m^3 (Benson, 2007). It was reported that the latter standard is exceeded more frequently in Khayelitsha than at the other air quality monitoring sites in Cape Town (Tessema, 2011). Although the term "episode" has no formal definition in air quality literature, it is used by Cape Town air quality management to describe a period when the daily average standard PM_{10} concentration is higher than the South Africa daily average concentration of 120 μg/m^3 or UK daily average Standard (50 μg/m^3). In Khayelitsha, both the South African and UK standards are exceeded at different times of the year. Days when these exceedences occur are considered as "episodes". Table 1 reports the number such episodes over a recent 10-year period.

Arsenic in air is generally not regulated under environmental standards, but is the subject of various occupational health guidelines, as shown in Table 2. The European Occupational Safety and Health Administration (OSHA) specifies that exposure to inorganic arsenic should not exceed 10 μg/m^3 in a working place averaged over an eight (8) hour period (Wu *et al.*, 2006).

This paper reports on an investigation of fuel wood smoke, undertaken in specific urban and peri-urban parts of Cape Town, in order to assess whether there might be thus far unrecognised health concerns, specifically related to occupational exposure by informally operating road-side caterers.

METHODS AND MATERIALS

Air Sample Collection

The sample collection campaign was executed. A MiniVol portable aerosol sampler (Air Metrics, USA) was used for PM_{10} collection. Smoke from wood fires was collected in three different urban areas in Cape Town (Nyanga, Khayelitsha and Langa) and one peri-urban area (Kayamandi in Stellenbosch). A total of 19 smoke samples were collected, but one of them was damaged during transportation, resulting in 18 samples composed as follows:

- 8 from Nyanga (5 close to wood fires and 3 from around the taxi rank area ± 100 m from where much wood burning happens)
- 3 samples from Khayelitsha (close to wood fires)
- 4 samples from Langa (close to wood fires) and
- 3 samples from Kayamandi (Stellenbosch) (close to wood fires)

The smoke samples were collected downwind from the fires over a duration of between 1–4 hours. The height at which samples were taken was approximately 1.50 m and the distance from the fire was generally 2 m except for three samples taken from Nyanga around the Taxi Rank where it was farther (± 100 m) from the fires. The MiniVol was operated at a flow rate of 5 L/min.

The filters used in the study were made of quartz. They were chosen for their resistance to carbon damage; complete digestion of the filter by acid was not required for Cr, Cu and As determination in captured particulate matter. The filters were 47 mm in diameter and the pore size was 0.5 μm, which is acceptable for PM_{10} sampling. The filters were weighed before and after the sampling using a microbalance with 10 μg sensitivity to obtain the particulate mass.

Digestion and ICP-AES Analysis (EPA SW 846 Method 6010B)

ICP-AES requires digestion (or an equivalent processing) of samples prior to analysis. Detection limits, sensitivity, and the optimum and linear concentration ranges of the elements can vary with the wavelength, spectrometer, matrix and operating conditions (Karthikeyan *et al.*, 2006; Wu *et al.*, 2006). The actual method detection limits are sample dependent and may vary as the sample matrix varies (Wu *et al.*, 2006). This method is applicable to the three CCA metals of concern in this project. The detection limit in this study was 1 ppb (10^3 μg/m^3) for arsenic and 0.7 ppb (7×10^2 μg/m^3) for both chrome and copper.

Reagents and Standard Reference Materials

For the preparation of reagents and standards, ultra pure water from a Maxima Ultra Pure Water system was used. Analytical grade reagents HNO_3 (Merck), was used for the

Table 1. Number of PM_{10} episode days in Khayelitsha based on South Africa and UK standards (Tessema, 2011).

Years	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009
SA standard	0	2	1	4	9	5	6	16	9	5	5
UK standard	91	90	29	91	185	139	147	157	151	151	142

Table 2. Standards and Regulations for inorganic arsenic (Wu *et al.*, 2006).

