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Migrating Levels of Toxic Heavy Metals in Locally Made Food Packaging Containers

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Abstract

Background/Objectives: Earth's crust contains heavy metals as natural ingredients. Heavy metals create a major health problem for the humans because of their persistence, highly toxic nature and tendency to accumulate in the ecosystem. The main aim of this study was to measure the concentration of heavy metals in the locally made food containers at three different temperatures, using various simulating solvents as per guidelines Bureau of Indian standard (BIS), by using Atomic Absorption spectroscopy (AAS).
Methods/Statistical analysis: The estimation of heavy metals such as Cd, Cr, Ni, Cu, Mn, Fe, Pb and Zn of plastic leachates were detected by using Atomic absorption spectrophotometer (AAS). The results were expressed statistically using mean ± standard deviation of triplicate reading of each sample and corresponding control solution. The dunnett comparison were made to assess the level of significance by applying one way analysis of variance (ANOVA) using computer based software 'Graph Pad PRISM-5'.
Findings: The level of migration of heavy metals above the permitted limit was in the following pattern:
• At Elevated Condition (60±2˚C for 2 h):
Pb(1.9-1.002ppm) > Cu(1.61-1.02ppm) > Ni(1.31-1.01ppm) > Zn(1.02-1.006ppm) > Mn(1.01-1.001ppm).
• At Ambient Condition (25±2˚C for 24 h):
Pb(1.9-1.01ppm) > Cu(1.61-1.01ppm) > Ni(1.31-1.01ppm) in S3, S5, S2, S4 > Mn(1.01-1.001ppm) >Zn(1.002ppm). Ni(1.01ppm) > Cu(1.009-1.003ppm) > Pb(1.007ppm) > Zn(1.001ppm).
• At Refrigerated Condition (4±1˚C for 72 h):
Ni(1.01ppm) in S2 > Cu(1.009-1.003ppm) in S4, S5, S2 > Pb(1.007ppm) inS1 > Zn(1.001ppm) in S1.
The results show that the amount of migration of heavy metals from food packaging containers followed the pattern: Elevated condition > Ambient condition > Refrigerated condition.
Novelty/Applications: This research aims to obtain a better understanding of locally made food packaging plastics having no specification of additives and their related potential hazards.
Keywords: Heavy Metals, Migration, Toxicity, Simulating Solvents, food packaging containers.

1. Introduction

Plastics have remarkably resourceful applications and food packaging is one of the most important applications [1]. The use of plastic in packaging of food is mainly due to their low cost, ease of processing and manufacturing. Apart from the basic monomeric units, all plastics contain an additional component known as additive [2]. These additives are usually added to improve physical and chemical properties of plastics. The commonly used additives in most of the plastics are fillers, plasticizers, antiblock agents, antioxidants, lubricants and antistatic agents etc. Each of the additives used has its own distinctive characteristics properties. Generally, food packaging plastics contain low concentrations of metallic compounds [3]. The heavy metals in plastics are present in the form of inorganic pigments, stabilizers and antioxidants etc [4-5].

The additives are present in plastic in high amount and thus make quantification of heavy metals very difficult. Generally, these metals are added to plastics as compounds, which often do not bond chemically to the matrix of the plastic materials and can migrate easily under the influence of physicochemical factors like sunlight, temperature, type of solvents and pH of the stored commodity and liberate toxic substances to

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air, water, food, food stimulants, saliva and sweat etc [5-8]. From various research, it has been reported that the leaching of heavy metals like lead(Pb), nickel(Ni), cadmium(Cd), chromium(Cr),copper(Cu), iron(Fe), manganese(Mn), zinc(Zn) from plastics food packaging can occur into the simulating solvents [9-12]. This can interrupt the normal physiological functions of the body cells and other organs.

