

Environmental Health: Evaluation of heavy metals pollution in Isfahan industrial zone from soils, well / eluent waters and waste water by microwave- electro-thermal atomic absorption spectrometry

Shahnaz Teimoori^{a,*}

^a Department of Environment and Natural Resources, Islamic Azad University, Science and Research Branch, Tehran, Iran

ARTICLE INFO:

Received 1 Jan 2019

Revised form 24 Feb 2019

Accepted 8 Mar 2019

Available online 20 Mar 2019

ABSTRACT

In this study, soils, well waters, drinking waters, and waste water in the Isfahan industrial area were sampled in spring and summer 2018. In 8 points of industrial zone, important toxic heavy metals such as, lead (Pb), Cobalt (Co), Nickel (Ni), Chromium (Cr), and Cadmium (Cd) were sampled from surface soil (up to 2 m), well/drinking waters and waste water. After sample preparation with micro-wave digestion technique, the concentration of heavy metals was determined by electro-thermal atomic absorption spectrometry (ET-AAS). According to the well water analysis, the mean concentration of Cr, Ni, Co, Cd, and Pb in well water were 95 $\mu\text{g L}^{-1}$, 146 $\mu\text{g L}^{-1}$, 185 $\mu\text{g L}^{-1}$, 12 $\mu\text{g L}^{-1}$, and 11 $\mu\text{g L}^{-1}$, respectively. In well water, the concentrations of Cd, Ni, Cr and Co were found much higher than Pb in comparison with the references of World Health Organization (WHO). Also, the concentrations of such elements in soils and drinking waters are less and near found in accordance to EPA and WHO references respectively. In addition, the concentration of metals in waste water of industrial area was more than well waters. Therefore, the pollution of heavy metals such as Cr, Co, Cd, and Ni in wastewaters of industries can be diffused to well waters and eluent waters in this region and cause many problems in plants and humans.

Keywords:

Heavy Metals

Environmental Pollution

Waters and Soils

Electro-thermal Atomic

Absorption Spectrometry

1. Introduction

Heavy metals are a group of elements with a mass density greater than 4.5 g cm^{-3} , which tend to release electrons in chemical reactions and form simple cations. Heavy metals such as, Cd, Ni, Co, Cr, and Pb is potentially toxic; in addition, their effects in water, plants, and soil are very important. Prolonged accumulation of heavy metals through food stuff may lead to chronic effect in the nerve system, kidney and liver of humans [1-4]. The sources of anthropogenic contamination or pollution of the

environment by heavy metals include different branches of industry, the power industry, transport, municipal waste management, waste dumping sites, fertilizers and waste used to fertilize soil. The heavy metals from these sources are dispersed in the environment and they contaminate soil and water. They also (directly or indirectly through plants) get into human and animal bodies. After entering heavy metals from water or soil to vegetables these metals can enter people's diet and consequently exert their effects. Soil chemical composition plays important role in composition of plant materials. Overall toxic metal availability in soil contributes to metal contents in vegetables. Soil eco-system throughout

*Corresponding Author: Shahnaz Teimoori
E-mail: sht9737@gmail.com
<https://doi.org/10.24200/amecj.v2.i01.44>