Agency	Focus	Level	Comments
Governmental Industrial Hygienists	Air: Workplace	10 μg/m^3	Advisory; TLV/TWA
National Institute for Occupational Safety and Health	Air: Workplace	2 μg/m^3	Advisory; 15 minute ceiling limit
Occupational Safety and Health Administration	Air: Workplace	10 μg/m^3	Regulation; PEL over 8-hour day

TLV/TWA (threshold limit value/time-weighted average): time weighted average concentration for a normal 8-hour workday or 40-hour workweek to which nearly all workers may be repeatedly exposed.
PEL (permissible exposure limit): highest level averaged, over an 8-hour workday, to which a worker may be exposed.

digestions. An ICP/AES multi- element standard was used for calibration. The standards used for recovery and quality control were approved by SABS. Quartz (QMA grade, 47 mm (dia.), Whatman® England) filters were used directly (without any pre-cleaning) for the collections of airborne particulate matter mainly close to wood burning fires.

In the preparatory experiment, the MiniVol was placed close to a controlled wood fire to sample its smoke. Particles in the smoke were thus collected onto the filter medium and analysed. The wood samples that were burnt in the controlled conditions were from a fire wood sample from Stellenbosch identified as H5 (Hazard class 5) and an H2 specimen supplied by the Epping Timber Treatment plant, as well as two wood samples considered to be untreated. This was done to confirm that elevated CCA concentrations would show in smoke collected on the filters when CCA-treated wood was burnt.

The levels of arsenic, chromium and copper in the H5 wood specimen were 3633, 6624, and 1761 mg/kg of wood, and for the H2 sample, 1077, 1275 and 608 mg/kg respectively. The untreated samples reported 8.84 and 8.30, 3.0 and 4.31, and 2.89 and 0.39 mg/kg of arsenic, chromium and copper respectively.

The treated samples were burnt on the 28th April starting with the H2, while the untreated samples were burnt on the 2nd May, to avoid contamination. Each wood sample was burnt separately. The mass of each wood sample used in the controlled burning is presented in Table 3. Each wood sample was burnt separately, resulting in 4 controlled fires.

RESULTS

It was noted that the concentration of arsenic volatilised from typical CCA-treated wood was significantly higher when CCA-treated timber was burnt, at 19 and 52 μg/m^3 for the H2 and H5 samples, respectively. Importantly also, the ratio of arsenic to the other two metals increased sharply from the normal ratios of 1:1.5 (Cu:As) and 1.5:1.7 (Cr:As) (Table 3), consistent with the higher volatility of this element (arsenic) and the findings of Rogers *et al.* (2007). The results obtained confirmed the results reported in literature and therefore showed that the MiniVol Sampler was suitable to collect smoke samples for this study.

The MiniVol was then taken to the field to different chosen areas (urban and peri-urban). PM_{10} results around the taxi rank were found to be considerably lower than close to wood fires (Table 4). The averages of the PM_{10} values recorded over the sampled areas were:

- 54.3 μg/m^3 for the 3 samples in the Nyanga taxi rank area;
- 2570 μg/m^3 for the 10 samples close to boiling applications (sheep head, chicken, maize or beer brewing); and
- 777 μg/m^3 for the 5 samples close to grilling ("braaing") applications.

The lowest concentration was found around Nyanga taxi

Table 3. CCA levels in the smoke from controlled wood burning.

Sample burned	Time (h)	mass of PM_{10} (mg)	Sample size (g)	PM_{10} (μg/m^3)	Cr (μg/m^3)	Cu (μg/m^3)	As (μg/m^3)	Cr:Cu:As ratio
H5	0.58	0.25	804.82	1388	6.52	1.53	51.9	4:1:34
H2	0.57	0.14	514.91	795	7.39	1.42	19.2	5:1:14
Sample 55	0.20	0.01	471.56	161	24	83.5	6	0.3:1:0.1
Sample 51	0.10	0.01	210.55	321	32	9	16	3.5:1:1.7

Table 4. PM_{10} concentration in urban and peri-urban areas and Cr:Cu:As ratios for the smoke samples.