Physicians and scientists believed that the no percentage of heavy metals in blood is safe or normal. Also, the exposure to very little amount may have prolonged and significant affects in children, though no characteristics indications are observed at low level exposure [13-28]. In order to safeguard the health of a consumer, the regulation guidelines [29-32] for the suitable use of plastic for food packaging application have been formulated all over the world. Bureau of Indian Standards (BIS) designed the national standards. In this regard, this research was designed to determine the concentration of heavy metals in locally made food packaging containers purchased from various districts of U.P, India.

2. Materials and Methods

In present study, 150 samples of five different brands of plastic food containers of Polyethylene terephthalate (PETE or PET) and Polypropylene (PP) were purchased from various districts of U.P, India and processed in the laboratory. Based on the nature of food, different food simulating solvents are used. All the samples were prepared in different simulating solvents in different temperature time conditions and then analyzed. The details of the simulating conditions are given in the table 1 and table 2.

Table 1: Food categorisation and Food simulants

Standard	Food categorisation	Food simulant
BIS/INDIA	Non-acidic (pH>5),including oil-in-water emulsions of low or high fat content.	Water(W) Double distilled water
	Acidic food (pH<5)	3%(v/v) Acetic Acid solution in double distilled water
	Alcoholic beverages(8% ethanol)	8%(v/v) Ethanol solution in double distilled water
	Saline nature of food	0.9%(w/v) NaCl and 5%(w/v) Na_2CO_3 solution in double distilled water.

Table 2: Time- temperature conditions in global migration tests.

STANDARD	TEST CONDITIONS	REMARKS
BIS/INDIA	a) 4 °C – 72h	Refrigerated condition
	b) 60 °C – 2h	Elevated condition
	c) 25 °C– 24h	Ambient condition

The food containers were washed thoroughly with double distilled water in order to reduce the migration of surface layer chemicals. The food containers were made to cut into 10x5 cm size pieces to expose them adequately to simulating solvents in a ratio of 1cm2 of plastic in 2ml of simulating solvent under various simulated conditions as provided by regulatory agencies.

In this method, 10ml sample solution was taken in a conical flask and digested with 1.0 ml concentrated HNO3. The digested sample was made to 10 ml using 1% HNO3. Parallel sets having simulating solvents (control) only were also prepared under similar conditions and were considered as basal control. The estimation of heavy metals such as Cd, Cr, Ni, Cu, Mn, Fe, Pb and Zn (USP) [33] of plastic leachates were detected by using atomic absorption spectrophotometer (AAS).

2.1. Statistical analysis

The results were expressed statistically using mean ± standard deviation of triplicate reading of each sample and corresponding control solution. The dunnett comparison were made to assess the level of significance by applying one way analysis of variance (ANOVA) using computer based software 'Graph Pad PRISM-5'. The p value less than 0.05 in figures are marked with * and are considered as significant.

3. Results and Discussion

In the production of polymers, including polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), polyethylene terephthalate (PET), polycarbonate (PC), acrylonitrile-butadiene-styrene (ABS) and polyamide (PA), different catalyst are used that can contain low levels of heavy metals. Generally, plastics used for food packaging foods also contain these metals in the form of pigments and stabilizers. The quantification of heavy metals is important because they have the potential to contaminate the food and causes toxicity [34-37]. The migrations of heavy metals in food containers were dependent on temperature as well as simulating solvent. The trend of leaching of heavy metals follows the order :

Elevated condition > Ambient condition > Refrigerated condition

All the samples were found migrating heavy metals in all simulating solvents at three different temperature conditions. Out of which few samples leached heavy metals which were above allowed limit. According to BIS, metal content should not be more than 1ppm except Cd which should not be more than 0.1ppm.

Elevated Condition (60±2˚C for 2 h)

The result shows that all samples were found containing Zn, Ni, Mn, Cu, Cr and Pb in varying concentrations are given in figure 1-5. Cd was not detected in any sample. The concentration of heavy metals above permissible limit shown in the table 3.