world has been contaminated with heavy metals by various human activities and movement of metals in food chain has become human health hazard [5, 6]. Nickel does not bio-accumulate to a great extent in animals. There is evidence of uptake and accumulation in certain plants. Nickel food intake in the United States ranges is between 69 and 162 μg per day for adults. The standard of United Nations Food for irrigation water is 200 $\mu\text{g L}^{-1}$. The US EPA primary drinking water standard is 0.1 mg L^{-1} [7]. The trace amount of nickel and cobalt, are indicated to be either necessary or toxic depending on their environment concentration range. For example, due to studies on chicks and rats, nickel is apparently essential for proper liver function, or cobalt is at the core of a vitamin B12. On the other hand, some of nickel and cobalt compounds are carcinogenic [8–10]. Lead is a common industrial toxin and environmental pollutant and can enter the human body. It can affect the nervous system significantly, especially on the central nervous system. Industrial development has paid attention to the adverse effects of lead pollution on people's health [11]. A series of literatures also showed that even if children's blood lead levels below 10 $\mu\text{g dL}^{-1}$, they can appear significant neurological dysfunction. Some researchers showed that many rivers had lost its self-purification capacity because of receiving so many industrial wastewaters [12–14]. Cadmium is highly toxic and has been implicated in some cases of poisoning through food. Minute quantities of cadmium are suspected of being responsible for adverse changes in arteries of human kidneys. The FAO-recommended maximum level for cadmium for irrigation water is 10 $\mu\text{g L}^{-1}$. USEPA drinking water standard for cadmium is 0.005 mg L^{-1} [15]. Chromium can enter the human body through breathing, food and drinking water. Chromium salts are used extensively in industrial processes and may enter a water supply through the discharge of wastes. Chromium may exist in water supplies in both the hexavalent and the trivalent state although the trivalent form rarely occurs in potable water. USEPA drinking water standard for chromium and FAO recommended the maximum

limit for irrigation water as 100 $\mu\text{g L}^{-1}$ [16]. The World Health Organization (WHO) states that the guideline values of 50 $\mu\text{g.L}^{-1}$ Cr (VI) are considered to be too high as compared to its Geno toxicity [17–19]. Thus it is obvious that determination of heavy metals, at trace level, in water and environmental samples is of great significance from the public health and environmental point of view. Wastewater irrigation has been practiced widespread in the world [20, 21]. Wastewater irrigation creates both opportunities and problems in agricultural source [22]. It provides important water resources and has the beneficial aspects of adding valuable plant nutrients and organic matter to soil [23]. However, excessive accumulation of heavy metals in agricultural soil through wastewater irrigation may not only result in soil contamination, but also affect food quality and safety [24]. It is necessary and important to develop sensitive methods for determining heavy metals in soil, and water samples and then, the results must be compared with World Health Organization (WHO) and Environmental Protection Agency (EPA) [25, 26]. Various techniques such as, inductively coupled plasma mass spectrometry [27,28], flame atomic absorption spectrometry (F-AAS) [29], electro-thermal atomic absorption spectrometry (ET-AAS) [30,31] and cold vapor atomic absorption spectrometry(CV-AAS) [32] have been applied for the determination of soil and water samples.

The aim of this study was to monitor the toxic heavy metals such as, Cd, Cr, Ni, Co, and Pb in well waters, drinking waters, waste waters and soils in Isfahan's industrial regions and evaluation of environmental pollution in this area. After microwave digestion of samples the concentration of heavy metals were determined by ET-AAS. The results of data were analyzed using SPSS statistical programmer, PHSTAT, and excel computer packages.

2. Experimental procedure

2.1. Apparatus and materials

Determination of heavy metals (Cd, Cr, Ni, Co, Pb) was performed with a spectra GBC electro-thermal atomic absorption spectrometer (Plus

Table 1. The instrumental conditions of ET-AAS for determination heavy metals.

Element	Cd	Co	Cr	Ni	Pb
Lamp current (mA)	4	7	7	4	5
Wave length (nm)	228.8	240.7	357.9	232.0	217.0
Slit width (nm)	0.5	0.2	0.2	0.2	1.0
LOD ($\mu\text{g L}^{-1}$)	0.05	0.6	0.1	0.8	0.25
LOQ($\mu\text{g L}^{-1}$)	0.2	3	1	5	3
Working range	0.2-1.8	3-45	1-16	5-65	3-40

932, Australia) using a graphite furnace module (GF3000, GBC). The operating parameters for the metal of interest were set as recommended by the manufacturer. All samples in ET-AAS were performed using 20 μL of samples. The pH values of the solutions were measured by a digital pH meter (Metrohm 744). Microwave digestions were carried out with a Multi-wave 3000 (Anton Paar, 100 mL, 20 bar; Austria). The instrumental and temperature programming for the graphite atomizer are listed in Table 1 and 2. All reagents were of ultra-trace analytical grade from Merck Germany. Cd, Cr, Ni, Co and Pb stock solution was prepared from an appropriate amount of the nitrate salt of this analyte as 1000 mg L^{-1} solution in 0.01 mol L^{-1} HNO_3 (Merck). Standard solutions were prepared daily by dilution of the stock solution. Ultrapure water (18 $\text{M}\Omega\cdot\text{cm}$) was obtained from Millipore Continental Water System (Bedford, USA).

