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Determination of Fe, Zn and Cu in ambient air by Combining pre-concentration Methods and FAAS

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ABSTRACT: The main sources of human exposure to trace metals for non-occupationally exposed individuals are inhalation and ingestion. Because the absorption rates of the metals by inhalation are significantly higher (up to 50-60%) than those by ingestion (between 3% and 10%), determination of trace metals in ambient air samples is of special interest. The main purpose of this study was to determine Fe, Zn and Cu in ambient air by combining pre-concentration methods and flame atomic absorption spectrophotometer (FAAS). In the pre-concentration step, adsorption reagents including 4-(2-pyridyl-azo) Resorcinol (PAR)-loaded XAD-7, thioureasulphonamide polymeric resin and cupferron-activated carbon were used sequentially. Under the optimum conditions, seasonal distributions of Fe, Zn and Cu concentrations in ambient air of Elazig City, Turkey, were determined. Concentrations of Fe, Zn and Cu were found to be in the ranges of 154-416, 101-323 and 12-75 ng/m^3, respectively. High Zn levels determined in March and April can be attributed to the burning of coal at the beginning of spring.

Key words: Air, Metals, Pre-concentration, AAS, Atmosphere

INTRODUCTION

Due to the rapid industrialization, urbanization, and increased use of automobiles, environmental contamination has increased gradually over the past 25 years (Nriago and Pacyna, 1988; Gucer and Yaman, 1992; Yaman, 1997). It is known that, metals as one group of environmental pollutants enter the human body mainly through inhalation and ingestion (Var *et al.*, 2000; Yaman and Cokol, 2004). Heavy metals in air are toxic even at low concentration. After inhalation, they form complexes with vital protein molecules, and then resulting in malfunction or death of cell can be observed (USEPA, 1996). Heavy metals are correlated with a number of serious health problems such as cancer, neurotoxicity, immunotoxicity and cardio toxicity leading to increased morbidity/mortality in community (Ozen *et al.*, 2002; Kumru *et al.*, 2003; Yaman *et al.*, 2007a; Yaman, 2006). Hence, it is clear that accumulation of metals in human body might have middle and long-term health risks and might adversely affect the physiological functions.

Because metals cannot be degraded or destroyed in human body, the assessment of health risks due to metals via ambient air and dietary intake is of great importance. Toxic metals in ambient air can be originated from various anthropogenic sources such as industrial processes, combustion of fossil fuel, vehicle exhaust, polluted soil and incinerators. To evaluate and reduce the health and environmental risks of toxic metals in inhaled ambient air and food matrices, it is vitally important to know both their chemical compositions and the way they vary in time and space. Therefore, there are continuing efforts to determine particularly toxic metals including Cu, Fe and Zn in air phases and food stuffs (Fang *et al.*, 2005; Kaya *et al.*, 2008; Yaman *et al.*, 2005). In particular, determination of different trace metals in ambient air samples is an issue of special interest because the absorption rates of metals by inhalation are significantly higher (up to 50-60%) than those by ingestion (between 3-10%) (Mulgrew and Williams, 2000). Zinc is one of the important elements for human being. It is a component of more than 300 proteins and 100 DNA-binding proteins with zinc fingers (Ames, 2001). This element is the prosthetic group of some metalloenzymes containing superoxide dismutase (SOD) which is an important antioxidant enzyme for cellular protection from reactive oxygen species (ROS) (Yaman *et al.*, 2005; Yaman *et al.*, 2007b). Zinc appears to be protective when Zn-deficient individuals are compared to those Zn-sufficient individuals while Zn appears to be harmful for those having Zn overload as a result of environmental exposure. Association between Zn levels and cancer risk has been also examined for several anatomic sites

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(Silvera and Rohan, 2007). Iron is also an essential element for all organisms. Although iron is essential for the living organisms as found in hemoglobin and myoglobin, its excessive exposure can cause some diseases. Dietary Recommended Daily Allowances (RDA) by authorized agencies for adults of 60 kg are in the ranges of 8 to 18 mg for Fe and 8 to 11 mg for Zn as depending on sex, age and some situations such as pregnancy (Goldhaber, 2003). Copper is also known as one of the essential trace elements. The interest in the determination of Cu in any matrices related with human being has been gradually increasing. Even though this element is essential for human health depending on its concentration, it might have adverse health effects for all living organisms (Fewtrell *et al.*, 2001; Yaman and Akdeniz, 2004; Theophanides and Anastassopoulou, 2002). The acceptable daily Cu intakes (ADI) recommended by authorized agencies such as the FAO/WHO) and the U.S. Recommended Daily Allowances (US-RDA) for adults were established as 2.0 to 4.0 mg/day (Noel *et al.*, 2012). The U.S. Environmental Protection Agency (U.S. EPA) has classified copper in Group D, or not classifiable as to human carcinogenicity (Silvera and Rohan, 2007; Goldhaber, 2003; Theophanides and Anastassopoulou, 2002). As a summary, copper and iron are essential but also toxic metals in high concentrations. Their essentiality is known, but their toxicity, except for the genetic overload diseases, Wilson's disease and hemochromatosis, is not well known.

