



## An investigation of heavy metal content from disposable batteries of non-U.S. origin from Butler County, Ohio: An environmental assessment of a segment of a waste stream

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### ABSTRACT

A sample set of 50 AA size disposable batteries, dominantly from China and other non-U.S. sources were investigated to assess the nature of heavy metal concentrations to determine if such batteries are of environmental concern. Inductively coupled plasma-mass spectrometry investigation indicates that all batteries analysed contain Ni, Cu, As, Sr, and Ba and most of the batteries have detectable quantities of Pb (92%), Cr (88%) and Co (88%). Roughly half of the batteries analyzed contain detectable quantities of Hg (52%) and V (56%). Tl occurs in 64% of batteries but at very low concentrations (0.1–1.1 ppm). Cd and Se were less common occurring in only 8% and 12% of batteries respectively. Some samples are arguably low in heavy metal content with 28% of the batteries having a sum of less than 100 ppm of the analyzed metals. The origin of the heavy metal concentrations is interpreted to be largely from original geologic sources of material. Scanning electron microscopy indicates that heavy metals are largely in solid solution in the phases in the battery materials and rarely exist as discrete particulate materials and suggests that mechanical separation of heavy metals for recycling purposes is therefore not feasible.

Although batteries from several sources have heavy metal concentrations of concern, batteries from China are generally characterized by having relatively high heavy metal content. These products are introduced into waste streams in countries where respective domestic manufacturers must meet a much higher environmental standard. Results of this study suggest an environmental global standard should be developed and the data presented here may serve as a reference for development of such a standard. The use of cleaner geologic source materials and manufacturing activities is suggested.

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### 1. Introduction

Disposable batteries are a major source of heavy metals in household waste streams globally. Heavy metal content in batteries arises from both manufacturing processes intentionally adding heavy metals for performance reasons and also potentially by unintentional inclusion via geologic sources of raw materials. Although well recognized as a source of heavy metals, there are comparatively few detailed studies that investigate the variation in elemental composition of these batteries. Although batteries produced in the United States are to be mercury free according to the Mercury-containing and Rechargeable Battery Management Act passed in 1996, a significant influx of batteries that are not of U.S.

origin are imported and are disposed of within the U.S. The mercury content and other heavy metal content of such batteries is not well characterized.

Heavy metal content is also a point of interest with respect to developing recycling of disposable batteries. Methods for recycling some battery technologies exist and some of these approaches are well established [1–8]. Specific methods exist for recycling spent alkaline batteries [9–15], however these are often not widely adopted owing to the very energy or material intensive nature of these processes or a lack of infrastructure or market for materials. Most methods of recycling spent alkaline batteries appear to be too costly to enable wide implementation. In addition to basic economic barriers, one specific challenge in spent alkaline battery recycling is that heavy metal content in these batteries are variable and when present may limit recycling potential both technically and from the perspective of being an environmental hazard. Complicating this issue is that some battery manufacturers adhere

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closely to European and U.S. regulations requiring no mercury, while manufacturers based in other countries or regions do not adhere to such regulations.

Fundamentally disposable alkaline batteries consist of two distinct parts, an anode and a cathode which are separated by a permeable membrane. The anodic region typically is composed of un-reacted metallic zinc, as well as an electrolyte solution which is commonly a KOH solution, gelling agents, and of course ionic zinc which accumulates during discharge of a battery. Electrolytic manganese dioxide (EMD) composes the cathode and is reported to consist of  $\text{MnO}_2$  (such as ramsdellite) and other manganese oxide or oxyhydroxide compounds including but not limited to  $\text{MnO}$ ,  $\text{Mn}(\text{OH})_2$ ,  $\text{Mn}_2\text{O}_3$  as well as aqueous ions [14,15]. Other investigations have investigated the inorganic phases that comprise EMD using Rietveld refinement techniques and transmission electron microscopy and found that  $\gamma\text{-MnO}_2$  and  $\varepsilon\text{-MnO}_2$  forms dominate with lesser amounts of  $\beta\text{-MnO}_2$  occurring [16].

Improvements in the recycling of alkaline batteries are clearly needed to make the processes more agreeable with pollution prevention protocols and also more profitable in general. In addition to identifying low energy and low material consuming processes, screening of environmental properties such as heavy metal content is greatly needed. If battery types can be identified with certainty as being environmentally hazardous, those may be rejected for recycling.

## 2. Materials and methods

Fifty disposable AA size batteries representing 27 labeled brands not of U.S. origin were investigated. These batteries were obtained from a battery recycling collection facility operated by Butler County Ohio in July 2010. Sample preparation and analytical work was carried out at Miami University. Battery samples were prepared by first carefully cutting a 1 cm section from each battery perpendicular to the length at the negative end with a Dremel tool utilizing a carborundum grinding wheel. The resulting plug of cathode and anode portions was then carefully cleaned by hand to prevent contamination from the metal casing. This plug of cathode and anode material was then homogenized and used for inductively coupled plasma-mass spectrometry (ICP-MS) work. This sampling strategy was selected because metals can migrate during discharge of a battery and the composition of casings (metals) is better defined. Selected samples had additional plugs cut for field emission scanning electron microscopy (FESEM) work.