2.2. Sampling

In this study, Cr, Co, Ni, Cd and Pb of soil, well water and drinking in eight different location of Isfahan industrial area were evaluated. For sampling, all glass tubes were washed with a 1 mol L^{-1} HNO_3 solution for at least 24h and thoroughly rinsed 8times with ultrapure water before use. As determination of heavy metals concentration in soil samples are very difficult, even contamination at any stage of sampling, sample storage and handling or analysis has the potential to affect the accuracy of the results. All samples prepared in the vicinity of Isfahan industries. Soil and water were sampled from eight points of Isfahan's industrial zone. All of samples prepared from south of Isfahan province (4*4 km^2) (Fig.1). Due to large study area Global Positioning System (GPS) was used to determine the actual coordinates of the sampling sites and to reconfirm the location of the sampling site during subsequent sampling periods.

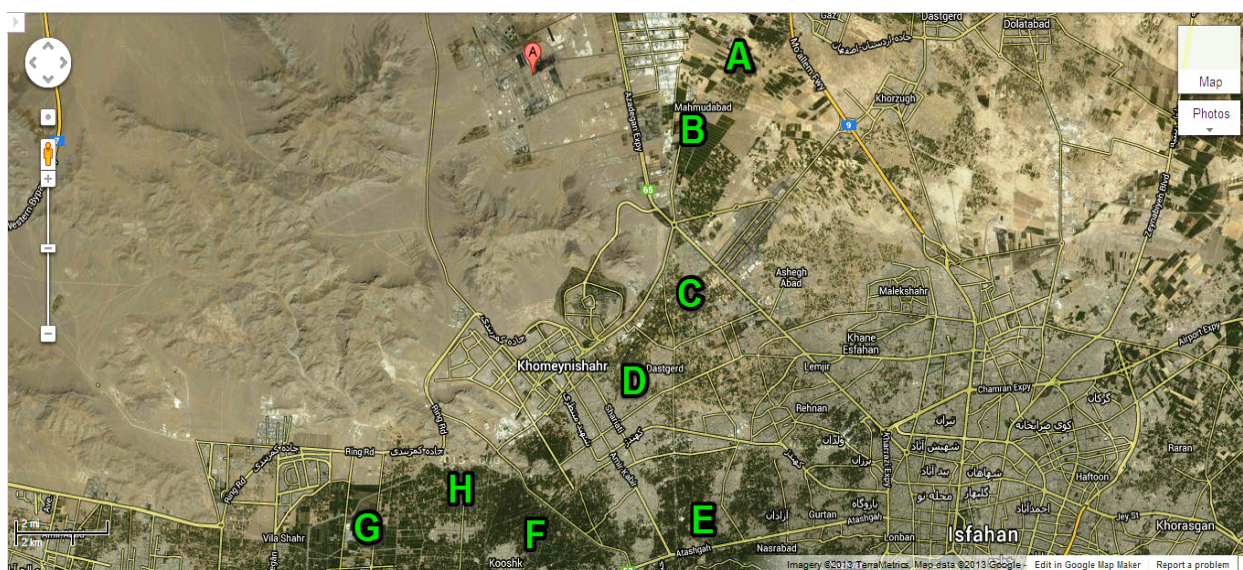


Fig. 1. Sampling water and soil in the Isfahan oil refinery area, and G point is oil refinery.

Table 2. temperature programming for the graphite atomizer of ET-AAS

Element	Cd	Co	Cr	Ni	Pb
Drying	130	130	130	130	130
Ashing	300	800	1100	900	400
Atomization	1800	2300	2500	2400	2000

In preliminary studies soil and water investigation consists of eight locations, in order to determine and to provide ground information for subsequent detailed planning of the future work. For soil sampling multiple sub samples were taken from each location and then samples were homogenized into composite sample with stainless spoon and then sub sampled by spoon into each sample container to get accurate results.