Sample no	Name of the area	Distance from the fire source	Time for sampling (h)	PM_{10} (μg/m^3)	Cr (μg/m³)	Cu (μg/m³)	As (μg/m³)	Cr:Cu:As ratio
1	Nyanga (taxi rank)	-	4	49	1	0.4	0.2	2.3:1:0.5
2	Nyanga (taxi rank)	-	4	81	1	0.3	0.2	3.7:1:0.6
3	Nyanga (braai fire)	± 25 m	3	173	1.1	0.3	0.2	3.7:1:0.8
4	Nyanga (braai area)	± 5 m	4	162	0.7	0.2	0.2	3.4:1:0.8
5	Nyanga (chicken boilers)	± 10 m	4	282	0.9	0.2	0.1	3.8:1:0.4
6	Nyanga (sheeps boilers)	± 2 m	1	2918	3	2	1.9	1.5:1:0.9
7	Nyanga (maize boiler)	± 3 m	1	1132	2.8	0.5	1.4	5.4:1:2.7
8	Nyanga (taxi rank)	-	1	33	4.3	1.3	0.6	3.4:1:0.5
9	Langa (beer vendor)	± 2 m	1	2529	3.3	1.5	0.7	2.2:1:0.5
10	Langa (beer vendor)	± 1 m	1	1657	3.2	0.9	0.5	3.3:1:0.6
11	Langa (braai fire)	± 2 m	1	1278	3.3	1.3	2.1	2.6:1:1.6
12	Langa (braai fire)	± 2 m	1	556	2.6	0.9	1.2	2.8:1:1.3
13	Stellenbosch (chicken boiler)	± 2 m	1	3485	0.7	0	11.8	01:00:17
14	Stellenbosch (sheeps boiler)	± 2 m	1	193	0.4	0	0	01:00:00
15	Stellenbosch (sheeps boiler)	± 2 m	0.66	880	0.5	0	0	01:00:00
16	Khayelitsha (braai area)	± 2 m	1	1715	0.2	0	0	01:00:00
17	Khayelitsha (sheeps boiler)	± 2 m	1	8139	1.2	0	11	01:00:09
18	Khayelitsha (sheeps boiler)	± 2 m	1	4452	0.2	0	3.9	00:19.5

rank at 33 μg/m^3, while the highest value of 8139 μg/m^3 was found in Khayelitsha close to wood burning fires.

After the determination of PM_{10}, further analysis was done to calculate the chromium, copper and arsenic concentrations in each smoke sample. Arsenic was detected in 15 samples with the lowest being 0.1 and the highest 11.8 μg/m^3 of arsenic (Fig. 1). The average of the arsenic positive samples was 2 μg/m^3 of arsenic, relative to 1.7 μg/m^3 of chromium and 0.5 μg/m^3 of copper.

The highest arsenic concentration was measured near wood burning fires in Stellenbosch (11.8 μg/m^3) where chicken was boiled in closed pots; the lowest arsenic level (0.1 μg/m^3) was measured from wood burning in Nyanga. Two samples from Stellenbosch and one from Khayelitsha did not show any arsenic, those are samples 14, 15 and 16. Considering other CCA constituents (chromium and copper), it was noted that those elements are also present in the smoke. Additionally, several smoke samples taken near such fires showed elevated Cr, Cu and As levels, with the As:Cu ratio increasingly significantly in samples 13, 17 and 18, as shown in Table 4.

DISCUSSION

Levels of PM_{10} in the Smoke

As reported in the literature, wood burning is one source of the PM_{10} in the ambient air (City of Cape Town, 2007). The use of treated wood generates a black smoke with a characteristic strong smell. This was initially noted during preliminary experiments when burning treated wood. Because of this, its use is mainly confined to applications involving boiling in closed vessels such as sheep-head preparation, chicken and maize boiling and brewing as seen in Fig. 1. Natural wood does not produce this distinctive smoke and is generally preferred for grilling and barbequing as it does not adversely affect the taste of the food being prepared. However during the rainy season, the use of treated wood increases as natural wood is wet and is difficult to ignite.

PM_{10} levels were found to be high close to open smoke sources (Table 4); for example, 8139 μg/m^3 was measured approximately ± 2 m from one of Khayelitsha's many wood fires over a 1 hour period. Whilst such a proximity to an open fire is more representative of a work-place exposure than to a public environmental exposure, the two are closely linked. This problem arises in areas like taxi ranks, where large numbers of people congregate. The daily PM_{10} standards of 50 μg/m^3 could possibly be exceeded by this activity, as PM_{10} average concentrations of 54.3 μg/m^3 (three samples around Nyanga taxi rank) was determined in 4-hour samples.