For FESEM work, carbon adhesive tabs were used to mount sample material on aluminum stubs. FESEM investigation was done with variable pressure Zeiss Supra 35VP FEG using nitrogen ( $\text{N}_2$ ) as the compensating gas. The instrument is equipped with a backscatter detector (BSD) and an energy dispersive spectrometry (EDS) detector EDAX2000 that has a detection limit of approximately 0.1 wt% for most elements.

Fifty representative batteries that previously had been cut, dried and crushed were prepared for inductively coupled plasma-mass spectrometry (ICP-MS) analysis by weighing out  $\sim 100$  mg of sample material into 30 ml Savillex teflon beakers to which was added 2 ml of twice distilled 70%  $\text{HNO}_3$ . These were tightly capped and placed on a fume hood hot plate at  $120^\circ\text{C}$  for one week. The entire contents of each were then transferred into 125 ml polypropylene bottles and diluted to 125 ml using distilled water made from a sub-boiling quartz still. Bottles and caps were pre-cleaned by rinsing in 1:1  $\text{HNO}_3$  acid, followed by a rinse with  $18.2\text{M}\Omega\text{-cm}$  deionized water, and then dried in an oven at  $60^\circ\text{C}$ . External calibration standards were made from  $10\ \mu\text{g ml}^{-1}$  solution standards purchased from Inorganic Ventures which were diluted to 500, 50, and  $5\ \text{ng ml}^{-1}$  using 1% nitric acid. A 100 ppb solution of Ge, In, Re,

and Bi was used for internal standardization. Five replicates of 20 readings each were averaged for each analytical solution.

## 3. Results

### 3.1. Inductively coupled plasma-mass spectrometry

ICP-MS analysis indicates that a variety of metals are detected in the batteries and results are reported in Table 1. Ni, Cu, As, Sr, Ba occur in all of the batteries analyzed. Most of the batteries have detectable quantities of Pb (92%), Cr (88%) and Co (88%). Approximately half of the batteries analyzed contained detectable quantities of Hg (52%) and V (56%). Tl occurs in 64% of batteries but at very low concentrations (0.1–1.1 ppm). Cd and Se were less common occurring in 8% and 12% of batteries respectively. With respect to total heavy metal content not all batteries were equal (Table 1) and some arguably are low in overall heavy metal content with 28% of the batteries having a sum of less than 100 ppm of the analyzed metals.

Multiple batteries of randomly selected brands were analyzed to ascertain if brands had distinctive elemental compositions. Some batteries of the same labeled brand show significant variation in elemental composition. For example four of the large brand batteries have only a few ppm of Ba and three have several thousand ppm of Ba. Similarly Pb content in High-Watt batteries varies from 0.2 ppm to 739.5 ppm. Other batteries have more consistent elemental compositions such as GP (Gold Peak) Green Cell Extra Heavy Duty (comparatively high transition metals, Ba and Pb), Sun beam mighty cell (low Ba and low Pb) and a battery consistently but ambiguously labeled (High Ba, Low Pb, moderate Sr). Toceba brand batteries are noted for the high levels of Cd compared to other brands in the study.

