Masterton H[1]*, O Pantos[1], J Bridson[2], G Northcott[3] and S Gaw[4]

[1]ESR, Christchurch Science Centre, 27 Creyke Road, Ilam, Christchurch 8041, New Zealand
[2]Scion, Te Papa Tipu Innovation Park, Rotorua, New Zealand
[3]Northcott Research Consultants Limited, 20 River Oaks Place, Hamilton 3200, New Zealand
[4]University of Canterbury, 20 Kirkwood Avenue, Upper Riccarton, Christchurch 8041, New Zealand

***Email: hayden.masterton@esr.cri.nz**

Bioaccessibility of Trace Elements Association with Beached Plastic Debris in New Zealand

Introduction

Plastic debris is present on nearly all New Zealand beaches, from remote locations to highly populated locations. This widespread distribution is of great concern due to the potential impacts on the environment. Potentially toxic trace elements are either inherent (as additives), or acquired (accumulated from the environment) in plastics. Recently published international studies have reported elevated concentrations of toxic trace elements on beached plastic debris. While in the environment this plastic may be ingested by organisms and lead to the release of these toxic trace elements into their digestive tracts.

This study aimed to determine the concentration and bioaccessibility of trace elements associated with beached plastic debris in New Zealand

Objectives

- **Determine trace element concentration associated with beached plastic debris from multiple sites around New Zealand**
- **Determine bioaccessibility of trace elements from commonly collected beached plastic debris**

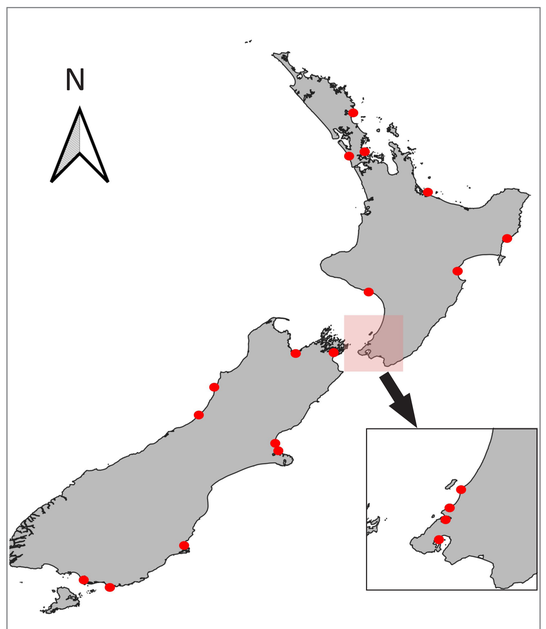

Figure 1. Location of the 20 different beaches sampled for beached plastic debris around New Zealand

Materials and Methods

- Collection of visible plastics from 10 x 50 m transects placed along the high tide mark of 20 beaches around New Zealand by citizen scientists (Figure 1).
- Each piece of plastic debris was rinsed with artifical seawater, dried, and characterised by length, weight, colour and polymer type by FTIR-ATR.
- Only samples greater than 2 g were analysed for trace element content.
- Samples were acid digested, diluted and analysed by ICP-MS for 20 trace elements (As, Au, Ba, Cd, Ce, Co, Cr, Cs, Cu, Hg, Mn, Mo, Ni, Pb, Pd, Pt, Sb, Sn, Sr, Zn).
- Two items commonly collected, lollipop sticks and firework casings, were used to assess trace element bioaccessibility from plastics. Brand new lollipop sticks were also used as a comparsion.
- Sections of each item was added to the two gastric fluid simulants, one for marine vertebrates and one for marine invertebrates, as well as a seawater control. These were then incubated to simulate the gastric conditions of marine vertebrates (24°C for 12 hours) and invertebrates (18°C for 6 hours) at 150 RPM.
- Samples were then diluted and analysed by ICP-MS for the same 20 elements.

Results

From the 20 sites a total of 957 pieces of plastic debris were collected. The average density of plastic was 0.1 items/m^2 with a maximum of 0.62 items/m^2.

- From the 957 plastic items, the dominant polymer types were PP > PE > PS > PET > PVC and the dominant colour was white (Figure 2). Proportions were similar for the subset used for trace element analysis.

Table 1. Mean and maximum concentration and detection frequency for each element in the beached plastic debris.

Element	Mean (mg/kg)	Maximum (mg/kg)	Samples detected
As	2.8	84.2	68
Ba	139.7	2532	155
Cd	182.3	1877	37
Ce	0.8	9.4	153
Co	1.8	46.2	66
Cr	35.1	454.1	32
Cs	0.3	1.4	26
Cu	23.7	594.5	137
Hg	6.3	13.4	5
Mo	5.8	179.1	36
Ni	1.0	11.0	141
Pb	96.7	4886.8	139
Sb	4.2	58.6	34
Zn	652.3	19674	126

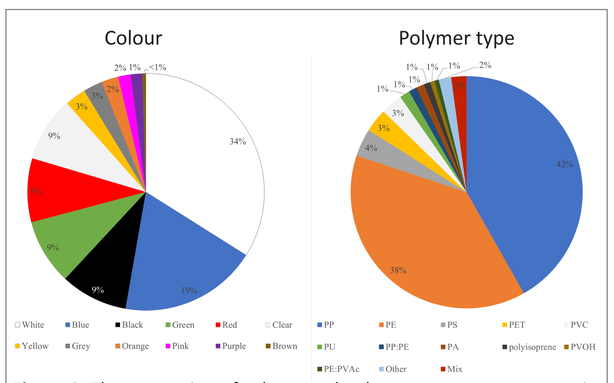

Figure 2. The proportion of colours and polymer types were present in the 957 pieces of plastic debris collected from around New Zealand

- 14 of the 20 trace elements were detected in the beached debris plastics.
- Detection frequencies followed the trend Ba > Ce > Ni > Pb > Cu > Zn > As > Co > Cd > Mo > Sb > Cr > Cs > Hg (Table 1).
- Mean concentrations followed the trend Zn > Cd > Ba > Pb > Cr > Cu > Hg > Mo > Sb > As > Co > Ni > Ce > Cs (Table 1).
- Significant correlations between Cr:Mo, Cr:Sb, Mo:Pb, Mo:Sb and Pb:Sb were identified (Table 2).
- Significantly higher concentrations of Cd, Cr, Mo and Sb in red debris compared to other colours, as well as Ce in orange and Cu in grey pieces of debris compred to all other colours.
- No signficant differences between other varibles such as polymer type, population density, individual sites, and geographical variations.