Arsenic Volatilisation during CCA-Treated Wood Combustion

The preparatory experiment confirmed that arsenic is enriched in the smoke relative to copper and chromium when CCA-treated wood is burnt. Chromium and copper are reported to remain in the ash, (Solo-Gabrielle *et al.*, 2002; Rogers *et al.*, 2007) and may be found in PM_{10} samples when such ash is sufficiently fine and suspended by air movement.

During the preliminary experiment the specimens considered to be untreated wood (samples 55 and 51 from Nyanga) were burnt after the CCA-treated wood burning. The ratios of those specimens are abnormal according to the literature. The Chromium is the highest, followed by copper then arsenic. These ratios do not match neither with

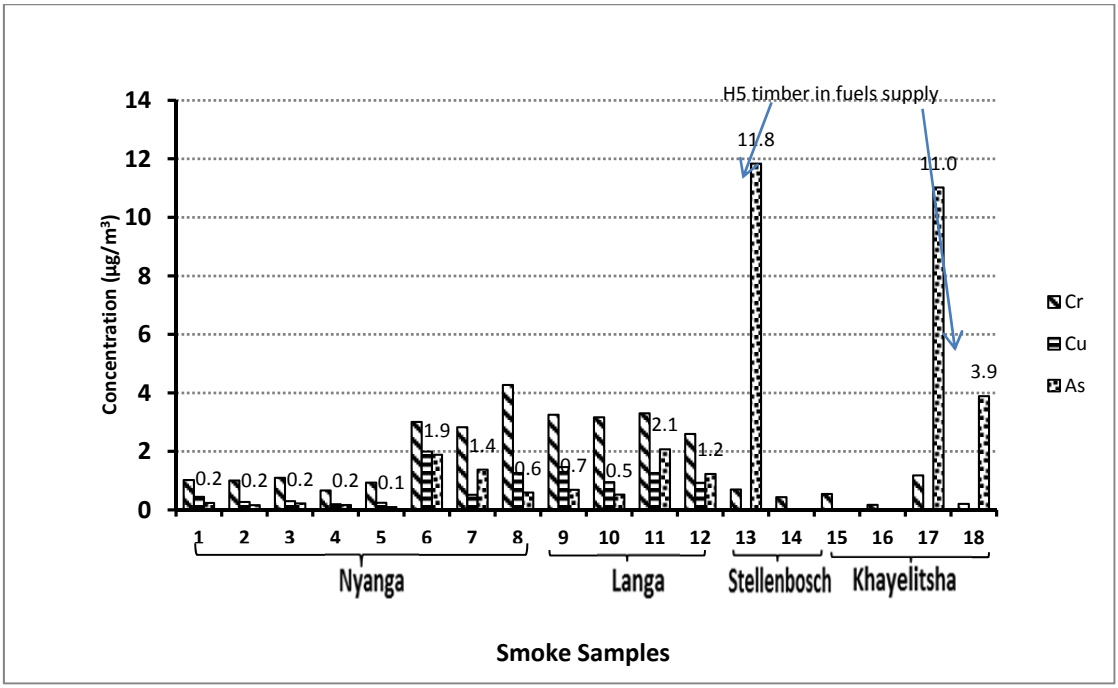

Fig. 1. CCA concentrations in smoke samples from in urban and peri-urban areas (with Arsenic concentrations shown numerically).

the ratios of smoke nor with the ratios of wood samples. This might be due to the fact that the remaining of the metal concentrations from the previous samples in the air probably affected the CCA levels in those smoke samples from untreated wood.

Of the analysed 18 smoke samples in this study, most showed much lower metals concentrations than the preliminary experiment. However, one sample from Khayelitsha and two from Kayamandi showed elevated arsenic levels and significant arsenic enrichment, similar to that observed when an H2 specimen was burnt in the preliminary experiment. At least one wood sample collected from those fires was identified to have been CCA-treated. This was confirmed after comparing the results with the blank sample (Niyobuhungiro, 2012).

A comparison of the results found in this study with normal background levels of arsenic in the air, which are 0.02–4 ng/m^3 in rural areas and 30 ng/m^3 in urban air (WHO, 2000), shows all the samples exceeding normal levels. The Occupational Hygiene Guideline of 10 µg/m^3 (8 h time weighted average) (EHC 224, 2001) could possibly be exceeded by this activity, as concentrations of 11 and 12 µg/m^3 (samples 17 and 13 collected in Khayelitsha and Stellenbosch respectively) were determined in 1-hour samples.