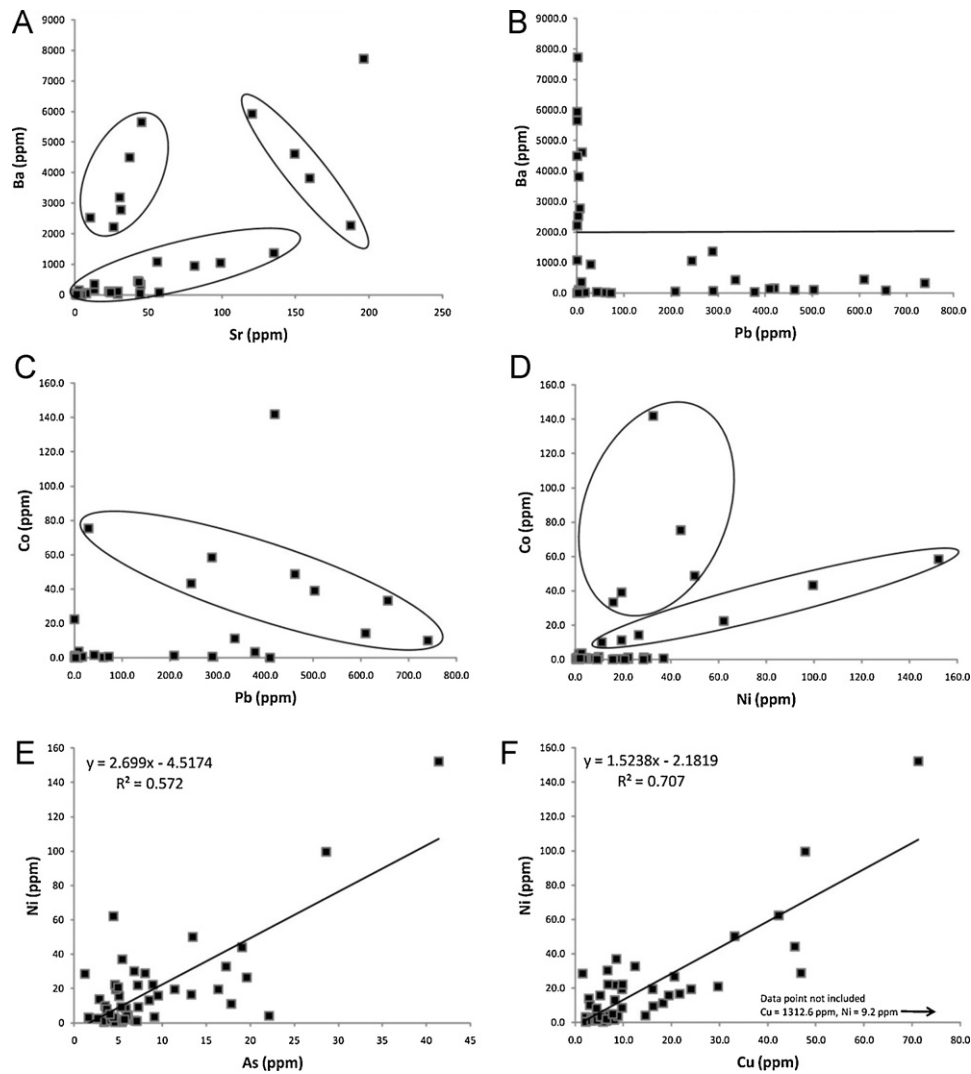
Observation of trends in the elemental concentration data are limited by of course the sample size and the fact that not all elements are present in each battery above the detection limit. Owing to these issues an extensive meaningful statistical analysis is difficult and may lead to problematic interpretation without (an unattainable) context such as knowledge of source materials, treatment and manufacturing processes and other unknown complicating factors. Simple statistics and qualitative groupings show some trends in the data of interest (Fig. 1). There are a few groups of analyses that can be delineated based on X–Y plots of Ba and Sr concentrations. There are two broad populations of high Ba and low Pb, and moderate or low Ba and high Pb. A few populations can be identified based on simple X–Y plots of Co and Pb and Co and Ni. Modest correlations of Ni and As ( $r^2 = 0.572$ ) and Ni and Cu ( $r^2 = 0.707$ ) are observed.

### 3.2. Scanning electron microscopy (SEM)

Sample material from both anodic and cathodic regions was investigated using BSD mode SEM. Although this investigation indicated several regions where Zn had concentrated and precipitated in Mn-oxide cathodic material as hetaerolite, discrete heavy metal bearing particles are not common or abundant (Fig. 2). Only one (sample 55.04) of several batteries that were investigated using BSD mode SEM had discernable heavy metal particles that are a Fe–Ni–Cr alloy which are embedded in the carbon rod portion of the battery (Fig. 3). These particles are irregular in texture and are approximately 1–10  $\mu\text{m}$  in maximum diameter. The cathode material had no such particles and the Fe–Ni–Cr alloy appears to be an impurity in the carbon rod. The sample was carefully separated and clean surface material was broken before SEM study and the Fe–Ni–Cr particulate is interpreted as originating from the manufacturing process.