2.3. General procedure

Five samples of well/drinking water(16×5), wastewaters (10) and soil(8×5) were collected from eight Isfahan's industrial region (N=130). Samples were placed in polyethylene bags and brought to laboratory of IPIHR for analysis. All samples were washed with tap water followed with DDW (double de-ionized distil water). In the laboratory, the soil samples after air drying at room temperature were sieved with nylon mesh (2 mm). The <2 mm fraction was grinded in an agate and pestle and passed through a 63 micron sieve. Selected physio-chemical properties of these soils were analyzed using standard methods. Soil pH was measured in suspension of soil to water ratio (1:2) using calibrated pH meter. Briefly, 1 g of the soil sample was placed in a decomposition polyethylene tube to which was added 1 mL of 10 % (w/w) H₂O₂ and 7 mL HNO₃ concentrate. The mixture was digested by heating and irradiating for 60 min by microwave digestion system (MDS). After heating the sample at 120 °C the volume of the digested sample was set to 0.5 mL and dilution up to 3 mL

with DDW. Following the instruction of Instrument operational manual provided by manufacturer, analysis of Ni, Co, Cd, Cr, and Pb was carried out using atomic absorption spectrophotometer coupled with graphite furnace assembly. The blank solutions proceeded the same way and are used for the preparation of the calibration solutions and for measurement of the blanks. Soil samples were prepared in 3 depth of surface earth (5 cm, 50 cm, and 100 cm). In order to quantitating analyze and confirm the relationship among soil properties and heavy metal content, the correlation analysis was applied to dataset.

3. Results and discussion

The results of determination of heavy metals in Isfahan's industries regions show that the concentration of Cr, Co, Ni, Cd and Pb in drinking water and soil were very low and did not exceed the permissible levels (TLV). In soil samples, all of heavy metals (Cr, Co, Ni, Cd, Pb) have low concentration in accordance to EPA and WHO references. In addition, soil samples collected from the land irrigated with waste water were higher than well water . Heavy metals accumulated in the surface soil layer may migrate into the deeper layers, and consequently pose a threat of well water contamination. The parameters of pollutants depend on the type of soil and its properties. The mean of concentration of Ni, Co and Cd in surface soil (5.23 ± 0.22 , 8.42 ± 0.42 , 0.35 ± 0.02) were higher than deeper layers (2.15 ± 0.12 , 3.28 ± 0.19 , 0.08 ± 0.01), but Pb and Cr were uniform in surface and

Table 3. Permissible limits of the metals in soil and water (FAO/WHO)

WHO	Ni	Co	Cr	Cd	Pb
Soila	2-40	0.1-50	1-180	0-0.2	1-200
Waterb	70.0	80.0	50.0	3.0	10.0

^a µg g⁻¹

^b µg L⁻¹

Table 4. Mean concentration of metals in soil and water of Isfahan's oil refinery regions (N=10)

Sample	Average Metal		Concentration ^a		
	Cr	Ni	Co	Cd	Pb
Waste Water ^b	95.24± 4.31	146.48± 7.12	185.48± 9.03	23.36 ± 1.33	11.64± 0.53
Well water ^b	28.35 ± 1.48	52.12 ± 1.86	68.53 ± 2.77	0.26 ± 0.01	1.08 ± 0.04
Soil ^c	3.38 ± 0.17	3.47 ± 0.18	5.17 ± 0.28	0.13±0.006	2.19 ± 0.14

^a Mean of three determinations ± confidence interval (P = 0.95, n=5)^b µg L⁻¹^c µg g⁻¹

Sample	Average Metal		Concentration ^a		
	Cr	Ni	Co	Cd	Pb
Wastewater ^a	377.3± 14.4	246.3± 11.8	299.7± 12.3	67.5 ± 4.2	94.1± 6.5

