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***Short Communication***

# Microplastics: A vector for heavy metal adherence and its transportation

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## Abstract

*Plastic particle with size less than 5mm (in diameter) are known as Microplastic. Nowadays it is becoming global threat for several water bodies and associated organisms hence considered as an alarming pollutant. On the other hand, heavy metals being persistent problem for aquatic body with high biomagnification capacity. In general, both Microplastic and Heavy metals acts as a stressor for the aquatic ecosystem and its biota. To explore the interactions, a short exposure study was conducted in which we examined the adsorption of two metals, Nickel (Ni) and Lead (Pb), taken places from a paint which has antifouling nature onto the surface of unexposed Polyethylene (PE) and Polyvinyl Chloride (PVC) beads. We have very clearly observed that both Ni and Pb was continuously released from paint into the tap water sample and adhered onto the surfaces of exposed microplastic beads but with specific preferential coexistence. Like, it was observed that Pb adsorption was appreciably greater in PE beads than in PVC further on the other side of Ni adsorption was significantly greater in PVC beads than in PE. This result strongly suggests that after degradation when a plastic convert into microplastic which has a high tendency to adhere heavy metals, further, act as a transport vehicle of such metals which moves one place to another in an ambient environment.*

**Keywords:** Microplastic, heavy metals, adherence, PVC, PE.

## Introduction

Worldwide rapid urbanization, industrialization and changing lifestyle of people has increased the demand of materials which are more durable, reliable, attractive and most importantly cost effective such as ‘plastics. Nowadays, people around the world prefer packed foods, plastic containers and plastic made carry bags as they can be more frequently use for a longer duration of time. Since past 50 years, the use and production of plastic goods have augmented progressively, reaching more than 300 million tons in the year 2014 at global scale production[1].In general scenario, Per capita consumption of plastics in different countries are different for example U.S. being on the lead with 109kg/person, whereas within Asia 38kg/person in China and 11kg/person in India[2].

According to CPCB report, regarding plastic waste scenario in India, maximum annual plastic waste production was reported in metropolitan cities like Delhi having 689.52 tonnes production followed by Chennai (429.39 tonnes), Mumbai (408.27 tonnes), Bangalore (313.87 tonnes) production and Hyderabad having 199.33 tonnes production[3]. Similar report was also discussed the problem associated with plastic waste management practices, like 9% of waste is been recycled and rest Left out 91% are unintentionally dumped into nearby open pits/landfills, flowing sewer drains and ultimately dumped into water bodies. And once the plastic waste enters into open environment in undergoes various processes which enhance all degradation in respect of chemical, mechanical and biological. These processes fragments macro sized plastic into micro sized plastic universally known as “Microplastic”. Such particles are found in different forms like spherical, fibers or granules. Generally, microplastics are classified into primary and secondary type in which primary ones are the engineered plastic like microsize beads, used in toothpaste and in cosmetics for the exfoliation purpose. On the other side secondary types are the one which fragment from large size plastic litter generated from sources like tourism (coastal), fishing (recreational or commercial), various marine industries or from associated vessels beside Waste Water Treatment Plants (WWTP) which also, ultimately end up into aqua-terrestrial environment[6]. Along with micro plastic, their lies another persistent toxic problem i.e., “heavy metals”. High concentrations of these metals are released into aqua-terrestrial environment through bedrock or sediment leaching, atmospheric deposition, urban and industrial runoff or discharge[7,8]. Due to larger surface area and hydrophobic nature of microplastic, various Persistent Organic Pollutants (POP’s) like Polychlorinated Biphenyls (PCBs), Polybrominated Diphenyl Ethers (PBDEs) or Perfluorooctanoic Acid (PFOA) etc which are already present in water body gets adhered to its surface and later on leads to persistent toxicity[9]. Therefore, it is expected that microplastic ingestion may introduce toxins to the food chain, gets bio accumulated and further its associated toxicity can be bio magnified from lower to higher trophic level. In general, there are limited number of studies have been reported to understand the adsorption of trace metals by the plastics present in an ambient environment[10,11]. Within the field of harbours and marinas, the metal pollution is predominately a common problem as it is originated by multiple sources[12], while considering bays and estuaries the pressure by anthropogenic activities is observed more, such that Zinc and Copper are leached into seawater from paint having antifouling properties[13].