Table 2. Correlations between different trace elements within individual items. undertaken using Pearson's correlation.

Trace element	Cd	Ce	Cr	Mo	Pb	Sb
Cd	1	0.15	0.18	0.12	0.1	0.11
Ce		1	0.0021	0.037	0.065	0.012
Cr			1	0.96	0.66	0.96
Mo				1	0.97	0.98
Pb					1	0.97
Sb						1

Table 3. Trace element concentrations present in beached lollipop sticks, firework casings and new lollipop sticks.
ND - not detected

Trace element, mean ± standard deviation (mg/kg)	New lollipop sticks	Beached lollipop sticks	Firework casings
As	ND	0.1	2.7 ± 0.3
Ba	148.9 ± 37.7	10.3 ± 13.0	880.3 ± 143.7
Cd	ND	ND	1.4 ± 0.2
Ce	ND	0.3 ± 0.06	2.2 ± 0.3
Co	ND	ND	1.3 ± 0.2
Cr	ND	ND	18.3 ± 8.2
Cs	ND	ND	0.2 ± 0.03
Cu	0.9	0.3 ± 008	237.8 ± 123.9
Mn	ND	2.4 ± 0.8	45.4 ± 3.5
Mo	ND	ND	0.9 ± 0.2
Ni	0.3	0.1 ± 0.02	3.1 ± 0.3
Pb	ND	0.3 ± 0.1	43 ± 6.2
Sb	ND	ND	1.2 ± 0.08
Zn	80.9 ± 19.3	15.9 ± 4.4	108.5 ± 13.4

- Firework casings had the highest concentration and widest range of trace elements present. While beached lollipop sticks had a wider range of trace elements than new lollipop sticks (Table 3).
- The release of these trace elements in gastric simulants followed the order vertebrate > invertebrate > seawater, with the exceptions of Ba, Ni and Zn which demonstrated the order of release, invertebrate > vertebrate > seawater (Figure 3).
- Of trace elements present in lollipop sticks and firework casings, a higher proportion was bioaccessible from the lollipop sticks (Figure 3).

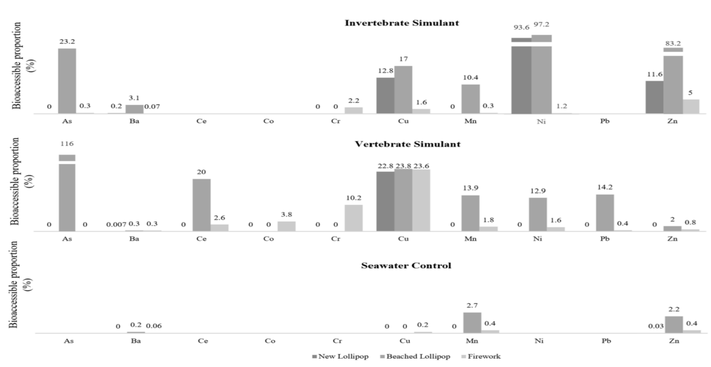

Figure 3. Proportion of each trace element made bioaccessible from beached lollipop sticks, firework casings and new lollipop sticks in a marine vertebrate, invertebrate gastric simulant as well as seawater.

Discussion and Conclusions

- Average density of plastic debris from this study was similar to another New Zealand study, but lower than international studies.
- Trace element concentrations were comparible to similar international studies. However, there were higher detection frequencies of elements in our study, likely due to lower detection limits in our method.
- The correlations between Cr:Mo, Cr:Sb, Mo:Pb, Mo:Sb and Pb:Sb is due to their use as red pigments or in mixtures for red pigments. Concentrations of Cd, Cr, Mo and Sb in red items compared to other colours. Common inorganic red pigments containing these elements are, CdS, CdSe, $Pb_3(SbO_4)_2$, $PbMoO_4$, and $PbCrO_4$.
- Signficantly higher concentrations of Ce in orange items may be due to the use of the pigment Ce_2S_3. With higher concentrations of Cu in grey items due to the complex mixture of pigments used to create grey, a hard colour to make, one of which is blue/green pigments containing Cu.
- Pigments are the cause of high concentrations of some trace elements (Cd, Cr, Cu, Mo, Pb and Sb). Therefore, the intentional addition of toxic trace elements to plastic during productions is likely of greater concern than those that adsorb to the plastics while in the environment.
- The bioaccessibility study demonstrated that trace elements are not bound to the polymer matrix and are bioaccessible to the organisms that ingest plastic items.

Acknowledgements

We wish to acknowledge the team at Sustainable Coastlines, especially Ben Knight, who through their litter intelligence program were able to collect beached debris from multiple sites around New Zealand with citizen scientists. The many technical staff at the University of Canterbury for their help in many different ways. This study was supported by the Aotearoa Impacts and Mitigation of Microplastics (AIM2) project (Ministry of Business, Innovation, and Employment, New Zealand, Endeavour Fund C03X1802).