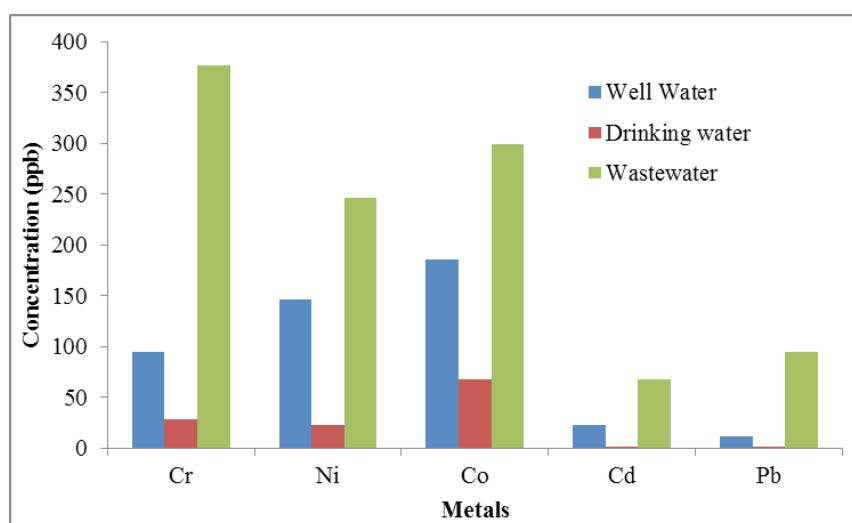
^a µg L⁻¹

deeper layers of soil. Concentrations of Cr, Co, Cd and Ni in waste water near industrial region (were higher than well water and lead was not significant effect (P<0.05). The dietary limit of metals in water and soil is very important and permissible limits of the metals in soil and water have reported by FAO/WHO [20-24] (Table 3). Mean concentration of Ni, Co, Cr, Cd and Pb in soil, well/drinking water obtained in Table 4.

Many industries located near agricultural land in Isfahan's regions. Some of points (A, B) was near to industries regions have higher concentration of heavy metals than other points (C-H). Nickel is a toxic metal that occurs naturally in environment. Results of our study show that maximum

concentration of nickel was found in waste water (246.32 µg L⁻¹) and the minimum concentration in well water and drinking water were obtained 37.43 µg L⁻¹ and 8.26 µg L⁻¹.

The mean concentration of nickel in drinking water, well water and soil were 22.12 ± 1.86 µg L⁻¹, 146.48±7.12 µg L⁻¹ and 3.47 ± 0.18 µg g⁻¹, respectively. Cobalt is an essential micronutrient for man, animals, and plants for a range of metabolic process. However, in any case the use of cobalt supplementation has been associated with toxic side effects such as cardiomyopathy. The high concentration of cobalt in human as compare to the maximum permissible limits (0.01 µg g⁻¹) can be affected on nervous system, bones, liver,

**Fig. 2.** Mean concentration of metals in well, drinking and waste water of Isfahan's industries regions.

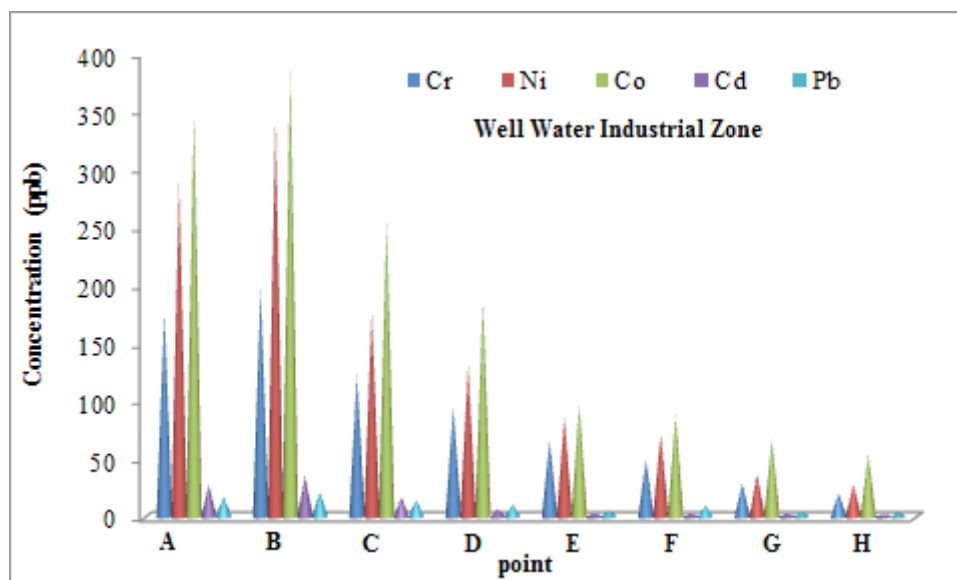


Fig. 3. Mean concentration of metals in sampling point of waste water in Isfahan's oil refinery regions.