In spite of all these facts, there are no many studies in literature to determine different metals in air samples if compared with food matrices. This is probably due to the excessively lower concentrations of those metals in aerial matrix, and their determinations would require high sensitive analytical methods such as electrothermal atomic absorption spectrometry (ETAAS), and inductively coupled plasma-mass spectrometry (ICP-MS). Different online and/or offline pre-concentration methods such as the slotted tube atom trap (STAT)-FAAS (Yaman, 2005; Kaya and Yaman, 2008a), liquid–liquid extraction, adsorption, solid phase extraction have been also used combined with FAAS to obtain lower detection limits for many metals (Kaya and Yaman, 2012; Yaman and Kaya, 2005; Bakirdere and Yaman, 2008; Kaya and Yaman, 2008b; Kaya *et al.*, 2010a; Kaya *et al.*, 2010b; Berg *et al.*, 2008). Nowadays, long-term monitoring programs are recognized as powerful tools for local, regional and global studies of atmospheric long-range metals transport processes (Berg *et al.*, 2008; Yaman, 2012). In this study, Fe, Zn and Cu concentrations in ambient air from Elazig city, Turkey were determined. For this purpose, ambient air was collected from air blowers within a period of one hour. The air volume was passed on-line to three adsorption solutions each in a washing bottle sequentially placed. After the application of pre-concentration processes described elsewhere (Yaman and Gucer, 1995; Senkal *et al.*, 2007; Ince *et al.*, 2008), clear solutions were analyzed for their metal contents by FAAS.

MATERIAL & METHODS

An ATI UNICAM 929 Model flame atomic absorption spectrophotometer (FAAS) equipped with hollow cathode lamps was used for the determinations of Fe, Zn and Cu. The acetylene–air flame in the FAAS was used as described in the manufacturer's instructions for the spectrophotometer. In the pre-concentration studies, magnetic stirrers and a centrifuge were used. The pH of the solutions was measured with an EDT GP 353 ATC pH meter (Dover, Kent, UK).

Metal stock solutions (1000 mg/L) were prepared from their nitrate salts (Merck, Darmstadt, Germany). Concentrated nitric acid (65%, Merck) and hydrogen peroxide (35%, Merck) were used for the sample digestion after the pre-concentration step. All of the chemicals used were of analytical reagent grade. Doubly distilled water was used in all preparations. All glass apparatus (Pyrex®) were kept permanently at full of 1 mol/L nitric acid when not in use. Representative locations city center and surrounding of Elazig having 320,000 population located at Eastern part of Turkey were selected for this study. Samples for the control site were taken far from the city center and a mountainous area of the city (Fig. 1). Air samples were collected in the period between March and August 2006. Air volumes were collected by using an air blower for one hour at a flow rate of 1.1 m^3/min. The air collected was passed through three adsorption suspensions which are sequentially placed in washing bottles in the order of 1-thioureasulphonamide polymeric resin at pH 2.50, 2- PAR-loaded XAD-7 at pH 5.50 and 3-cupferron-activated carbon at pH 4.75 previously optimized for pre-concentration of metals described elsewhere (Yaman and Gucer, 1995; Senkal *et al.*, 2007; Ince *et al.*, 2008). Then, adsorption solutions of 250 mL were filtered, and the solid phase on the filter paper was dried at 70 °C for one hour. Dried sample was digested by using a hot mixture of concentrated nitric acid/hydrogen peroxide by occasionally stirring as described elsewhere (Yaman and Gucer, 1995; Senkal *et al.*, 2007; Ince *et al.*, 2008). After removing the acid mixture by evaporation, 3.0 mL of 1.50 M of nitric acid was added to the residue, stirred, and centrifuged. The clear solution obtained was analyzed by FAAS. To obtain calibration plots at the same conditions, the

model metals solutions were also pre-concentrated as described elsewhere (Yaman and Gucer, 1995; Senkal *et al.*, 2007; Ince *et al.*, 2008). The results from calibration graphs were transformed into metal concentrations in ambient air taking into consideration of the collected air volume of 66 m^3 for 1.0 hour.