Table-3 Migrating concentration of heavy metal above permissible limit in different simulating solvent.

Simulating solvents	Heavy metals (concentration in parts per million (ppm))				
	Pb	Cu	Ni	Zn	Mn
Double distilled water	1.9	1.02	1.31-1.21	-	1.008-1.001
3% Acetic acid	1.2-1.002	1.61	1.102-1.006	1.02	-
8%Ethanol	1.029	1.36-1.02			
0.9% Sodium chloride		1.30	1.08	1.006	1.01
5% Sodium carbonate	1.1-1.04		1.02		

The differences were significant between mean concentrations of metals in different food container samples using the above mentioned simulating solvents.

•The result also shows that higher level of migration of heavy metals above allowed limit follows the pattern:

Pb(1.9-1.002ppm) in S1, S3, S5, S1, S2 > Cu(1.61-1.02ppm) in S5,S4,S3 > Ni(1.31-1.006ppm) in S4,S3,S2,S5,S4 > Zn(1.02-1.006ppm) in S2,S4 > Mn(1.01-1.001ppm) in S5,S2,S3.

Ambient Condition (25±2˚C for 24 h)

The result shows that all samples were found containing Zn, Ni, Mn, Cu, Cr, Cd and Pb in varying concentrations is given in Figure 6-10. The concentration of heavy metals above permissible limit shown in the table 4.

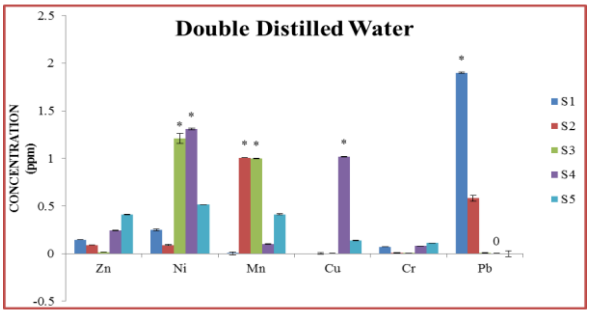


Figure-1 The concentration of metals (ppm) in double distilled water at 60±2˚C for 2 h.

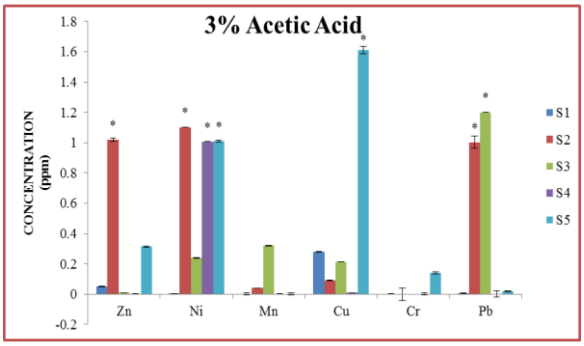


Figure-2 The concentration of metals (ppm) in 3% acetic acid at 60±2˚C for 2 h.

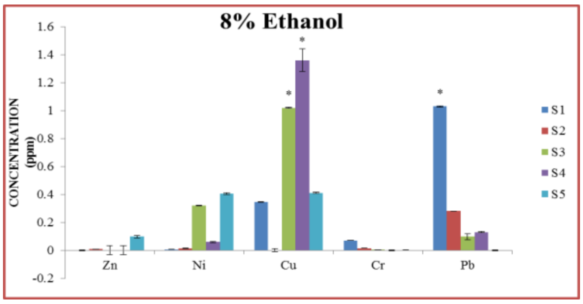


Figure-3 The concentration of metals (ppm) in 8% ethanol at 60±2˚C for 2 h.