pancreases, teeth and causes blood diseases. Results of our study show that maximum concentration of cobalt was found in waste water ($357.7 \mu\text{g L}^{-1}$) and the minimum concentration in well water and soil ($32.12 \mu\text{g L}^{-1}$, $0.38 \pm 0.01 \mu\text{g g}^{-1}$). The mean concentration of cobalt in well water, waste water and soil were $185.48 \pm 9.03 \mu\text{g L}^{-1}$, $299.7 \pm 12.3 \mu\text{g L}^{-1}$ and $5.17 \pm 0.28 \mu\text{g g}^{-1}$ respectively. Cobalt and nickel have a high concentration in waste water as compared with WHO references. USEPA drinking water standard for chromium and FAO recommended the maximum limit for irrigation water as $100 \mu\text{g L}^{-1}$. Results of chromium show that maximum concentration was found in waste water ($483.53 \mu\text{g L}^{-1}$) and the minimum concentration in well water and soil ($17.09 \mu\text{g L}^{-1}$, $1.08 \pm 0.07 \mu\text{g g}^{-1}$). The mean concentration of Cr in well water, waste water and soil were $95.24 \pm 4.31 \mu\text{g L}^{-1}$, $377.3 \pm 14.4 \mu\text{g L}^{-1}$ and $3.38 \pm 0.17 \mu\text{g g}^{-1}$, respectively. Speciation chromium in waste water showed that the Cr (VI) has high concentration than Cr (III) ($C < 65\%$) and in well water had more less 10%. Cadmium and lead have a high concentration in waste water as compared with WHO references. In waste water, maximum / minimum concentration of Cd and Pb were found ($91.3 \pm 5.3 \mu\text{g L}^{-1}$ / $24.4 \pm 1.9 \mu\text{g L}^{-1}$) and ($135.7 \pm 7.2 \mu\text{g L}^{-1}$ / 36.5 ± 2.2

$\mu\text{g L}^{-1}$), respectively. The mean of Cd and Pb in well waters, drinking waters and wastewaters was achieved (12.37 ± 1.33 ; 0.26 ± 0.01 ; 67.5 ± 4.2) and (11.64 ± 0.53 ; 1.08 ± 0.04 ; 94.1 ± 6.5), respectively.

4. Conclusion

In this study, the concentration of heavy metals such as Cr, Co, Cd, Pb, and Ni in soil, well water and waste water in Isfahan's industries regions were analyzed. After digestion the soil and waste water samples with microwave, the concentration of heavy metals determined by ET-AAS. The concentrations of Cr, Co, Cd, Pb and Ni in drinking water and soil have low TLV with compared to WHO/FAO references. But the same metals except lead have high concentration in well water. Lead concentration was not significant in samples ($P < 0.05$). Figure 1 showed that the A,B points have higher concentration of heavy metals than other points in Isfahan's regions. The mean concentration of Cr, Ni, Co, Cd, and Pb in well water were 95.24 ± 4.31 , 146.48 ± 7.12 , 185.48 ± 9.03 , 12.37 ± 1.33 , and 11.64 ± 0.53 , respectively. Therefore, Cr, Co, Cd, and Ni in well water from these regions can probability cause pollution in environmental and humans. In addition, the concentrations of such elements in soils and well/drinking waters are less

and near found in accordance to EPA and WHO references, respectively. Therefore, the pollution of heavy metals such as; Cr, Co, Cd and Ni in Isfahan industrial regions can be diffused to well waters and eluent waters and cause many problems in plants and humans.

