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Studies and Determination of Heavy Metals in Waste Tyres and their Impacts on the Environment

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Abstract

Uncontrolled burning of waste vehicle tyres causing environmental pollution has become a popular practice in developing countries like Nepal. Such activities were banned in many countries considering the environment and public health hazards but the official ban was ignored in many countries like Nepal. An experiment was conducted in a laboratory scale in an attempt to understand the potential discharge of trace metals content in Kathmandu Valley due to scrap tyre fires. For this purpose, four tyre types viz., CYCN, CSKR, BTIN and BBJP were collected representing the first two categories from passenger car and the last two from motorbike. An Atomic Absorption Spectrophotometer (AAS) was used for determination of metal concentration. Among the five heavy metals determined, Zn was detected in significantly high levels in all the tested tyre samples whereas Cd and Cr were found significantly less in many of them. The concentrations of Cd, Cr, Fe, Pb and Zn ranged from 0.020 - 27.1 μg/g, 0.14 - 1.18 μg/g, 17.8 - 381 μg/g, 0.96 - 458 μg/g and 3.95 – 8.21 mg/g respectively. It was found that the metal concentration also varied with the tyre types and qualities. The potential discharge of the metals per representative scrap tyre mass was also estimated. Results indicate that the metal pollutants due to the uncontrolled burning of the scrap tyres could significantly contribute to deteriorate the environmental condition of the Valley.

Key words: Heavy metals, Waste tyre, Environmental Pollution, Kathmandu Valley

Introduction

Uncontrolled burning of waste tyres poses a serious public health and an environmental threat [1]. Since a large number of decomposition products can be given off from the uncontrolled, open, waste tyre fires, its effect on soil, water and air is a major concern [2]. Accumulation in the street dust due to the waste tyres is one of the major way through which heavy metals may find their way into soils and water, enter the food chain and subsequently living tissues of plants, animals and human beings [3]. Heavy metals are stable and persistent environmental contaminants since they can not be biologically and chemically degraded or destroyed unlike many other organic toxic pollutants [4]. Their effects on the environment and human health have been well-established [5]. The metal contamination of the environment is a significant worldwide phenomenon.

Kathmandu, the very capital of a developing country, Nepal in South Asia has a population of 2.5 million. It is located between 27^0 45'– 27^0 47' N latitude and 85^0 20' – 85^0 25' E longitude. The Kathmandu Valley is known for its deteriorating environmental status due to the uncontrolled and open tyre fires, which has become a popular practice particularly in the narrow streets of the Valley. Such activities are gaining momentum these days and the Government of Nepal has officially banned them considering the environment and public health hazards. Besides, some people also use the tyre fires for cooking purpose as well as to avoid chilly weather during winter in the Valley and outside. Therefore, it has become an additional contributing factor for environmental pollution in the country. Hence, study on the source of pollutants is very important considering the vital aspects of the environment and human health.

There are several studies on water, soil and air quality monitoring due to the transport, industrial and domestic sectors in the Kathmandu Valley and elsewhere [6]. But very limited study is known regarding the studies on discharge of heavy metals due to the uncontrolled burning of the scrap vehicle tyres as a potential contributor for environmental degradation. Hence, the aim of the present study is to understand the environmental status in the Valley through determination of trace metals content due to the scrap tyre fires.

Experimental

Sample collection

Tyre samples were collected from tyre repairing workshops. Only passenger car and motor bike tyres were selected because they were easy to handle and store for the experimental purpose. Among many tyre types, qualities and popular manufacturing companies available in Kathmandu today, four different widely used tyre types, two each of the above vehicle category were selected as representative samples (Table 1). Each of the collected tyre samples was selected from the waste or among the used ones that has already reached the end of tyre life. The end of life tyre is a waste or used tyre that cannot or be reused for its originally intended purpose. Such tyres may have a further use as raw material for other processes or be destined for final disposal. End-of-life tyres are called "scrap tyres" in the United States. The details of the representative samples are given in Table 1.

Table 1. Description of the collected tyre samples.