**Table 1**  
Concentrations of elements analyzed by ICP-MS for samples.

Brand as labeled	Origin	Sample	V, ppm	Cr, ppm	Co, ppm	Ni, ppm	Cu, ppm	As, ppm	Se, ppm	Sr, ppm	Cd, ppm	Sb, ppm	Ba, ppm	Hg, ppm	Tl, ppm	Pb, ppm
Phillips long life	China	3	0.2	1.9	1.0	2.8	3.1	4.6	b.d.	23.2	b.d.	0.7	111.0	0.1	0.1	3.8
High Power Heavy Duty	Not available	4	4.1	3.6	0.8	4.1	14.6	22.1	0.5	57.5	b.d.	1.0	74.0	0.2	0.5	289.1
Ignite	China	7	1.5	3.5	142.0	32.7	12.5	17.2	b.d.	13.1	b.d.	1.3	157.2	b.d.	0.7	419.5
Fujitsu	Indonesia	11	0.2	0.8	1.2	2.0	3.0	4.7	3.6	4.6	b.d.	0.4	39.9	0.1	0.1	2.7
PowerFuel	China	13	0.2	1.3	3.4	1.5	8.1	6.9	b.d.	44.4	b.d.	0.1	36.9	b.d.	0.4	378.0
Winners Extra Heavy Duty	China	15	b.d.	b.d.	0.3	21.8	8.5	7.2	b.d.	29.2	12.3	b.d.	21.3	b.d.	b.d.	61.2
Power.com	China	17	0.3	1.6	0.2	8.4	9.8	5.9	b.d.	149.5	b.d.	0.1	4621.3	b.d.	0.3	10.2
Toshiba	Not available	23	0.1	0.7	0.9	4.5	6.2	6.1	b.d.	1.7	b.d.	b.d.	0.9	b.d.	0.8	3.7
Maxcell Alkaline	China	24	b.d.	2.1	0.3	16.6	21.7	13.3	b.d.	31.3	b.d.	b.d.	2780.7	b.d.	0.4	5.7
Maxcell SuperPower Ace	Not available	25	b.d.	b.d.	b.d.	3.2	2.2	1.6	b.d.	4.4	b.d.	b.d.	9.2	b.d.	b.d.	b.d.
Vivitar	China	27	b.d.	1.2	b.d.	2.1	3.4	3.2	0.3	2.1	b.d.	b.d.	2.7	b.d.	b.d.	0.5
Maxcell Alkaline Ace	Japan	28	b.d.	1.2	0.6	37.0	8.5	5.4	b.d.	1.1	b.d.	b.d.	6.4	0.1	0.3	72.3
Dishy	China	29	b.d.	b.d.	b.d.	13.9	2.8	2.9	b.d.	187.7	b.d.	b.d.	2273.3	0.1	0.1	b.d.
Super Power Heavy Duty	China	30	b.d.	0.9	0.1	0.5	6.0	5.4	1.5	2.9	b.d.	0.1	138.2	0.1	0.3	410.0
Universal Electronics	China	33	b.d.	0.6	0.3	0.4	2.2	3.4	b.d.	1.1	b.d.	b.d.	43.7	0.3	b.d.	7.8
Phillips long life	China	35	0.2	0.6	1.4	1.0	6.6	7.1	b.d.	7.2	b.d.	0.6	54.1	0.1	0.4	209.2
HW Alkaline	Not available	38	0.1	3.5	0.6	3.5	8.9	9.1	b.d.	3.7	b.d.	b.d.	2.1	b.d.	0.3	6.8
Everready Super Heavy Duty	Singapore	41	0.2	1.0	1.4	9.9	3.1	3.5	b.d.	7.5	b.d.	0.2	43.3	0.1	b.d.	42.0
Mitsubishi	China	43	b.d.	0.9	3.8	2.7	4.8	2.7	2.4	13.2	b.d.	0.1	355.9	0.1	0.1	9.3
Panasonic Industrial Alkaline	Japan	44.12	0.2	1.6	0.1	15.6	5.2	5.1	b.d.	0.8	b.d.	b.d.	1.6	0.1	0.5	3.3
Panasonic Industrial Alkaline	Japan	44.15	b.d.	0.1	b.d.	13.1	8.3	8.5	b.d.	1.6	b.d.	b.d.	5.3	0.1	b.d.	1.6
Chaobei	China	47.01	b.d.	1.2	1.1	28.8	47.0	8.0	b.d.	4.0	b.d.	b.d.	3.2	0.1	b.d.	1.3
No clear label	China	50.02	b.d.	0.2	0.3	19.4	9.7	4.7	b.d.	30.5	b.d.	b.d.	3197.0	1.2	b.d.	b.d.
No clear label	China	50.03	b.d.	0.7	0.5	30.1	6.8	6.8	b.d.	10.5	b.d.	b.d.	2527.4	0.5	b.d.	2.4
No clear label	China	50.04	b.d.	0.8	0.3	5.1	4.4	3.7	2.7	37.4	b.d.	b.d.	4490.5	0.1	b.d.	0.3
No clear label	China	50.05	b.d.	b.d.	0.3	4.1	6.5	6.0	b.d.	26.3	b.d.	b.d.	2220.7	b.d.	0.1	0.4
No clear label	China	50.07	b.d.	0.5	0.5	8.2	4.4	3.7	2.4	45.5	b.d.	b.d.	5649.6	0.1	b.d.	0.4