5. Nomenclature

DDW: double de-ionized distil water

WHO: Water Health Organization

6. References

- [1] L. Jarup, Impact of environmental pollution on health, balancing risk, *Br. Med. Bull.*, 68 (2003) 167-182.
- [2] Agency for Toxic Substances and Disease Registry (ATSDR), Interaction profile for arsenic, cadmium, chromium, and lead, (2004).
- [3] National Health and Nutrition Examination Survey, Atlanta centers for disease control (ACDC), GA 30333, (2010).
- [4] Agency for Toxic Substances and Disease Registry (ATSDR), Toxicological profile for Zinc (update), Atlanta, US department of public health and human services (2005) 1-2.
- [5] S. Uchida, T. Keiko, H. Ikuko, Soil-to-plant transfer factors of stable elements and naturally occurring radionuclides, upland field crops collected in Japan, *J. Nucl. Sci. Technol.*, 4 (2007) 628-640.
- [6] M. Abbas, P. Zahida, Muhammad Iqbal, M. Riazuddin, S. Iqbal, A. Mubarik, R. Bhutto, Monitoring of toxic metals (cadmium, lead, arsenic and mercury) in vegetables of Sindh, Pakistan, Kathmandu University, *J. Sci. Eng. Technol.*, 2 (2010) 60-65.
- [7] G. Amrita, S. Das, S. Dhundasi, K. Das, Effect of garlic (*Allium sativum*) on heavy metal (Nickel II and Chromium VI) induced alteration of serum lipid profile in male albino rats, *Int. j. Environ. Res. Pub. health*, 3 (2008) 147-151.
- [8] A. Safavi, N. Iranpoor, N. Saghir, Safieh M. Glycerol-silica gel: a new solid sorbent for preconcentration and determination of traces of cobalt (II) ion, *Anal. Chim. Acta*, 569 (2006) 139-144.
- [9] A. Safavi, H. Abdollahi, M. R. Hormozi Nezhad, R. Kamali, Cloud point extraction, preconcentration and simultaneous spectrophotometric determination of nickel and cobalt in water samples, *Spec. Acta*, *Mol. Biomol. Spec.*, 12 (2004) 2897-2901.
- [10] J. L. Manzoori, A. Bavili-Tabrizi, Cloud point preconcentration and flame atomic absorption spectrometric determination of cobalt and nickel in water samples, *Microchim. Acta*, (2003) 201-207.
- [11] T. Sanders, Neurotoxic effects and biomarkers of lead exposure: a review, *Rev. Environ. health*, 24 (2009) 15-46.
- [12] M. Jakubowski, Low-level environmental lead exposure and intellectual impairment in children, the current concepts of risk assessment, *Int. j. Occup. Med. Environ. health*, 24 (2011) 1-7.
- [13] L. D. Wang, F. Y. Zhou, X. M. Li, L. D. Sun, X. Song, Y. Jin, J. M. Li, Genome-wide association study of esophageal squamous cell carcinoma in Chinese subjects identifies a susceptibility locus at PLCE1, *Nat. Gen.*, 9 (2010) 759.
- [14] Y. L. Liu, K. L. Luo, X. X. Li., X. Gao, R. X. Ni, S. B. Wang, X. L. Tian, Regional distribution of longevity population and chemical characteristics of natural water in Xinjiang, China *Sci. Total Environ.*, 473, (2014), 54-62.
- [15] A. H. Arias, J. Eduardo Marcovecchio, Continent Derived Metal Pollution Through Time: Challenges of the Global Ocean, *Marine Pollution and Climate Change*, CRC Press, (2017) 107-125.
- [16] M. Krishnamurthy, P. Ramalingam, K. Perumal, L. P. Kamalakannan, J. Chinnadurai, R. Shanmugam, K. Srinivasan, V. Venugopal, Occupational heat stress impacts on health and productivity in a steel industry in southern India. *Safety and health at work*, (2017) 99-104.
- [17] M. H. França, E. Carasek, Chromium speciation and preconcentration using zirconium (IV) and zirconium (IV) phosphate chemically immobilized onto silica gel surface using a flow system and F AAS, *Talanta*, 2 (2005) 537-542.
- [18] J. Sunderman, F. William, M. Sidney Hopfer, T. Swift, W. N. Rezuze, L. Ziebka, P. Highman, B. Edwards, M. Folcik, H. R. Gossling, Cobalt, chromium, and nickel concentrations in body fluids of patients with porous-coated knee or hip prostheses, *J. Orth. Res.*, 7 (1989) 307-315.
- [19] H. Shirkhanloo, A. A. Beigi, M. M. Eskandari, B. Kalantari, Dispersive liquid-liquid microextraction based on task-specific ionic liquids for determination and speciation of chromium in human blood, *J. Anal. Chem.*, (2015) 1448-55.

