



Modeling heavy metal mass releases from urban battery litter

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ABSTRACT

Consumer batteries littered on urban pavements release metals of environmental significance (Ag, Cd, Cr, Cu, Hg, Li, Mn, Ni, Pd, Ti, Zn) to stormwater runoff. Predicting the mass loading of any one metal is difficult because of the random composition of battery litter. However, when littering is modeled as a conditional filtered Poisson process, bounds may be estimated for the mean and variance of site mass loading for any metal if the site litter rate and battery product contributions are known. Site-specific data on the battery brand distribution in litter can improve load estimates, but statistics computed from 5500 littered batteries collected in the Cleveland area may be used to approximate the brand distribution. Zinc load calculations based on battery litter size, type and brand discretizations are implemented in a model titled BLML and illustrated for a case-study location. Results indicate that, at some urban sites, zinc released from battery litter can be the largest source of zinc in urban pavement runoff.

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Software availability

Name: BLML (Battery Litter Mass Loading)

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Coefficient updates available at: <http://civil.case.edu/batterylitter>

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Hardware: Personal Computer

Software: Microsoft Office Excel

Program Size: 450 kb + text file CD

Cost: Free

1. Introduction

Urban stormwater can be contaminated from a great many sources and much of this contamination comes from materials intentionally or unintentionally released directly to urban pavements. Unintentional releases include atmospheric particulate deposition, vehicle liquid discharges (gas, grease, oil, break fluid, steering fluid, coolants, etc.), vehicle wear debris (tire wear, break pad wear, tire balancing weights, lug nuts, etc.), product “spills” and pollutants washed onto pavements from other locations. Components from all of these sources can be found in pavement stormwater discharges. There is also a class of material generically characterized

as “litter” that is intentionally released to urban pavements. Much of this is paper/plastic products, food containers or cigarette-related materials, but there is an unexpected component of this litter that has a unique potential for yielding heavy metal contamination. Field work conducted in the Cleveland, Ohio area has demonstrated that urban pavement litter can contain a surprising number of consumer batteries capable of releasing metals worthy of environmental concern (Ag, Cd, Cr, Cu, Hg, Li, Mn, Ni, Pd, Ti, Zn, ...). Since little is known about the nature of this source, researchers at Case Western Reserve University have been conducting studies to evaluate the significance of battery metal releases relative to other sources of urban stormwater contamination.

This manuscript presents a stochastic mass loading model that can be used to estimate the magnitude of site heavy metal loading from urban battery litter. The model may be calibrated using data from simple field surveys and default coefficients, or may be refined to produce site-specific predictions adjusted for local distribution of battery products and site-specific battery deterioration rates. Information on new battery types may also be added as product innovations emerge. Stochastic modeling is required because the source (individual battery litter events) is strongly random in time and the objects of these events (individual consumer batteries) vary in size, power chemistry, structural construction, and resistance to environmental damage, all of which impact the rate and magnitude of each cell's releases. However, because this is a little known and unexpected source of pollution, Sections 2–7 summarize background information on the problem of urban battery litter. These are followed by presentation and illustration of the stochastic mass loading model.

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2. Origins of battery litter research at Case Western Reserve University (CWRU)

The potential for environmental problems associated with consumer battery litter was first identified at CWRU in the summer of 2001 by a team of students sampling brownfield soils (Jennings et al., 2002) for heavy metal contamination. Field sampling activities were staged from nearby retail parking lots, and in several lots, littered batteries were noted. Because the project focused on heavy metal pollution, the team became watchful for battery litter as a possible source of sample contamination. This led to pavement surveys to count the number of littered batteries as a rough measure of their significance. In one initial survey, 56 batteries were recovered from a single Wal-Mart parking lot, and many of these were so deteriorated that it was clear they had already released their contents to the pavement's stormwater runoff.

The initial results of 2001 led to efforts to formalize the methods of quantifying battery litter (Jennings and Clark, 2002; Jennings and Kiedrowski, 2002; Kiedrowski and Jennings, 2002) and to a series of projects to examine the phenomena that govern littered battery deterioration and pollutant release (Kiedrowski, 2003; Hise, 2003; Rozsa, 2003; Barns, 2003; Jennings et al., 2003; Felix, 2004; Krouse and Jennings, 2005). Details of this work are summarized here to emphasize the need for the heavy metal mass release model presented.

3. The consumer battery industry

To understand the complexity of the urban battery litter problem, one must consider the structure of the consumer battery industry. Batteries come in many sizes (lantern, button, button stack, K, P, R, S, J, N, etc.), but most sales are in the “big 5” sizes of D, C, AA, AAA, and 9v. There is intense competition for these sales and market data are difficult to obtain, but it is believed that about \$10 billion in consumer batteries are sold in the U.S. each year (Batteries Digest, 2006). The worldwide market is predicted to climb to \$70 billion by 2010 (Freedonia Group, 2006). The U.S. annual per capita consumption is estimated to be between 10 and 50 batteries (Sanyo/GE, 2003; EHSO, 2006) so as many as 15 billion consumer batteries are sold in the U.S. each year. The vast majority of these are disposable. The battery market doubled in the 1990s growing at 6–10% per year and at 15% in 1999 due to Y2K fears (Lee, 2001). Growth on the order of 7% per year is predicted through 2010 with China surpassing the U.S. as the world's largest battery market (Freedonia Group, 2006).