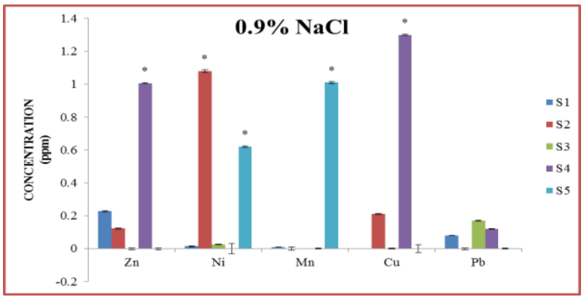
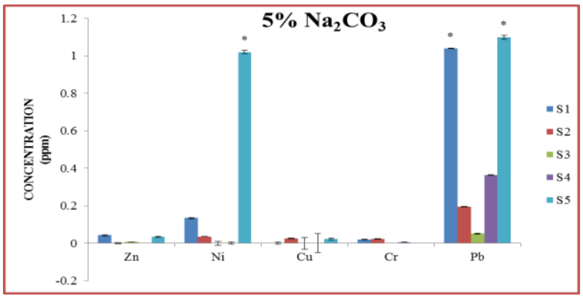


Figure-4 The concentration of metals (ppm) in 0.9% NaCl at 60±2˚C for 2 h.



Figure–5 The concentration of metals (ppm) in 5% Na2CO3 at 60±2˚C for 2 h.

Table-4 Migrating concentration of heavy metal above permissible limit in different simulating solvent.

Simulating solvents	Heavy metals (concentration in parts per million (ppm))				
	Pb	Cu	Ni	Zn	Mn
Double distilled water	1.9	1.02	1.31-1.21	-	1.01-1.001
3% Acetic acid		1.61-1.30	1.01		-
8%Ethanol	1.2		1.102	1.002	
0.9% Sodium chloride	1.029	1.36			1.01
5% Sodium carbonate	1.04-1.01	1.02	1.02		

The differences were significant between mean concentrations of metals in different food container samples using the above mentioned simulating solvents.

Thus, the result shows that higher level of migration of heavy metals above allowed limit follows the pattern:

Pb(1.9-1.01ppm) in S1, S3, S5, S1 >
Cu(1.61-1.02ppm) in S4, S3, S5 >
Ni(1.31-1.01ppm) in S3, S5, S2, S4 >
Mn(1.01-1.001ppm) in S2, S4, S5 >
Zn(1.002ppm) in S2.

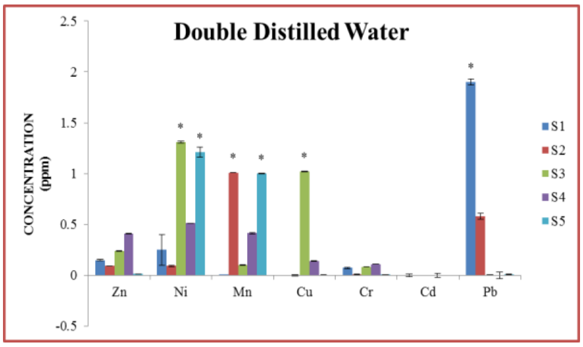


Figure-6 The concentration of metals (ppm) in double distilled water at 25±2˚C for 24 h.

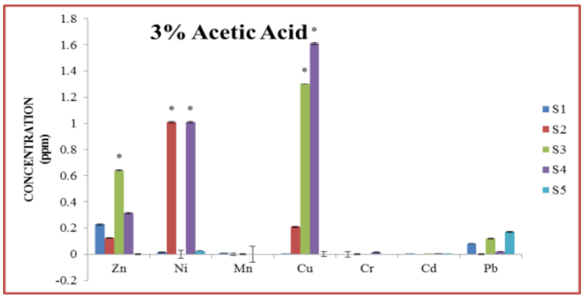


Figure-7 The concentration of metals (ppm) in 3% acetic acid at 25±2˚C for 24 h.