RESULTS & DISCUSSION

Linear calibration plots were obtained by using the solutions of the studied elements at different concentrations. Equations of linear calibration plots with the concentration ranges were as follows:

$y = 0.064x + 0.43$ $R^2 = 0.99$ for Fe (0.20–4.0 mg/L)

$y = 0.302x + 0.75$ $R^2 = 0.99$ for Zn (0.1–2.0 mg/L)

$y = 0.098x + 0.54$ $R^2 = 0.99$ for Cu (0.07-4.0 mg/L)

In addition to optimum values in the previous studies (Yaman and Gucer, 1995; Senkal *et al.*, 2007; Ince *et al.*, 2008), the recovery results depending on pH for Fe by using 60 mg of the PAR-loaded XAD-7 and 45 min of stirring period were given in Fig. 2. It was found that maximum recoveries were in the pH ranges of 5.0-6.0. The blank values were subtracted from the obtained values to eliminate the effects of contamination. Limit of detection (LOD) values for Fe, Zn and Cu in solution were found to be 0.72, 0.36 and 0.25 ng/mL, respectively, by using the combination of optimum pre-concentration method with FAAS system.

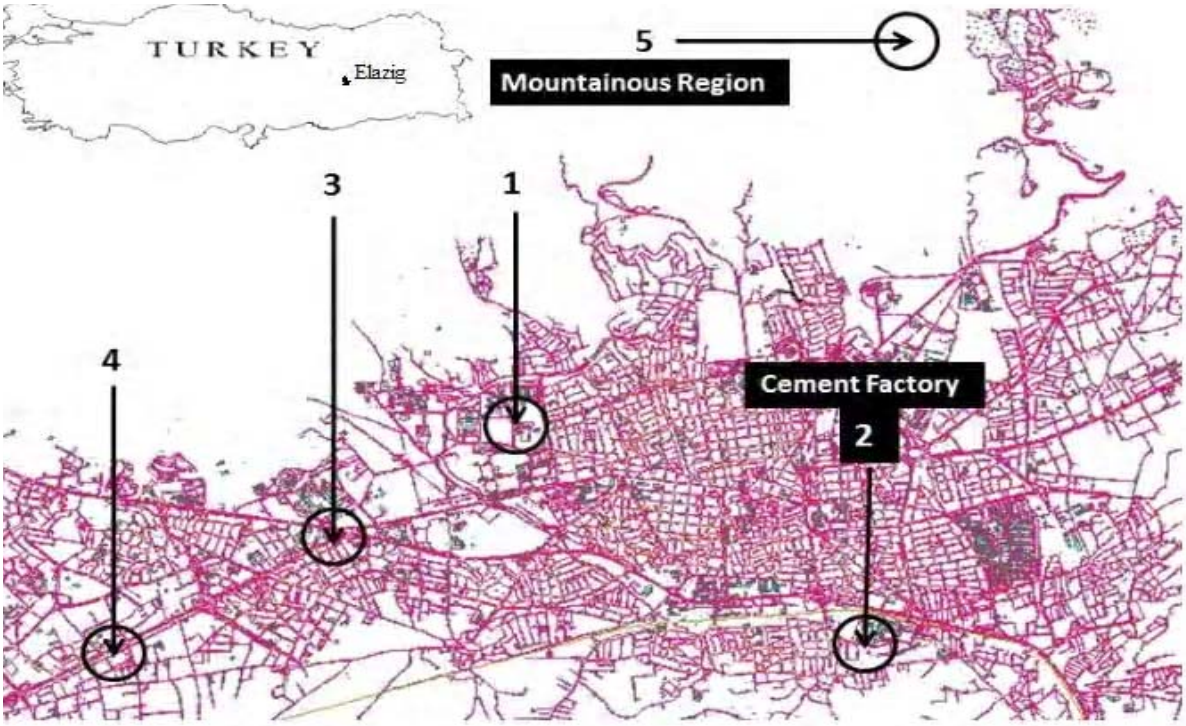

Fig. 1. Map of the study area

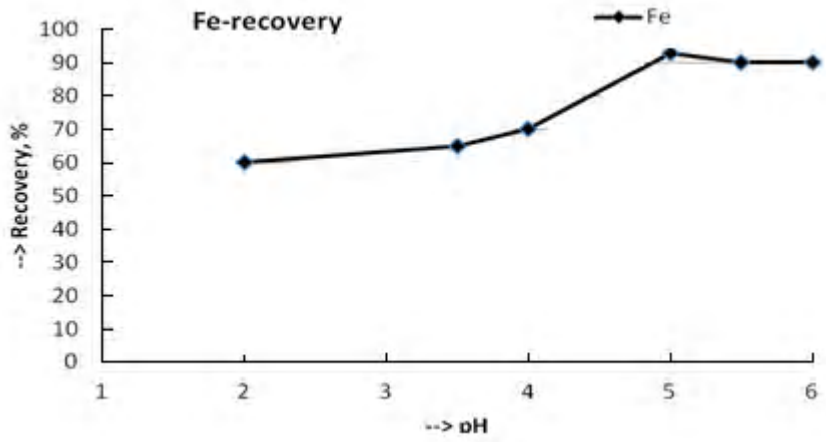

Fig. 2. Effect of pH on the recovery of Fe using PAR-loaded XAD-7

Table 1 presents the obtained average monthly results for Fe, Zn and Cu concentrations as ng/m^3 in ambient air. Seasonal changes in metal concentrations for Stations 2 and 3 are given in Figs 3-4. Zinc concentrations in ambient air taken from Stations 2 and 3 showed a decline trend from the beginning of the spring season to the summer season. In other words, concentrations of zinc peaked in the spring period. This can be attributed to the burning of coal at the beginning of the spring and cement dusts. In the rainless season, the emissions of cement dusts and flue gases can be transported to sites further away. The observed increase tendency in Fe and Cu concentrations of air samples collected in summer season might be attributed to this transportation. In the literature, the levels of Fe, Zn and Cu in ambient air from cities and urban areas range from 261 to 4800, 61 to 733 and 6.8 to 154 ng/m^3, respectively (Odabasi *et al.