In the current study, we have tried to investigate the interface between two different types of recognized polymers and two heavy metals like Nickel (Ni) and Lead (Pb) which are abundantly available in the urban backdrop. Among all water pollutants, some hazardous one are known as Potentially Toxic Elements (PTEs). PTEs are naturally occurring, pervasive elements originating from weathering of parent material and causal anthropogenic activities like mineral resource development, metal processing, smelting, industrial emissions, application of fertilizers and pesticides, sewage irrigation, as well as through atmospheric deposition and runoff. Some of these metals in small quantities function as essential elements due to its importance in living organism sustenance. PTEs like As, Co, Cr, Cu, Fe, Mn, Mo, Se, V are essential while Sb, Be, Cd, Pb, Hg, Ni, Ti and Sn are non-essential elements (having no use in human body). Among all, Ni and Pb were selected as Nickel (in $Ni^{+2}$ oxidation state) and Lead (in $Pb^{+2}$ oxidation state) are highly abundant both in soil and water of Delhi, NCT also they leachin to tap water from water supply pipes and fittings. Lead based additives are used as stabilizers by most Indian manufacturers for strengthening and increasing the life span of pipes. Both Nickel and Lead being non-essential when introduced into water act as neurotoxic, genotoxic, and carcinogenic agent which may further causes serious health problems[4,5].

The simulated experiment was conducted under controlled laboratory condition, in which we applied paint with antifouling property onto the PVC settling plates and two known polymers were considered i.e. virgin beads of Polyethylene (PE) and Polyvinylchloride (PVC). To understand whether microplastics can adsorb metals leached from such paints, PE and PVC microplastics were exposed separately in different experimental units having water from tap and treated them with painted settling plate, for 4 weeks period.

## Materials and methods

**Experimental setup:** In the experimental setup, we had exposed two types of microplastics, Polyethylene (PE) and Polyvinyl Chloride (PVC) beads which were less then <5mm in size and spherical in shape. PVC Settling plate (5 X 10 cm) was painted one side with non-toxic commonly used oil based red colour paint (manufactured by Asian paints). All glass containers used in experimental units were prior rinsed with diluted Hydrochloric acid and deionized water to exclude prior interference of any heavy metals. One glass container (250ml beaker) was considered as one experimental unit with an antifouling paint coated plate along with microplastic beads. Approximately 0.5g of each PE and PVC beads (50 in number) were procured from Jhilmil Industrial area, Delhi manufactured by G-Lex, GAIL (India) Limited and then added to each respective unit. Six set up of each plastic type (PE/PVC) were arranged and water was exchanged weekly. During water exchange, 10 beads from each of the PE and PVC set up along with respective water sample were also sampled. This simulated study will mimic the process of micro plastic adherence capacity in a metal contaminated aquatic ecosystem.

**Metal Analysis:** For heavy metal analysis, procured water samples were acidified immediately with conc. Nitric acid and stored at 2°C for further analysis. Glass bottles were used for storage and afterward analysis. For plastic pellets preservation, they were freeze dried, 24 hrs prior to extraction. Two marker metals, Nickel (Ni) and Lead (Pb) were extracted from microplastic surfaces using a modified Aqua Regia extraction method[10]. 12 M HCL and 16 M $HNO_3$ in a ratio of 3:1 was mixed for the preparation of Aqua Regia. After preparation, the pellets collected from each unit was stored in 10ml HDPE (High Density Polyethylene) vials, to which 10ml of 20% (v:v) Aqua Regia was added. For the release of heavy metal adhered to microplastic surface, the stored vials were shaken for 24hrs at 150 rpm on centrifuge machine. The extraction occurred at room temperature. After which, samples were filtered using GF/F Whatman filter paper number 1 to retain the pellets and immediately acidified with $HNO_3$ (9ml of sample to 1ml of $HNO_3$, to adjust pH<1). Atomic Absorption Spectrometry (AAS) (model: Shimadzu, AAS (AA-6300) was used for both the heavy metal analysis. Concentration of Nickel (Ni) and Lead (Pb) were measured in the tap water and beads samples (considered as laboratory blank) at initial day 0, before adding any paint into the system. Further, the samples for water and beads were collected at day 7, 14, 21 and 28.

## Results and discussion

**Adherence of Ni and Pb on different plastic types:** In this setup, throughout 4 weeks, the averaged concentration of Nickel (Ni) in water was found to be 245.25±0.166µg/l. Further, Ni concentration adhered on PE pellets ranged from 68-129µg/g whereas its concentration on PVC pellets were in the range of 64-138µg/g as shown in Figure-1. An increasing trend of Ni adherence was noticed in the exposure study till 21 days in both the pellets (PVC and PE) types. But after 28 days interestingly the trend started decreasing in both the case (with almost similar adherence capacity), probably due to the saturation of surface binding site for both pellet type. This confirms that Ni adheres very easily on plastic type (PE and PVC) from the surrounding water.