- [20] Singh S., M. Kumar, Heavy metal load of soil, water and vegetables in peri-urban Delhi, *Environ. Monit. Assess.*, 120 (2006) 79-91.
- [21] P. J. Li, X. Wang, G. Allinson, X. J. Li, X. Z. Xiong, Heavy metals, *J. Hazard. Mater.*, 161 (2009) 516.
- [22] R. K. Yadav, B. Goyal, R. K. Sharma, S. K. Dubey, P. S. Minhas, Post-irrigation impact of domestic sewage effluent on composition of soils, crops and ground water, a case study, *Environ. Int. J.*, 28 (2002) 481-486.
- [23] W. H. Liu, J. Zhao, Z. Ouyang, L. Söderlund, G. Liu., Impacts of sewage irrigation on heavy metal distribution and contamination in Beijing, China., *Environ. Int. J.*, 31 (2005) 805-812.
- [24] Muchuweti, Maud, J. W. Birkett, E. Chinyanga, R. Zvauya, Mark D. Scrimshaw, J. N. Lester, Heavy metal content of vegetables irrigated with mixtures of wastewater and sewage sludge in Zimbabwe: implications for human health, *Agriculture, Ecosystems Environ.*, 112 (2006) 41-48.
- [25] L. Schenk, S. O. Hansson, C. Rudén, M. Gilek, Occupational exposure limits: A comparative study, *Reg. Toxicol. Pharm.*, (2008) 261-270.
- [26] World Health Organization (WHO), Boron in drinking-water: Background document for development of WHO Guidelines for drinking water quality, Geneva, (2009).
- [27] S. Sarkar, A. Tanveer, K. Swami, D. Christopher, B. Abdul, A. Vincent, H. Liaquat, History of atmospheric deposition of trace elements in lake sediments, *J. Geophys. Res.: Atm.*, 11 (2015) 5658-5669.
- [28] JI N. Kumar, H. Soni, R. N. Kumar, I. Bhatt, Macrophytes in phytoremediation of heavy metal contaminated water and sediments in Pariyej Community Reserve, Gujarat, India, *Turkish J. Fish. Aqu. Sci.*, 2 (2008) 193-200.
- [29] K. Mortazavi, M. Ghaedi, M. Roosta, M. Montazerzohori, Chemical functionalization of silica gel with 2-((3-silylpropylimino) methyl) phenol (SPIMP) and its application for solid phase extraction and preconcentration of Fe (III), Pb (II), Cu (II), Ni (II), Co (II) and Zn (II) Ions." *Indian J. Sci. Technol.*, 5 (2012) 1893-1900.
- [30] H. Mizuguchi, T. Takahashi, A. Sasaki, S. Junichi, Ultra-trace determination of lead (ii) in water using electrothermal atomic absorption spectrometry after preconcentration by solid-phase extraction to a small piece of cellulose acetate type membrane filter, *Anal. Sci.*, 27 (2011) 85-89.
- [31] S. Z. Mohammadi, T. Shamspur, M. A. Karimi, E. Naroui. "Preconcentration of trace amounts of Pb (ii) ions without any chelating agent by using magnetic iron oxide nanoparticles prior to ETAAS determination, *The Scientific World J.*, (2012).
- [32] D. A. Skoog, F. J. Holler, R. Stanley, Crouch instrumental analysis, Belmont: Brooks/Cole, Cengage Learning, 47 (2007).