Sample No.	Types of vehicle tyres	Manufacturing company/Country	Abbreviated as
1	Passenger Car	Yin Zhu/China	CYCN
2	Passenger Car	Samyang/South Korea	CSKR
3	Motor bike	TVS/India	BTIN
4	Motor bike	Bridgestone/Japan	BBJP

Preparation of Samples and Stock Solutions

All the representative scrap tyre samples were cleaned, thoroughly washed and shade dried to remove dust particles. A small portion of each of the tyre samples was cut into fine pieces so that they could be burnt completely to ash without difficulty.

Preparation of stock solutions and heavy metal analysis were carried out by following the method as described in ASTM Designation: 4185-90 (modified) [7]. Accordingly, 2.0 g of the finely cut pieces of CYCN was accurately weighed and burnt to ashes in a porcelain basin. The residue left after burning the tyre sample was ignited at about 650-700^{o}C in a furnace till complete ashing. After complete ashing, it was digested with (1:1) nitric acid. The volume was adjusted to 10 ml with double distilled water. The prepared solution is known as stock solution and then it was preserved in a polyethylene bottle. The stock solution of all other samples were prepared and preserved in similar ways. All the experiments were carried out in triplicate.

Reagents and Equipment

The chemicals such as HNO_3, $CdSO_4.H_2O$, $K_2Cr_2O_7$, $FeSO_4(NH_4)_2SO_4.6H_2O$, $Pb(NO_3)_2$ and $ZnSO_4.7H_2O$ were purchased from E. Merck, India. The standard solutions of each metal were prepared as follows: Cadmium(II): 0.500, 1.00, 2.00, 4.00 and 6.00 mg/L; Chromium(VI): 1.00, 2.00, 3.00, 4.00 and 5.00 mg/L; Iron(III): 0.500, 1.00, 2.00, 4.00 and 6.00 mg/L; Lead(II): 1.00, 2.00, 3.00, 4.00 and 5.00 mg/L; Zinc(II): 0.500, 1.00, 2.00, 3.00, 4.00 and 5.00 mg/L. Double distilled water was used throughout the experiment. A SOLAAR M5 Dual Automizer Atomic Absorption Spectrophotometer with a standard photomultiplier, 180 – 900nm, Thermo Elemental, UK was used to analyze all the samples.

Determination of Trace Metals

Initially, the Atomic Absorption Spectrophotometer (AAS) was sufficiently warmed up for about 30 minutes. Hollow cathode lamps manufactured by Photron Pvt. Ltd., Australia were used for determination of the trace metals. The AAS was then calibrated with a series of the standard solutions of each specific metal already prepared before the concentration of specific metal was determined in all the samples of the stock solutions. For instance, the AAS was calibrated with a series of the prepared standard solutions of cadmium (II) and then the cadmium level was determined in all the samples one after another. The concentration of all other metals was also determined in similar ways. A reagent blank was run during the determination of each metal. Dilution of the stock solutions was made whenever necessary and multiplied the concentration by dilution factor wherever applicable during the calculation.

Metal concentration was calculated using the working formula given below:

$$\text{Concentration of metal, } \mu g/g = \frac{\text{Observed Conc. (ppm) * Vol. of Sample Prepared (mL)}}{\text{Wt. of Tyre Sample (g)}}$$

Results and Discussion

Heavy metals in the representative tyre ash

The concentrations of the heavy metals obtained in the tyre ash of the representative tyre sample are summarized in Table 2. Zinc exhibited significantly high levels in all the tested tyre types. Iron ranked the second higher level whereas the concentration level of lead was significantly below the zinc and iron in many of the tested tyre samples. Although cadmium and chromium levels were found relatively low in almost all the samples, they have significant effect on the environment as well as on human health. It was found that the concentration level of the metals also varied with the vehicle tyre types and qualities.

Results revealed that CYCN exhibited significantly high level in terms of all its' metal concentration among all the tyre samples. Indeed, the metal concentration in the tyre ash followed the order as Zn > Pb > Fe > Cd > Cr (Table 2). Like CYCN, CSKR was also found to contain higher level of zinc, however the metal concentration was in the order as Zn > Fe > Pb > Cr > Cd. Cadmium and chromium levels were almost negligible in CSKR but they were obtained in considerable amount in CYCN. Similarly, lead level was also found significantly low as compared to CYCN. The variation of the metals level may probably be due to the difference in the material composition of the respective tyre types.