*, 2002). In this study, iron concentrations in ambient air during the study period for all sampling stations ranged from 155 ng/m^3 to 416 ng/m^3 (Table 1 and Figs 3-4). The highest value (416 ng/m^3) was recorded at Station 3 in March 2006 while the lowest one was obtained at Station 5 in August 2006 as control site. ANOVA results of iron levels showed significant variation among the seasons. Zinc levels found in samples varied between 101-323 ng/m^3 (Table 1, Figs 3-4). The highest value (323 ng/m^3) was found at Station 3 in March 2006 as similar to Fe while the lowest value (101 ng/m^3) was obtained at Station 4 in August 2006. ANOVA result of Zn concentration showed significant variation among the seasons. Yatin et al. (2000) reported that Zn concentrations in fine fraction of air particles from winter to summer season decrease between 1.0 and 3.5 times. In our study, similar decreases were observed for Zn levels in ambient air from winter to summer season. Copper concentrations in the sample of interest were found in the range of 12-75 ng/m^3 (Table 1, Figs 3-4). The highest Cu result (75 ng/m^3) was found at Station 3 in April 2006 while the lowest value was recorded as 12 ng/m^3 at Station 5 in August 2006 for control site. It was figured out that ANOVA results of Cu levels showed significant variation among the seasons. Similar results were reported for the effect of burning of poor-quality coal on Ni concentrations in soil and *Cedrus libani* leaves taken from the same city (Karaaslan *et al.*, 2013). Var et al. (2000) also reported similar variations in 16 Japanese cities depending on seasons.

Table 1. The obtained Fe, Zn and Cu concentrations in ambient air, ng/m^3. N=4

Sampling location/Month	Fe	Zn	Cu
Location 1: June, 2006	276±45	134±17	49±8
Location 4: August, 2006	312±41	101±14	53±9
Location 5: Control/ August, 2006	155±19	114±16	12±2
Location 2. Average of Fig. 3	193±27	154±21	39±6
Location 3. Average of Fig. 4	357±59	174±29	63±10