Relation between Arsenic and PM_{10} Levels

In this study a generally strong association was found between the PM_{10} concentration and arsenic concentration (Fig. 2). Samples with low PM_{10} concentrations also reported low arsenic concentrations – although for several samples above the reported normal concentrations in urban air. The three smokiest fires also had the highest arsenic contents. In the PM_{10} concentration range of 500–3000 µg/m^3 range, four samples showed elevated and enriched arsenic concentrations, whilst two showed no detectable arsenic and two showed arsenic in a 'normal CCA' ratio to Cu and Cr.

CONCLUSION

This study has confirmed levels of PM_{10} close to wood fires to be high. Considering the health effects associated with the PM_{10} reported in the literature, continuing controls over emissions should particularly benefit people living with HIV and AIDS, and TB, and result in health cost savings.

Arsenic was detected in 15 of the 18 smoke samples collected near or next to wood-fires, in all cases exceeding the reported normal background level of 30 ng/m^3 for urban air.

The literature states that there is no safe level of arsenic inhalation that can be recommended. The 1 hr smoke samples from Stellenbosch and Khayelitsha, reporting 11.8 and 11.0 µg/m^3 of arsenic respectively, are of the order of an European occupational hygiene guideline, setting a limit of 10 µg/m^3 (8 h time weighted average) (EHC 224, 2001).

It is concluded that where CCA-treated timber is burnt by informally operating caterers, significantly elevated arsenic levels have been found. Moreover, even where this is not directly the case, arsenic was measured at elevated levels, possibly indicative of burning of CCA-treated timber elsewhere or recently in the studied areas.

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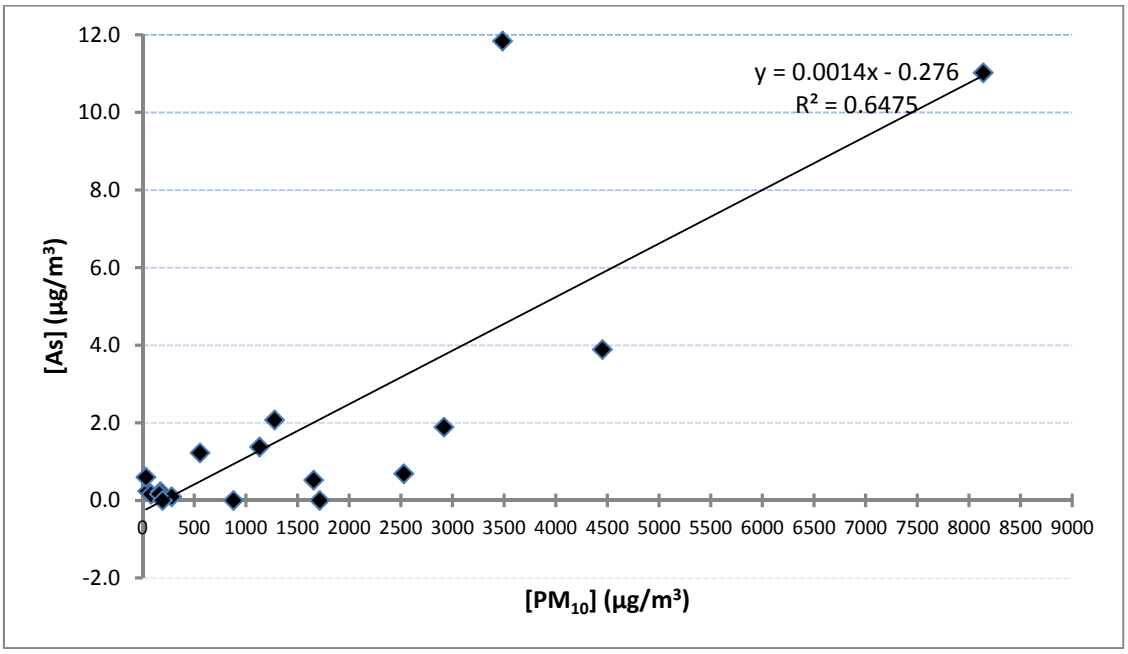

Fig. 2. Relation between arsenic and PM_{10} level for 18 smokes samples.

the alignment of this work with the university's new strategic objectives and the associated financial support. We applaud the volunteering work of the "caterers" working group of the Engineers without Borders branch at the University of Cape Town, which has worked to introduce efficient wood stoves to Nyanga-based caterers alongside our research.