Sun Beam Mighycell	Canada	53.01	0.1	1.0	0.3	1.1	3.4	3.5	b.d.	2.1	b.d.	0.3	22.7	b.d.	0.2	4.8
Sun Beam Mighycell	Canada	53.02	0.1	1.3	0.1	1.6	4.1	4.1	b.d.	1.4	b.d.	0.2	14.4	b.d.	0.2	4.5
Sun Beam Mighycell	Canada	53.03	b.d.	0.2	0.1	28.5	1.6	1.2	b.d.	0.6	b.d.	b.d.	6.5	0.1	b.d.	6.6
Sun Beam Mighycell	Canada	53.04	0.2	1.1	0.6	0.4	5.7	4.6	b.d.	2.2	b.d.	0.5	23.4	b.d.	0.2	15.8
Sun Beam Mighycell	Canada	53.05	0.1	1.5	0.6	1.2	4.5	5.5	b.d.	2.4	b.d.	0.5	26.6	0.3	b.d.	16.9
Large	China	54.01	0.1	2.0	0.2	22.2	6.8	4.6	b.d.	4.5	b.d.	0.1	2.0	b.d.	0.1	1.1
Large	China	54.02	b.d.	0.6	b.d.	9.3	16.2	5.3	b.d.	1.7	b.d.	b.d.	0.5	b.d.	b.d.	0.4
Large	China	54.03	b.d.	3.6	0.2	9.2	1312.6	7.3	b.d.	2.8	b.d.	b.d.	3.2	b.d.	0.1	1.6
Large	China	54.04	b.d.	b.d.	0.2	3.3	5.3	4.4	b.d.	120.5	b.d.	b.d.	5933.1	b.d.	b.d.	0.1
Large	China	54.05	b.d.	0.7	1.4	22.2	9.9	8.9	b.d.	196.4	b.d.	b.d.	7722.2	b.d.	0.1	1.4
Large	China	54.06	0.4	1.8	0.7	2.0	6.5	5.7	0.6	159.9	b.d.	b.d.	3810.2	0.1	0.8	4.1
Large	China	54.07	b.d.	b.d.	b.d.	4.9	7.8	4.0	b.d.	1.2	b.d.	b.d.	0.3	b.d.	b.d.	b.d.
High-Watt	Not available	55.03	13.8	6.8	75.5	44.1	45.7	19.0	b.d.	81.5	b.d.	0.7	936.0	0.1	1.0	29.2
High-Watt	Not available	55.04	0.1	0.2	22.5	62.3	42.3	4.5	b.d.	56.2	1.7	b.d.	1073.8	0.3	b.d.	0.2
High-Watt	Not available	55.05	2.5	1.3	9.9	11.1	18.3	17.8	b.d.	44.7	b.d.	0.1	331.9	0.1	0.5	739.5
GP (Gold Peak) Alkaline	China	57	0.2	2.2	0.1	20.8	29.7	5.0	b.d.	1.3	b.d.	b.d.	4.7	b.d.	b.d.	2.7
GP (Gold Peak) Green Cell Extra Heavy Duty	China	58.01	5.0	1.9	14.3	26.6	20.6	19.6	b.d.	43.0	b.d.	0.4	445.7	b.d.	0.4	610.0
GP (Gold Peak) Green Cell Extra Heavy Duty	China	58.02	6.1	2.1	11.2	19.4	16.1	16.4	b.d.	43.5	b.d.	0.5	420.3	b.d.	0.3	336.5
GP (Gold Peak) Green Cell Extra Heavy Duty	China	58.03	3.9	3.6	48.9	50.1	33.1	13.5	b.d.	23.9	b.d.	0.4	102.4	b.d.	0.4	462.1
GP (Gold Peak) Green Cell Extra Heavy Duty	China	58.04	3.0	2.1	39.0	19.5	24.0	11.4	b.d.	29.2	b.d.	0.3	107.7	4.1	0.3	503.7
GP (Gold Peak) Green Cell Extra Heavy Duty	China	58.05	2.2	1.6	33.3	15.9	19.4	9.5	b.d.	24.1	b.d.	0.3	82.0	b.d.	0.6	655.9
Toceba	Not available	68.01	23.7	6.6	43.4	99.6	47.8	28.6	b.d.	98.9	32.2	0.4	1049.4	11.7	0.7	244.7
Toceba	Not available	68.02	43.9	16.3	58.5	152.2	71.3	41.4	b.d.	135.5	85.2	0.1	1366.5	31.5	1.1	288.4
	V ppm	Cr ppm	Co ppm	Ni ppm	Cu ppm	As ppm	Se ppm	Sr ppm	Cd ppm	Sb ppm	Ba ppm	Hg ppm	Tl ppm	Pb ppm		
n = positive	28	44	44	50	50	50	8	50	4	24	50	26	32	46		
% positive	56	88	88	100	100	100	16	100	8	48	100	52	64	92		
Min	0.1	0.1	0.1	0.4	1.6	1.2	0.3	0.6	1.7	0.1	0.3	0.1	0.1	0.1		
Max	43.9	16.3	142.0	152.2	1312.6	41.4	3.6	196.4	85.2	1.3	7722.2	31.5	1.1	739.5		
Ave	4.0	2.0	11.9	18.4	39.6	8.5	1.7	36.4	32.9	0.4	1047.1	2.0	0.4	127.7		