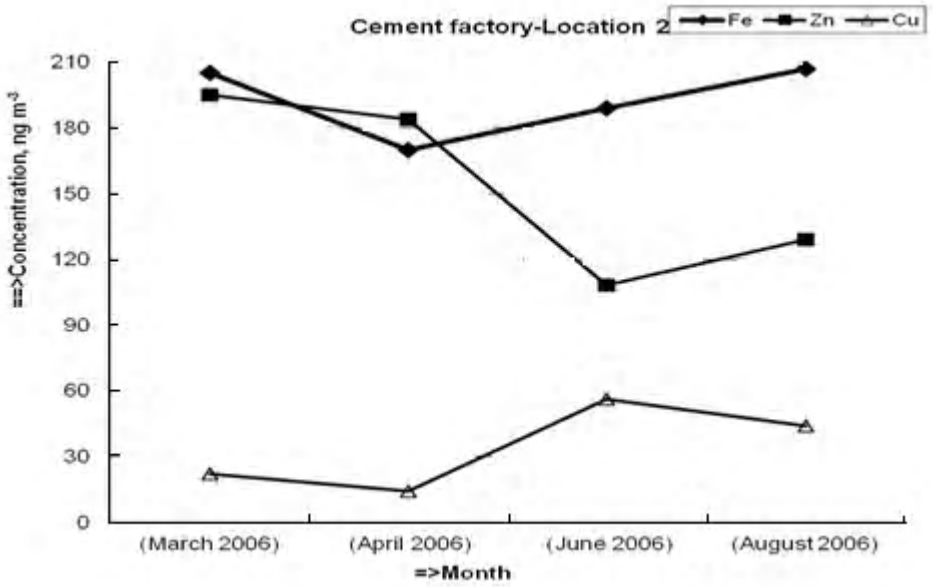

Fig. 3. Seasonal changes in Fe, Zn and Cu concentrations in ambient air taken around cement factory-location 2

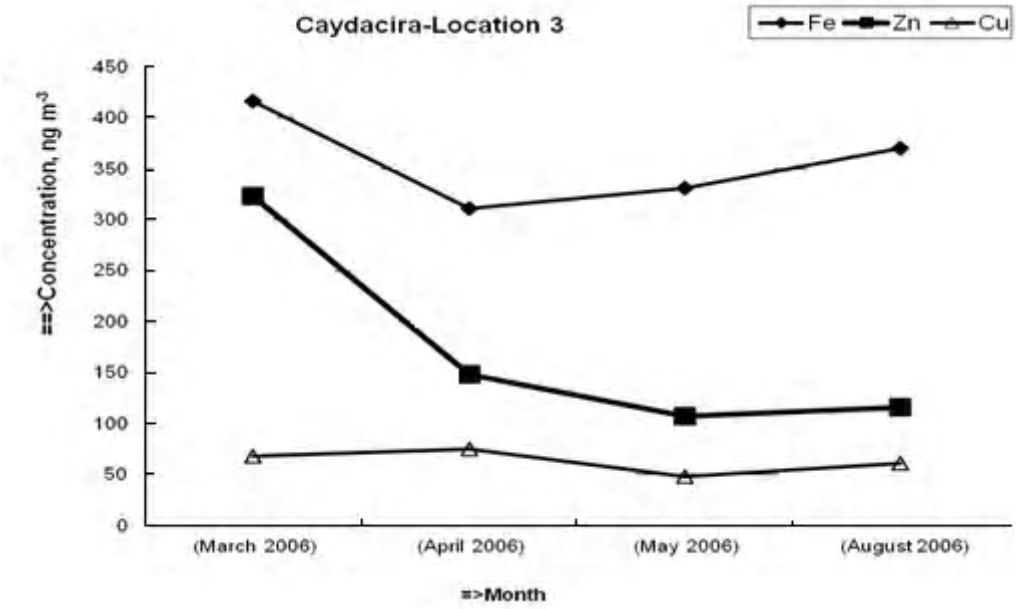

Fig. 4. Seasonal changes in Fe, Zn and Cu concentrations in ambient air taken from location 3

CONCLUSION

Determination of different metals in ambient air at trace levels has a great importance because of the fact that absorption rates for many metals by inhalation are higher (up to 50-60%) than those by ingestion (between 3-10%) as well as their common use in our life and their undestroyed properties. In order to obtain lower detection levels for the elements of interest in ambient air, optimized pre-concentration methods were successfully combined with FAAS system. Limit of detection (LOD) values for Fe, Zn and Cu in solution were found to be 0.72, 0.36 and 0.25 ng/mL, respectively, by using the combination of optimum pre-concentration method with FAAS system. Under the optimum conditions, all of the samples collected were analyzed and it was observed that metal concentrations in the samples were under the permissible levels.

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