REFERENCES

Benson, S.E. (2007). Physical and Chemical Characteristics of Airborne Particulate Matter in Khayelitsha, Cape Town, Department of Chemistry, University of Cape Town (Masters Thesis).

Chong, N.S., Sivaramakrishnan, K., Wells, M. and Jones, K. (2002). Characterization of Inhalable Particulate Matter in Ambient Air by Scanning Electron Microscopy and Energy - Dispersive X-ray Analysis. *EJEAFChe* 1: 145–164.

City of Cape Town (2007). *Air Quality in Cape Town: What We Can Do to Clear the Air*, City of Cape Town.

Environmental Health Criteria 224 (2001). *Arsenic and Arsenic Compounds,* World Health Organization, Geneva.

Fang, G.C., Lin, C.C., Huang, J.H., Huang, and Y.L. (2011). Measurement of Ambient Air Arsenic (As) Pollutant Concentration and Dry Deposition Fluxes in Central Taiwan. *Aerosol Air Qual. Res.* 11: 218–229.

Habeck, M. (2007). *Toxicological Profile for Arsenic*, Eco-USA.

Kapaj, S., Peterson, H., Liber, K. and Bhattacharya, P. (2006). Human Health Effects from Chronic Arsenic Poisoning - A Review. *J. Environ. Sci. Health., Part A* 41: 2399–2428.

Karthikeyan, S., Josh, U.D. and Balasubramanian, R. (2006). Microwave Assisted Preparation for Determining Water-Soluble Fraction of Trace Elements in Urban Airborne Particulate Matter: Evaluation of Bioavailability. *Anal. Chim. Acta* 576: 23–30.

Maas, R.P., Patch, S.C. and Berkowitz, J.F. (2004). Integrated Studies of the Dynamics of Arsenic Release and Exposure from CCA-Treated Lumber, UNC-Asheville Environmental Quality Institute, Environmental Impacts of Preservative-Treated Wood Conference, Orlando, Florida.

Niyobuhungiro, R. (2012). An Investigation of CCA-treated Wood in Informal Caterers' Fuel Stocks and Related Airborne Arsenic in the Cape Town Region, Masters Dissertation, Chemical Engineering Department, University of Cape Town.

Niyobuhungiro, R., Naidoo, S., Dalvie, M.A. and von Blottnitz, H. (2012). Occurrence of CCA-treated Timber in Caterers' Fuel Wood Stocks in the Cape Town Region, University of Cape Town. *S. Afr. J. Sci.* (under Review).

Solo-Gabrielle, H.M, Townsend, T., Messick, B. and Clitu, V. (2002). Characteristics of Chromated Copper Arsenate Treated Wood Ash. *J. Hazard. Mater.* 89: 213–232.

Tessema, M.A. (2011). Particulate Matter (PM_{10}) Pollution in Khayelitsha, Cape Town, African Institute for Mathematical Sciences (AIMS), Submitted in Partial Fulfilment of a Postgraduate Diploma at AIMS.

Von Blottnitz, H., Fedorsky, C. and Bray, W. (2007). Air Quality, In *Environmental Management in South Africa*, 2nd edition, Strydom, H.A. and King, N.D. (Eds.), Juta Legal and Academic Publishers, South Africa.

WHO (2000). Guidelines for Air Quality, Geneva.

WHO (2005). Air Quality Guidelines for Particulate Matter, Ozone, Nitrogen Dioxide and Sulfur Dioxide Global Update, Summary of Risk Assessment, WHO/SDE/PHE/OEH/06.02

Wu, C.Y., Townsend, T., Solo-Gabriele, H., Misra, A. and Dubey, B. (2006). Evaluation of Thermal Processes for CCA Wood Disposal in Existing Facilities, Florida Center for Solid and Hazardous Waste Management, Contract No. 00053522, Project No. 00050891.

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