**Fig. 1.** Several X–Y plots of selected elements showing chemical trends grouped qualitatively. (A) Groupings of compositions based on Ba and Sr content. (B) X–Y plot showing significant variation in Ba and Pb concentrations with a mutually exclusive relationship. (C) A plot of Co and Pb where some compositions appear to follow a specific trend. (D) A similar plot for Co and Ni with groups delineated. (E) A plot of Ni and As concentrations showing a modest correlation. (F) A plot of Ni and Cu concentrations (with one point culled for the regression), showing a moderate correlation.

## 4. Discussion

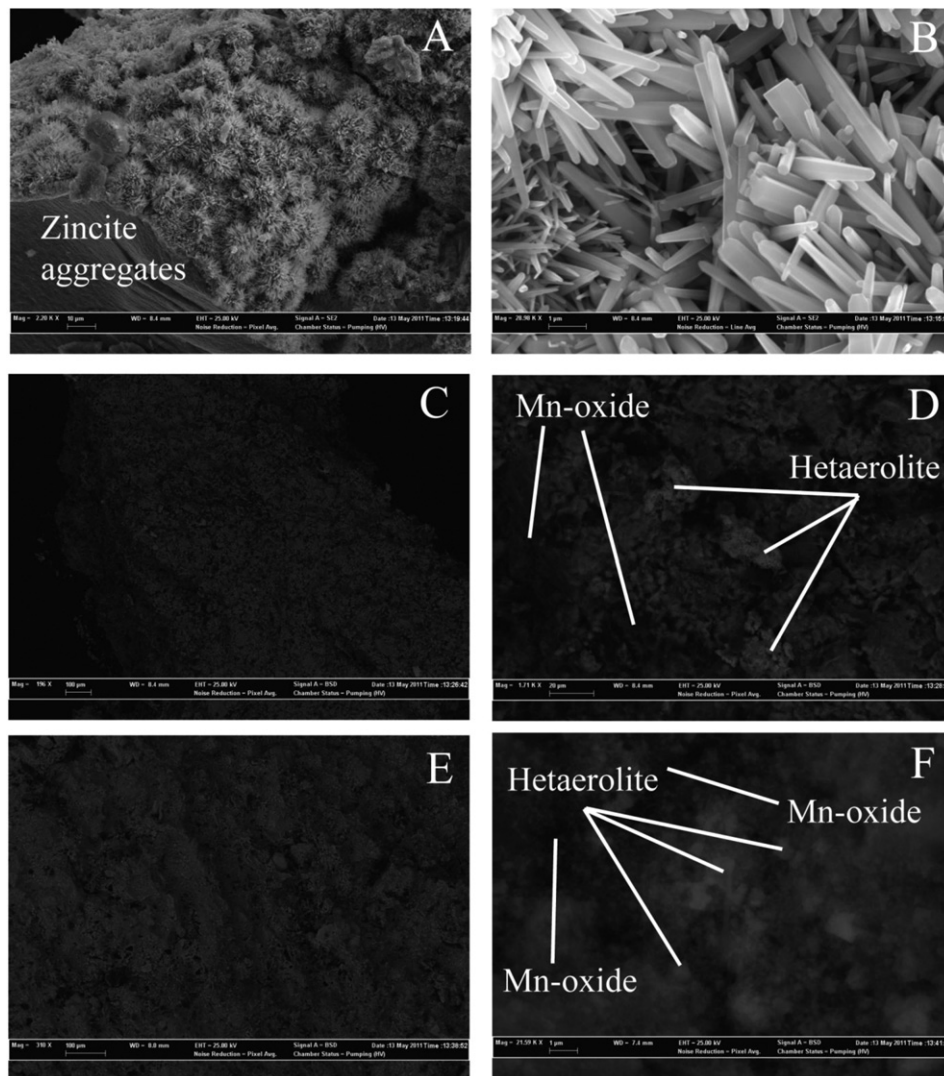
### 4.1. Interpreted causes of heavy metal concentrations and variation among brands

The variation in metal content is extensive and this is interpreted to arise from numerous sources of materials. Although groups of chemical compositions are evident, attributing a specific source or cause of that variation is problematic. Variation in metal content may be a function of manufacturing processes as certain heavy metals are added to increase performance or aid in anti corrosion. Cd, Hg, Pb and other metals are sometimes added to the Zn anode to decrease corrosion. In addition to corrosion control, heavy metals may be added to cans to alter mechanical properties and aid in manufacturing and this is common in some Zn–C cells. Other metals are added for increasing electrical performance as Hg and In for example are added to some batteries to promote electrical connections between Zn particles and the current collector. Variation and co-variations of analyzed metals observed may be reflections of specific manufacturing processes.

The cause of heavy metal content of batteries is however fundamentally linked to geologic sources of ore for producing manganese

oxides and natural manganese oxides and oxyhydroxides are well recognized as materials that absorb a wide range of heavy metals [17]. Much of this work starts in the early 1960s and the first major association in natural systems was described by work by Taylor and McKenzie [18] who found in their soil extraction studies that Ba, Co, Cr, Mo, Ni, Pb, V, and Zn appear to be more concentrated in manganese oxides, and that Co had a major specific affinity for the Mn-oxide minerals. Detailed studies of heavy metal sorption have primarily focused on the Mn-oxides of birnessite and cryptomelane. Several workers over the past 40 years have indicated that cryptomelane can absorb metal cations with an effective ionic radius of approximately 1.4 Å into the  $2 \times 2$  ( $4.6 \text{ \AA} \times 4.6 \text{ \AA}$ ) tunnel structures [19–22]. The radii for many transition metals are smaller than this and accordingly many of the transition metals exchange in some way with cryptomelane.