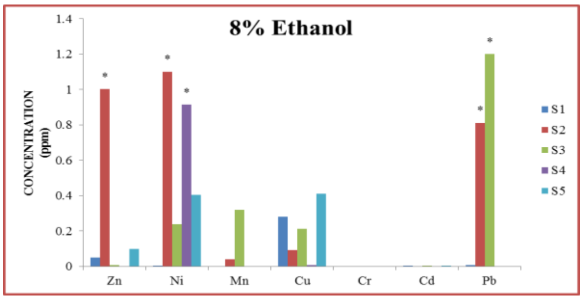


Figure-8 The concentration of metals (ppm) in 8% ethanol at 25±2˚C for 24 h.

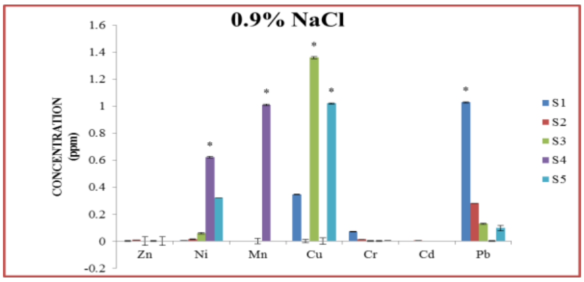


Figure-9 The concentration of metals (ppm) in 0.9% NaCl at 25±2˚C for 24 h.

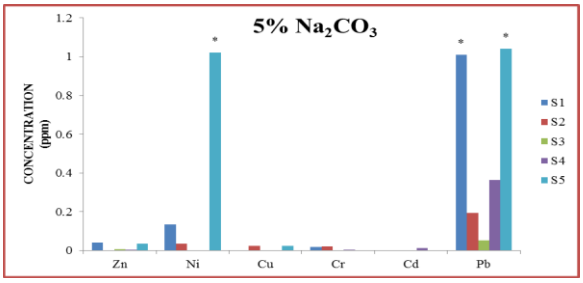


Figure-10 The concentration of metals (ppm) in 5% Na2CO3 at 25±2˚C for 24 h.

At Refrigerated Condition (4±1˚C for 72 h)

The result shows that all samples were found containing Zn, Ni, Mn, Cu, Cr and Pb in varying concentrations are given in Figure 11-15. The concentration of heavy metals above permissible limit shown in the table 5.

Table-5 Migrating concentration of heavy metal above permissible limit in different simulating solvent.

Simulating solvents	**Heavy metals (concentration in parts per million (ppm))**				
	Pb	**Cu**	**Ni**	**Zn**	**Mn**
Double distilled water	1.007	1.008	1.01	-	1.003-1.002
3% Acetic acid		1.009-1.007		1.001	-
8%Ethanol					
0.9% Sodium chloride		1.009-1.003			
5% Sodium carbonate					

The differences were significant between mean concentrations of metals in different food container samples using the above mentioned simulating solvents.

Thus, the result shows that higher level of migration of heavy metals above allowed limit follows the pattern:

Ni(1.01ppm) in S2 > Cu(1.009-1.003ppm) in S4, S5, S2 > Pb(1.007ppm) in S1 > Mn (1.003 – 1.002) in S3, S4 > Zn(1.001ppm) in S1.

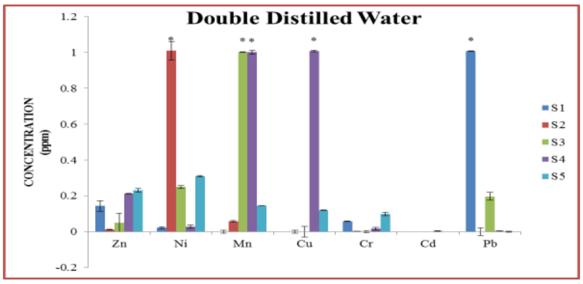


Figure-11 The concentration of metals (ppm) in double distilled water at 4±1˚C for 72 h.