Interestingly, from another setup, similar trend was also observed in the case of Lead (Pb), its average concentration in water was found to be, almost double 443.96±0.053µg/l. Pb concentration adhered on PE pellets ranged from 125-302µg/g whereas on PVC pellets ranged from 162-281µg/g as shown in Figure-2. This confirms that both the PE and PVC plastics adheres Pb from the surrounding water and comparatively in higher concentration than Ni exposure. A similar study for 8 weeks was conducted in South West England, where virgin polyethylene pellets was deployed and was observed that heavy metals like Manganese (Mn), Aluminium (Al), Copper (Cu), Silver (Ag), Zinc (Zn) and Lead (Pb) were adsorbed at plastic surface. In general, the mechanism behind metal adsorption observed was that cations or complexes directly adsorbs onto charged or neutral sites present on plastic surface[14]. It was also found that plastic pellets been collected from beaches of south west England contained variable concentrations of trace metals (Cr, Co, Ni, Cu, Zn, Cd and Pb) which in some cases, exceed local estuarine sediments concentrations[10]. Plastic surface properties and porosity plays a vital role when heavy metals are released into a water column. Further it is noticed that the adsorption rate and surface area along with reactivity are directly proportional to each other[10]. It is also observed that mechanism of heavy metal adsorption by functional groups like Amines is done by process of "chelation". This depends on binding capacity, surface force, morphology and electric charge of polymer which connects to electric charge, binding capability, surface forces and so on.

Also, the chemical used in plastic manufacturing units (such as catalysts, fillers, plasticizers), different type of degradation and aquatic plastic debris fouling due to microbial biofilms formation and algae or invertebrate's colonization, can lead to generation of active sites for further sorption and/or metals bioaccumulation.