U.S. battery manufacturing is dominated by Duracell, Eveready/Energizer and Rayovac, who produce their own brand and “private label” batteries labeled for major U.S. retailers. There are also many international manufacturers that produce brand name and private label batteries for the U.S. market (Sony, Fuji, Panasonic, Maxell, Sanyo, Toshiba, Varta, etc.) and many international brands that do not identify their manufacturer. Batteries made in the U.S., Belgium, Brazil, Canada, China, Costa Rica, France, Germany, Hong Kong, India, Indonesia, Israel, Japan, Korea, Macau, Malaysia, Mexico, Poland, Singapore, Thailand and the U.K. have been found in the Cleveland area. The vast array of product sizes, ages, types and origins greatly complicates the problems of predicting their pollutant discharges.

4. Consumer battery power chemistry

Consumer batteries also employ several electrochemical power systems. The most common are summarized in Table 1 (see Powerstream, 2003; Linden, 1995; BAJ, 2004). Of these, “alkaline”, zinc chloride (Zn–Cl) and zinc–carbon (Zn–C) are most common. Most batteries made in the U.S. are “alkaline”. Many imported “discount”

Table 1

Common consumer battery electrochemical power reactions.

| Battery type | Principal electrochemical power reaction |
|-----------------------------|--|
| Zinc–carbon (Zn–C) | $\text{Zn} + 2\text{NH}_4\text{Cl} + 2\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3 + \text{Zn}(\text{NH}_3)_2\text{Cl}_2 + \text{H}_2\text{O}$ |
| Zinc chloride (Zn–Cl) | $\text{Zn} + 2\text{MnO}_2 + \text{ZnCl}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{MnOOH} + 2\text{Zn}(\text{OH})\text{Cl}$ |
| Alkaline–manganese dioxide | $\text{Zn} + 2\text{MnO}_2 \rightarrow \text{ZnO} + \text{Mn}_2\text{O}_3$ |
| Lithium (manganese dioxide) | $\text{Li} + \text{MnO}_2 \rightarrow \text{LiMnO}_2$ |
| Lithium carbon monofluoride | $n\text{Li} + (\text{CF})_n \rightarrow n\text{LiF} + n\text{C}$ |
| Lithium–iron | $2\text{Li} + \text{FeS} \rightarrow \text{Li}_2\text{S} + \text{Fe}$ |
| Alkaline zinc–air | $2\text{Zn} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Zn}(\text{OH})_2$ |
| Silver oxide | $\text{Zn} + \text{Ag}_2\text{O} \rightarrow \text{ZnO} + 2\text{Ag}$ |
| Nickel–metal hydride (NiMH) | $\text{MH} + \text{NiO}_2\text{H} \rightarrow \text{Ni}(\text{OH})_2 + \text{M}$ |
| Nickel/cadmium (NiCd) | $\text{Cd} + \text{NiO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Ni}(\text{OH})_2 + \text{Cd}(\text{OH})_2$ |
| Lead acid | $\text{Pb} + \text{PbO}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O}$ |
| Mercuric–Cd Oxide | $\text{Cd} + \text{HgO} + \text{H}_2\text{O} \rightarrow \text{Cd}(\text{OH})_2 + \text{Hg}$ |
| Mercuric–Zn Oxide | $\text{Zn} + \text{HgO} \rightarrow \text{ZnO} + \text{Hg}$ |

batteries are Zn–Cl or Zn–C cells. These can sometimes be identified by the words “Heavy Duty” or “Super Heavy Duty” on their label, but these cells are sometimes labeled “alkaline” when they are not (Jennings, 2004). The cell chemistry can often be inferred from external construction details and from the cell mass, but the most dependable method is to disassemble the cell to examine internal details and to measure its electrolyte pH. Alkaline cells have a steel barrel and an electrolyte pH > 12. Zn–Cl and Zn–C cells have a softer zinc barrel (that is eventually consumed in the power reaction) and an electrolyte pH < 7.5.

Battery chemistry continues to evolve. Panasonic (2003), Kodak (2004), Duracell (2006a) and Camelon (Jada Products, 2006) have recently introduced “Oxy-alkaline” disposable batteries in the U.S. market that substitute nickel oxy-hydroxide for a portion of the manganese dioxide (MnO_2) to provide higher capacity. These blur the line between alkaline and nickel–metal hydride (NiMH) cells, and alter the nature of battery pollution potential.

5. Battery disposal

Discussions of battery litter often lead to questions about the classification of consumer battery waste, proper battery disposal techniques and the roll of recycling in battery waste management.

In the U.S., upon disposal, consumer batteries generally become solid, universal or hazardous waste. Alkaline, Zn–Cl, and Zn–C cells are classified as solid waste by USEPA rules, but some states apply more stringent tests (which alkaline batteries may fail) to the definition of hazardous waste. Industry instructions are that they be treated as solid waste and discarded in the trash (Duracell, 2006b; Energizer, 2006). Many recycling programs exist, but with the exception of California, they are voluntary efforts not required by state or federal regulation. Beginning in 2006, consumer battery disposal was banned from California landfills (CIWMB, 2006), and several other states are considering “e-waste” rules that may further restrict battery disposal. Most other battery types (NiMH, nickel/cadmium, etc.) become hazardous or universal waste (USEPA, 1995), and should be collected for recycling or secure disposal. Universal waste batteries are collected by several retail outlets and in voluntary household hazardous waste collections. Products such as rechargeable alkalines (Rayovac, 2004; Grandcell, 2004; Pure Energy, 2004) and oxy-alkaline cells blur the distinction between solid and universal waste batteries. It is not yet clear how they will be managed.

Elsewhere around the world regulations vary considerably. There are at least 11 countries with “takeback” laws that require consumer battery recycling (Raymond Communications, 2002). Six EU countries (Austria, Belgium, France, Germany, Sweden and the

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