Like CYCN and CSKR, comparatively high zinc level (5.92 and 3.95 mg/g) was found in BTIN and BBJP respectively (Table 2). However, cadmium and chromium levels were almost negligible in both tyre types compared to the rest of the metals. Zinc, iron and lead levels in BTIN were found significantly higher to that of BBJP whereas Cd and Cr were found in more or less the same level in both the tyres. Interestingly, the order of metal concentration (Zn > Fe > Pb > Cr > Cd) in BTIN and BBJP followed similar trend as CSKR (Table 2). Release of the metals in such levels depends probably on the material composition of each tyre wear type and quality as described above. A study made by Weckwerth (2001) revealed that an abraded tyre material released about 3% of the metals such as Zn, Mo, Cu and Sb in the environment whereas the significant contribution was made by vehicular exhaust, brakes and vehicle services [8]. Kakar and Gupta (2007) studied Cr, Zn, Pb, Cd, Ni, Mn and Fe as the seven toxic trace metals in the particulate matter (PM_{10}) from the industrial (Cossipore) sites of an urban region of Kolkata, India [9]. They apportioned 8% to tyre wear and the remaining was attributed to the vehicular emissions and coal combustion. Since the source of the trace metals in the present study is entirely due to the waste tyres, further investigation is required in order to mention the proportionate contribution of the trace metals in the environment. However, it is obvious from our findings that different tyre types release different levels of the trace metals such as Cd, Cr, Fe, Pb and Zn in the environment.

The trace metals released due to the tyre wear or waste tyre accumulate in the road dusts. Habib et al. (2006) reported the higher concentration of iron while analyzing Cu, Fe, Pb and Zn in the road dust of different sampling stations in Dhaka city [10]. The highest level of Fe in the road dust samples was reportedly due to the high abundance of Fe in the nature and partly due to tyre wears and roadside artisans' activities. Homady et al. (2002) had noticed the significant increases in the total contents of Fe, Cu, Pb, Zn, Ni, Mn and Cr in ambient dusts at some vehicular service stations in Jordan [11]. They also found the highest level of Fe and the lowest level of Cr in the ambient dusts, which was reportedly due to the vehicle sources, petroleum residue and tyre repair. The present study also shows comparatively low levels of Cr in almost all the tyre ash and is, therefore partly in agreement with the above findings. This may probably be due to the least content of Cr in the material composition either in tyre wear or in vehicle sources. However, our study reveals that all the tyre wear releases the highest level of Zn and then Fe whereas the levels of Cd, Cr and Pb are comparatively low. Hence, the contribution of the metals in the ambient and road dusts due to the waste tyre is justified apart from a number of other sources.

Tripathi et al. (1993) measured the atmospheric deposition of trace metals like Pb, Cd, Cu and Zn at Deonar, Bombay [12]. The bulk deposition flux for these metals was found to vary from 0.3 to 102.1 kg $km^{-2}yr^{-1}$ with the deposition velocities which varied from 0.05 to 2.5 cm s^{-1}. They suggested that the atmospheric deposition of the trace metals in Bombay was mainly due to increasing vehicular emissions. Devkota et al. (1997) studied air pollution of the Kathmandu valley due to Cd and Pb using lichens as biomonitors [13]. They found higher accumulation of Cd and Pb in the lichens collected from the vicinity of the Valley than those from remote areas. However, Pb was obtained in higher level compared to that of Cd suggesting that the polluted air of the valley was mainly due to increasing vehicular emissions. Similarly, it was studied that the transport sector emitted about 5 tons of Pb in the Kathmandu Valley in 2005 and estimated 6 tons of Pb by 2010 [6]. The present research has some study limitations and hence may not truly be comparable with the above findings. However, our results show that almost all the waste tyres release significant levels of Pb compared to that of Cd and Cr. Hence, the waste tyres or tyre wear might also contribute to the metal pollution in the Valley to some extent along with the vehicular emissions. In other words, the trace metals released due to the waste tyres or tyre wear accumulate in the road dust. The road dust blown up in the atmosphere by wind or vehicular movements may travel several distances and finally return to the soil or water causing environmental pollution. Also, the uncontrolled and open tyre fires may partly contribute to atmospheric deposition of the trace metals.