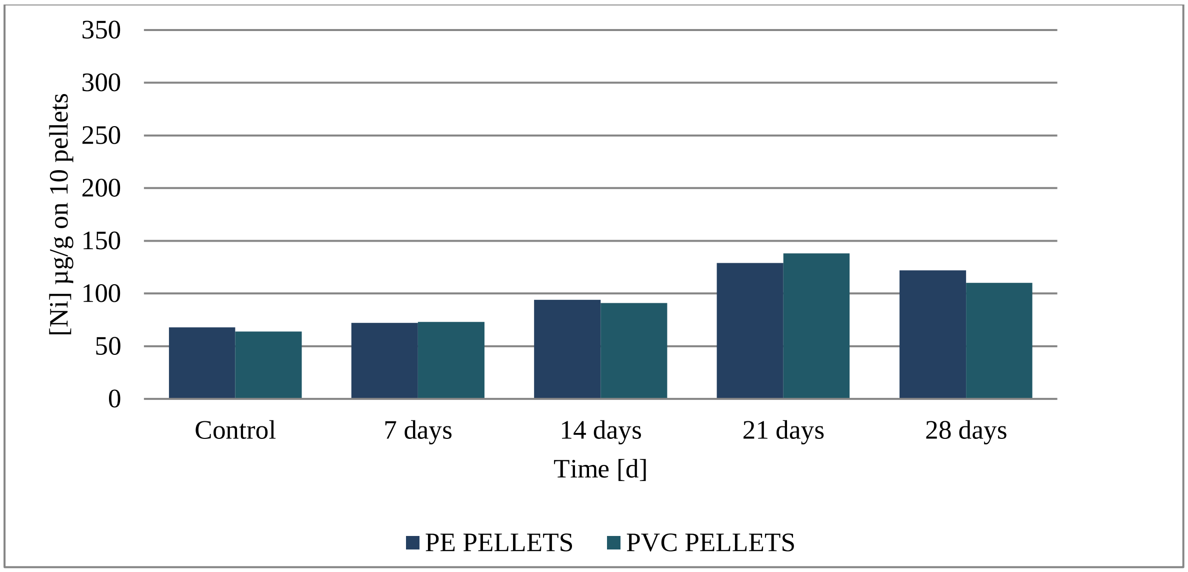


**Figure-1:** Adsorption of Ni on PE and PVC pellets.

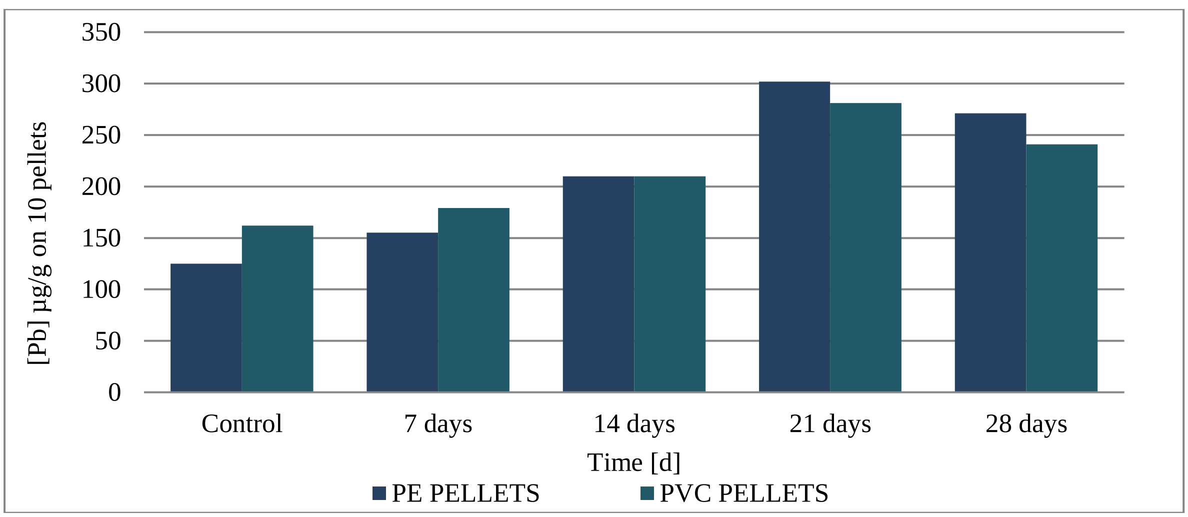


**Figure-2:** Adsorption of Pb on PE and PVC pellets.

Since in this study, we specially considered virgin plastic pellets only, but it has been also observed that the aged (environmentally exposed) pellets adhere more amount of heavy metals over its surface as they are on higher state of degradation which can contribute to high capacity of adsorption[15]. Along with surface area, shape of plastic also plays a major role in determining the plastic adsorption capacity. Toxicity potential of an aquatic system increases; as aquatic organisms ingest such metal adhered micro plastic particles which is not only leads to "pseudo-satiation" but also releases adhered heavy metals into their body. This further leads to bioaccumulation and ultimately biomagnification of these persistent metals[16]. It has been also reported that the adherence and the toxicity effect of plastics on aquatic organisms is not an acute phenomenon but it could have chronic effects depending upon water's metal concentration and the proportion of it been adhered on plastic surface[16].

In our study, it was also observed that adsorption of Pb was more in PE pellets in comparison to PVC pellets. A long-term study conducted in San Diego Bay, USA, examined the metal sorption between five plastic types: Low-Density Polyethylene (LDPE), High-Density Polyethylene (HDPE), Polyethylene Terephthalate (PET), Polyvinyl Chloride (PVC) and Poly-propylene (PP)[12]. Investigated metal concentration in the study showed that the concentration though increased but for metals like Cobalt and Lead for in Polyethylene (PE) plastic type equilibrium was not attained. Concluding the fact that they can adhere more of such metals when exposed for longer duration of time[12].

So, in reference to findings it was observed that heavy metals (Ni and Pb) where adhered on both the plastic type (PVC and PE), and among both of them Pb had shown more affinity towards adherence and most importantly Pb adsorption was significantly greater in Polyethylene (PE) beads than in Polyvinyl Chloride (PVC). Further on the other side, the adsorption of Ni was considerably greater in PVC beads than in PE beads. So, the finding supports the fact which has been already referred by different authors that pellets can represent as an important vehicle for metal transport in the aquatic environment[11].

## Conclusion

Heavy metals and microplastics are two major contributors towards ambient pollution either in water or in soil. Heavy metals have a tendency to get adsorbed or absorbed over any surface either organic or inorganic components leading to bioaccumulation and further biomagnifications. Microplastic on the other side is more persistent as it takes years to degrade so one cannot ignore the fact that microplastic undegraded will continue adsorbing such toxic components and hence transferring it from one place to another and from water or sediment source to ultimately in biological organism. Our study also indicates higher metal adherence capacity of micro plastic particles, further longer duration studies are needed for better understanding the attainment of the equilibrium state and the saturation point of the plastic.

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