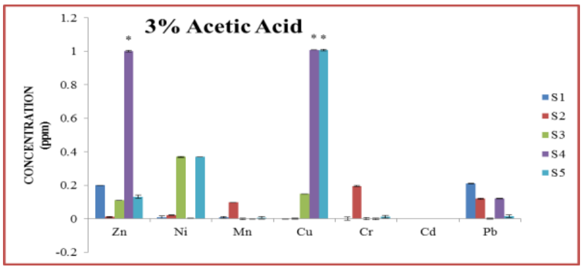


Figure-12 The concentration of metals (ppm) in 3% acetic acid at 4±1˚C for 72 h.

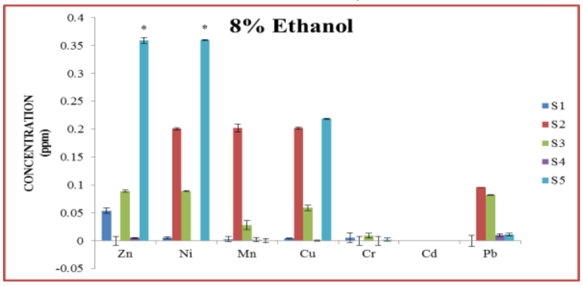


Figure-13 The concentration of metals (ppm) in 8% ethanol at 4±1˚C for 72 h.

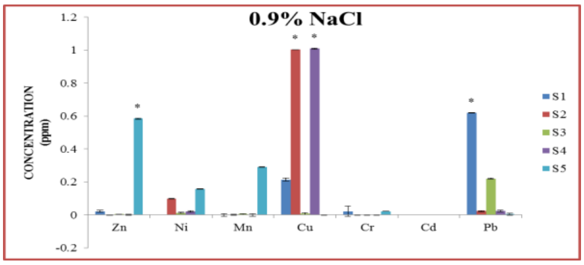


Figure-14 The concentration of metals (ppm) in 0.9% NaCl at 4±1˚C for 72 h.

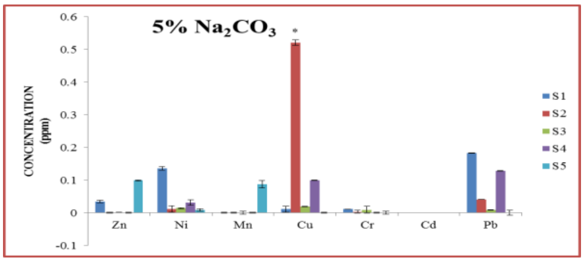


Figure-15 The concentration of metals (ppm) in 5% Na_2CO_3 at 4±1˚C for 72 h.

Table-6 Migration level of heavy metals in different temperature-time condition.

Metals	**Migration concentration at Elevated condition**	**Migration concentration at Ambient condition**	**Migration concentration at Refrigerated condition**
Pb	1.9-1.002ppm	1.9-1.01ppm	1.007ppm
Cu	1.61-1.02ppm	1.61-1.02ppm	1.009-1.003ppm
Ni	1.31-1.006ppm	1.31-1.01ppm	1.01ppm
Zn	1.02-1.006ppm	1.002ppm	1.001ppm
Mn	1.01-1.002ppm	1.01-1.002ppm	1.008-1.002ppm

From the results, it was also concluded that the migrations of heavy metals from food packaging container follows the pattern: Pb > Cu > Ni > Zn > Mn. Moreover, it was also concluded that maximum percentage of migration occur at elevated condition than ambient condition and least at refrigerated condition.

4. Conclusion

From the results, it was concluded that all the samples were found containing Zn, Ni, Mn, Cu, Cr and Pb in varying concentrations. Out of which most of the samples contain heavy metals above allowed limit. According to IS, metal content should not be more than 1ppm except Cd should not be more than 0.1 ppm.

The concentration of Pb, Cu, Ni, Zn and Mn above allowed limit in all simulating solvents at three different temperature-time conditions ranges from 1.9 ppm- 1.002ppm. The following Table-6 show the level of migration of heavy metals at different temperature-time condition.

5. Acknowledgement

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