As cited in a report [14], Malmqvist (1983), Hewit and Rashed (1990), Brewer (1997), VROM (1997) and Legret and Pagotto (1999) had analyzed the metal content of tyres with high way-run off. They found the concentration range of 0.28-0.96 mg/kg (Cd), 0.4-6.73 mg/kg (Cr), 2.12-533 mg/kg (Fe), 1.0-160 mg/kg (Pb) and 8378-13494 mg/kg (Zn) respectively in the tested run off samples. The results of the present study are partly in agreement with the above findings. Only iron and lead levels obtained in all the tested tyre samples fall within the above concentration range whereas the other metals varied in their concentrations. In fact, the results of the present study may not likely be compared with the above results. It is because that the present study was entirely based on the model use of known vehicle tyre types and qualities unlike the above studies in which the concentration of metals were analyzed in highway run-off only irrespective of the tyre types and qualities. However, this comparison was taken as informative only.

Tyres contain total of approximately 1.5% by weight of hazardous waste compounds as stated in Basal Convention report [2]. These compounds, outlined as Cu, Zn, Pb, Cd, organohalogens and many others are encased in the rubber compound or present as an alloying element. The copper compounds are used as alloying constituent of metallic reinforcing material. The zinc compound as zinc oxide is retained in the rubber matrix. Cadmium as cadmium compound present in trace levels is used as an attendant substance of the zinc oxide. Similarly, lead and lead compounds present in trace levels are used as attendant substance of the zinc oxide. Reportedly, the content (% weight) of these hazardous constituents is approximately 0.02% and 1.0% for Cu and Zn respectively. Similarly, the contents of Cd, Pb and halogens are 0.001%, 0.005% and 0.10% at the maximum respectively as mentioned in the above report.

Although, analysis of copper and organohalogens is not included in the present study but almost all the representative tyre samples had their hazardous metal constituents level within the above outlined percentage. However, CYCN exceeded the outline value in case of lead whereby 0.005% is the outline value as mentioned in the Basel Convention report and 0.046% was the experimentally observed value (Table 2). The reason for the above observations may probably be due to an appropriate composition of the metals content in the respective tyre samples. Nevertheless, experimental errors cannot be avoided in some cases. Above all, the content of Zn (% weight) was found almost in the comparable ratio (Table 2) and the high level of Zn in all the samples is justified.

Table 2. Metal concentration in the tyre ash of each representative sample. Each value in the Table is the mean ± SD of three replicates

Heavy Metals	Concentration* (μg/g)			
	CYCN	CSKR	BTIN	BBJP
Cd	27.1 ± 4.5	0.020 ± 0.001	0.10 ± 0.01	0.10 ± 0.01
Cr	1.18 ± 0.17	0.24 ± 0.06	0.14 ± 0.04	0.21 ± 0.06
Fe	381 ± 21	182 ± 9	137 ± 11	17.8 ± 2.9
Pb	458 ± 83	5.45 ± 0.84	5.23 ± 0.73	0.96 ± 0.21
Zn*	8.21 ± 0.11	4.46 ± 0.44	5.92 ± 0.63	3.95 ± 0.36

Zn concentration, mg/g

Potential discharge of the metals due to the uncontrolled burning of an entire representative scrap tyre mass and their impacts on the environment

Based on the above experimental ratio at laboratory scale, potential discharge of the metals in the environment due to the uncontrolled burning of an entire scrap tyre mass was also estimated. The weights of CYCN, CSKR, BTIN and BBJP scrap tyres were found to be approximately 6.5 kg, 6.5 kg, 2.0 kg and 2.5 kg respectively (Tyre repairing workshops – personal communication). Hence, cadmium, chromium, iron, lead and zinc levels to be discharged through complete ashing of the representative tyre samples would proportionately increase with their respective scrap tyre mass as shown in Table 3. Accordingly, zinc is expected to be discharged in the environment in significantly high level of all. These results suggest probable common source of the toxic metals in the environment in the Kathmandu Valley is due to the uncontrolled tyre fires.

Table 3. Potential discharge of the metals per scrap tyre mass of each representative sample through complete ashing.