There is a strong association with lead sorption and manganese oxides in general. Lead has been reported by many workers to be more strongly absorbed by manganese oxides than other metals such as Ba, Cd, Co, Cu, Mn, Ni, and Zn [23–27]. Some studies suggest that manganese oxides absorb more Pb than many clay minerals and organic matter [23,25,26,28,29]. O'Reilly and Hochella [30] conducted a comparative study of natural and synthetic Mn- and



**Fig. 2.** Representative SEM images of materials investigated. (A) A low magnification (scale bar = 10  $\mu\text{m}$ ) secondary electron image of zincite crystals from an oxidized anode portion. (B) A higher magnification (scale bar = 1  $\mu\text{m}$ ) secondary electron image. (C) Back-scatter electron image at low magnification (scale bar = 100  $\mu\text{m}$ ) of a cathode showing a few areas of moderate contrast. (D) A higher magnification image (scale bar = 20  $\mu\text{m}$ ) of the left center portion of C showing moderate contrast regions identified as hetaerolite ( $\text{ZnMn}_2\text{O}_4$ ) and lower contrast regions identified as Mn-oxide (phase undetermined). (E) Back-scatter electron image at low magnification (scale bar = 100  $\mu\text{m}$ ) of a cathode showing a comparatively higher concentration of moderate contrast regions. (F) A higher magnification image (scale bar = 1  $\mu\text{m}$ ) of center portion of E showing abundant moderate contrast regions identified as hetaerolite ( $\text{ZnMn}_2\text{O}_4$ ) and lower contrast regions identified as Mn-oxide (phase undetermined).

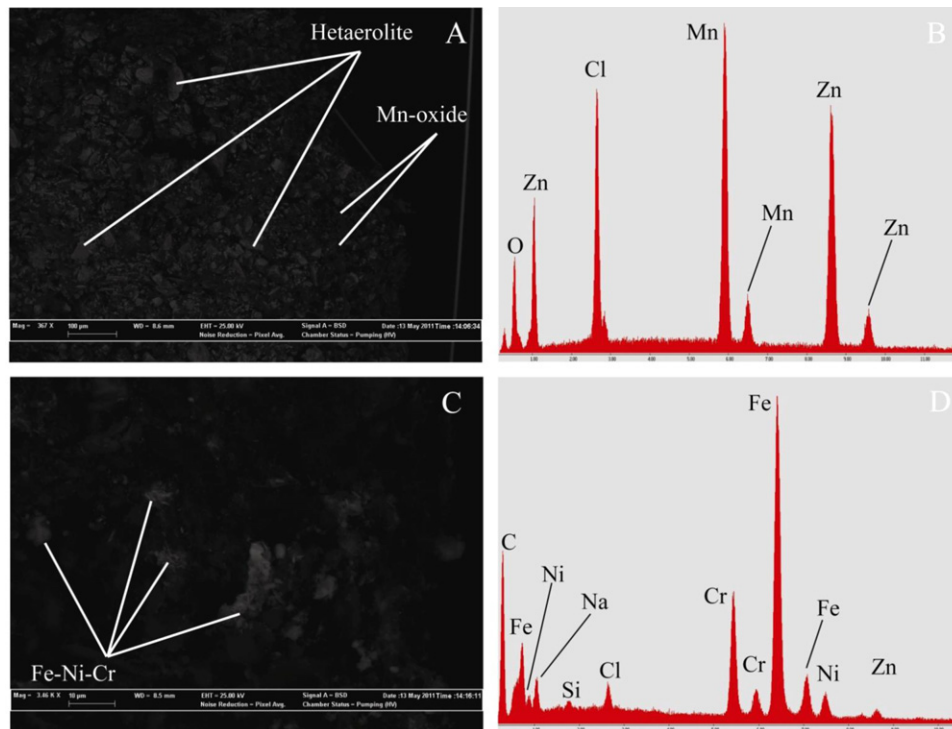
Fe-oxide materials using a 10 ppm solution of Pb in either  $\text{NaNO}_3$  or  $\text{KNO}_3$  solutions at pH = 5.5. Here they found the synthetic Mn-oxides have a higher affinity for Pb than natural Mn-oxides and both have higher affinities than natural or synthetic Fe oxides [30].

Significant variation between and among battery brands occurs and clearly generalizations regarding heavy metal content regarding AA are speculative at best. Certain brands appear to be very low in overall heavy metal content such as Sun Beam Mighty Cell, where many others have variable heavy metal content and others such as GP (Gold Peak) Green Cell Extra Heavy duty and Toceba clearly have high heavy metal content.

However these assessments are made only on a small sample size and without detailed provenance of samples. It is unreasonable to identify environmentally “better” or “worse” brands as sample size is small. Additionally one complicating factor in the analysis of consumer goods is that counterfeit labeling can occur. Counterfeit products are common globally and from Asia [31–33] and as such counterfeit products are substandard with respect to adherence to environmental regulations or industry standards. The brand

labels of batteries in this investigation are assumed to be accurate as there may be no advantage to counterfeiting the specific apparent brands of this study because they are not major brands, but there is no absolute assurance or reasonable reliable way to authenticate the brands. Discussion with Duracell staff indicate that counterfeit activity mimicking their products is known and it should be acknowledged for the present investigation that there is the possibility that the brand labeled is not the manufacturer for some small undetermined percentage of samples. This raises important and complex regulatory compliance issues in that imposing policy enforcement activities on companies that actually produce batteries that exceed stipulated metal contents may not be attainable.

However, based on the limited number of analyses, it does appear that companies producing batteries should easily be able to prove the quality of battery materials from their chemical stock. Future or current regulatory compliance should be assessed at the manufacturing sites or the EMD suppliers – not at the end waste stream product to clearly identify the contributor to heavy metal concentrations.