Heavy Metals	Amount per scrap tyre* (kg)			
	CYCN	CSKR	BTIN	BBJP
Cd	1.76×10^{-4}	1.30×10^{-7}	2.00×10^{-7}	2.50×10^{-7}
Cr	7.67×10^{-6}	1.56×10^{-6}	2.80×10^{-7}	5.25×10^{-7}
Fe	2.48×10^{-3}	1.18×10^{-3}	2.74×10^{-4}	4.45×10^{-5}
Pb	2.98×10^{-3}	3.54×10^{-5}	1.05×10^{-5}	2.40×10^{-6}
Zn	5.34×10^{-2}	2.90×10^{-2}	1.18×10^{-2}	9.88×10^{-3}

The figure in each column denotes an estimated metal concentration per scrap tyre that could be discharged into the environment upon complete burning. The values are presented on the basis of the experimental ratio and the reference weight of each scrap tyre as: CYCN (6.5 kg), CSKR (6.5 kg), BTIN (2.0 kg) and BBJP (2.5 kg).

Release of such metals is one of the most significant environmental problems caused by the anthropogenic activities. Recently, there has been an increased concern regarding the occurrence of the heavy metals because of their toxicity. Due to high concentration in the environment, these metals may not only pollute the environment but also enter the food chain from soils [3]. Exposure to the metal ions in sufficient quantities can have serious impacts on human health that may include cancer, endocrine-disrupting effects, reproductive system disorders, nervous system disorders, several acute toxicity etc. [15].

Iron and zinc are some of the metals, which are essential at very low concentrations for life because they have important roles in metabolic processes taking place in living cells. Cadmium and lead are nonessential metals, which are known to cause severe damage in living organisms even at low concentrations [16]. The presence of these metals ions at elevated levels in the environment is often toxic to living organisms [17]. This involves blocking essential functional groups, displacing essential metal ions, or modifying the active confirmation of biological molecules resulting in the inhibition of a variety of metabolic as well as enzyme activities in living organisms. The metal toxicity has a direct effect on various physiological and biochemical processes such as photosynthesis, chlorophyll content and reduction in plant growth [18].

Large quantities of cadmium and zinc can be found in soils. The metal ions bind strongly to soil particles and some of these dissolve in water causing metal pollution. Hence, they accumulate in the bodies of water and soil organisms. They can interrupt the activity in soils, as they negatively influence the activity of soil microorganisms and earthworms. The breakdown of organic matter in the soil may seriously slow down because of this. On zinc-rich soils only a limited number of plants have a chance of survival. Water soluble zinc that is located in soils can contaminate groundwater. Zinc ions may also increase the acidity of water [19].

Body functions of phytoplankton can be disturbed when metal like lead interferes. Phytoplankton is an important source of oxygen production in seas and many larger sea-animals eat it [18]. Fishes can also accumulate lead in their bodies, when they live in the metal-contaminated waterways. The metal that enters the bodies is able to bio-magnify up the food chain. Iron (III)-O-arsenite, pentahydrate may be hazardous to the environment. Chromium (III) is an essential element at trace level whereas Chromium (VI) is mainly toxic to living organisms. High concentrations of chromium can cause respiratory problems in animals, a lower ability to fight disease, birth defects, infertility and tumor formation [20].

Although the present study has not covered the research aspect regarding the impacts of the heavy metals on the environmental status in the Kathmandu Valley, the metal pollution however brings about the consequences as described above. A future work, however, will be needed to study in the related area.

Conclusions

The present study conducted in the laboratory scale was a model application showing the potential discharge of various hazardous heavy metals in the Kathmandu environment due to the uncontrolled burning of waste tyres. Based on the experiments, our findings conclusively demonstrate that these toxic metals could also be an additional source for the environmental degradation of the Valley. However, several factors affect in field and laboratory conditions. Indeed, the uncontrolled and open-air burning of waste tyres can never be an environmentally sound or acceptable management practice in the Valley. It is because humans are exposed to them in several ways for short or long terms and then gradually get their health affected.

The present study is probably the first ever research conducted in the related area in a developing country like Nepal. The study would, therefore provide significant information for redressing the environmental pollution due to the uncontrolled burning of waste tyres. Moreover, the present study may open a wide prospect as well as provide a guideline for further investigation into the related areas elsewhere in developing countries.

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