**Fig. 3.** (A) representative back-scatter electron image of a cathode from a zinc carbon battery with hetaerolite and Mn-oxide regions identified with (B) EDS spectra taken over the region with peaks labeled. (C) Back-scatter electron images of carbon rod with high contrast Fe-Ni-Cr metal particulate identified. (D) EDS spectra from point analysis of center bright particle. Na, Cl and Si are interpreted to originate from matrix material surrounding the metal particles.

#### 4.2. Comparison to previous investigations

Direct measurement of heavy metal content in batteries is challenging. In addition to the need or desire to measure multiple metals, a variety of choices exist in selecting material to analyze such as whole content or contents of different discrete components. We have elected to measure the mixture of anode and cathode materials together as it is well recognized that ions may migrate in a cell and it is reasonable to expect that heavy metals may exhibit similar behavior. Technical challenges exist as well such as measuring true total mercury concentration which is problematic owing to the liquid nature of the metal and the potential for volatilization. Given these issues exact quantitative comparisons to elemental compositions in the literature are problematic however some qualitative comparisons can be made.

The most comparable study in the literature is that of Recknagel et al. [34] who investigated heavy metal content of disposable zinc-carbon and alkaline batteries for the purpose of regulatory compliance in Germany. They analyzed the Cd, Pb, and Hg content in 25 batteries of various sizes using ICP-MS. They report only a summary of their data and found for all batteries that Pb concentrations vary from 3 to 1910 mg kg<sup>-1</sup>, Cd concentrations vary from 0.1 to 135 mg kg<sup>-1</sup> and Hg in all analyses were <3.9 mg kg<sup>-1</sup>. Our analyses of these metals are broadly consistent with this previous work.

Richter et al. [35] investigated selected heavy metals in zinc-air button cells also for the purpose of regulatory compliance in Germany. These are a different class or group of battery, however some general comparisons can be made. For mercury they found concentrations of approximately <1–21 g kg<sup>-1</sup>, with 17 or 18 values being over 7 g kg<sup>-1</sup>, a substantial difference from values determined for the AA batteries of the current investigation. They report very consistent concentrations of approximately 200 mg kg<sup>-1</sup> for Pb in each sample. The heavy metal content of these batteries is clearly

different that of this or Recknagel et al.'s [34] study and the similarity in Pb concentration and Hg suggest a dominant single source or manufacturer.

Nnorom and Osibanjo [36] investigated content of Co, Cr, Ni and Cd in rechargeable lithium ion and nickel metal hydride batteries used for mobile phones using atomic adsorption (AA). They report averages for Co (361,284 mg kg<sup>-1</sup>), Cr (25.3 mg kg<sup>-1</sup>), Ni (75,272 mg kg<sup>-1</sup>), and Cd (2.8 mg kg<sup>-1</sup>). The AA population of the current investigations is broadly similar with respect to Cr and Cd content, however clearly differs in Co and Ni content largely owing to differences in the primary composition of the battery types of course.

#### 4.3. General implications for environmental policy

Environmental problems associated with consumer products generated in China are well noted and include issues with drywall [37,38], melamine [39] and lead in paint [40]. The high levels of heavy metals found in many of the batteries from China are another example of a consumer product that is of environmental concern. Given the dominance of manufacturing of consumer goods in China, there is some concern regarding the amounts of heavy metals in batteries and policy actions to reduce heavy metal content are suggested. For example the same rigor of European, German and U.S. manufacturing standards should apply and in some way be enforced as these batteries make it into these countries and from some perspectives circumvent the regulatory intentions of those countries.

Batteries from countries of other origins are of course not without significant heavy metal content. Adoption of a global standard of maximum heavy metal content would be beneficial for reducing the amount of heavy metals in the waste stream and although preliminary in nature our work provides some reference for further development of such a standard.

## 5. Conclusions

This preliminary analysis of heavy metal content in batteries of non U.S. origin indicates concentrations and diversity exhibits a wide range and the limited survey of sample materials indicates that some batteries have very low heavy metal content, while others are of significant environmental concern. It is very probable that some if not much of the heavy metal content is derived from original manganese oxide ore whereas other content is very likely introduced during the manufacturing process. SEM indicates that most of the heavy metals do not occur as discrete particles but as minor content in solid solution with Mn-oxide or other phases. Mechanical separation of heavy metal content is not feasible thus batteries with high heavy metal content are not tractable for recycling by phase separation.

A much larger, broader study of batteries with very well defined provenance from many global locations with multiple analyses of each brand is suggested as well as systematic investigation of component suppliers globally. Such an investigation would identify sources and manufacturers of batteries with particular environmental concern and would produce groundwork for potential global environmental standards.

Although preliminary in nature, the results of this investigation strongly suggest that batteries originating from China continue to introduce large amounts of heavy metals into the U.S. Furthermore the limited analyses of this investigation suggest a generalization that batteries produced in China are likely not acceptable for recycling purposes based on the concentrations and variability of heavy metal content.

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