Analysis of metals leached from smoked cigarette litter

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ABSTRACT

Background Littered cigarette butts represent potential point sources for environmental contamination. In areas with substantial amounts of cigarette litter, environmental hazards may arise as chemical components are leached from the filters and smoked tobacco.

Objective The three main aims of this study were: (1) to quantify the amount of Al, Ba, Cd, Cr, Cu, Fe, Pb, Mn, Ni, Sr, Ti and Zn leached from cigarette butts, (2) to determine the relationship between the pH of the aqueous soaking solution and metal concentration leached and (3) to determine the relationship between the period of soaking in aqueous solution and metal concentration leached.

Methods Smoked cigarette butts and unsmoked cigarettes were added to phials containing aqueous solutions of pH 4.00, 5.00 and 6.00 (± 0.05). The metal concentration of the resultant leachates was measured via inductively coupled plasma optical emission spectroscopy (ICP-OES) 1 day, 7 days and 34 days after sample addition.

Results All metals were detected in leachates 1 day after sample addition (with the exception of Cd) and were released at varying rates. No clear relationship between pH within the range typical of precipitation and metal concentration leached was observed.

Conclusions Based on the gradual release of multiple metals over the full 34-day study period, cigarette litter was found to be a point source for metal contamination. The apparent rapid leaching of other metals may increase the risk of acute harm to local organisms.

Cigarette butts are among the most common forms of litter. Worldwide, approximately 4.95 trillion cigarette butts are estimated to be littered each year.¹ Of the 10 million pieces of litter collected during the 2009 International Coastal Cleanup campaign, 21% were cigarette butts and filters,² twice as much as any other type of litter. Water channelled by sewer systems and streams acts to accumulate cigarette litter in localised areas and leach its chemical components into the environment. Although many may argue that a single piece of cigarette litter would not inflict serious environmental damage, the cumulative effect of many cigarette butts littered in a centralised area may present a significant threat to local organisms. Indeed, several studies^{3–5} have found cigarette litter toxic to some aquatic species.

Although the compounds in cigarettes and mainstream smoke have been extensively researched, few studies have attempted to identify and quantify the components leached from

cigarette butts^{3–6} or assess the leaching behaviour of these components. Micevka *et al.*⁵ suggest that the toxicity of cigarette butt leachates is in part due to heavy and trace metals. The occurrence of metals in cigarettes can largely be attributed to the growth and cultivation of tobacco (*Nicotiana tabacum*), as tobacco is known to readily accumulate metals from underlying soil.⁷ The metal composition of soil primarily reflects the mineral composition of the bedrock from which it was derived. Fertilisers, however, may also introduce metals to soil. Case studies of the use of municipal sludge containing heavy metals as fertiliser found significant increases in the concentration of many heavy metals in the sludge-amended soils and the plants grown in these soils.⁷ The application of pesticides, insecticides and herbicides also introduce metals to the tobacco leaf.⁸ Further introduction occurs during cigarette manufacture, particularly via the addition of casing materials to the cured leaves^{9–10} and the use of brightening agents on the wrapping paper.^{11–13}

The response of biota to metal contamination is highly varied.^{14–15} Whereas increased levels of trace and heavy metals in soils and water adversely affect some organisms, contamination enhances the metal tolerance of other species (eg, bioaccumulators). Environmental conditions, such as pH, further vary biological responses to contamination by affecting the mobility of metals in soils and the bioavailability of metals to plants.¹⁴ To better predict how metals leached from littered cigarette butts affect local biota, investigation of their leaching behaviour is required. The main aims of this study, therefore, were: (1) to determine the concentration of Al, Ba, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sr, Ti and Zn leached from cigarette butts in aqueous solution; (2) to assess the relationship between pH of the leaching solution and metal concentration leached; and (3) to assess the relationship between soaking time and metal concentration leached. The metals listed above were selected for study based on their presence in smoked filters,^{12–16–17} toxicity to living organisms,¹⁸ and/or ability to be reliably analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES).

METHODS

Sampling

Smoked cigarette butts were collected from covered cigarette receptacles adjacent to buildings on the campus of the University of Tennessee-Chattanooga, USA. Following collection, the filters were manually separated from the remnant tobacco on the cigarette butts. These components were stored separately in disposable plastic containers.

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Cigarette butts were not collected after local precipitation events to reduce the loss of analyte prior to sampling. Packs of the three most popular cigarette brands in the USA¹⁹ were also purchased from convenience stores. The unsmoked cigarettes were stored in their original packaging and sealed inside a disposable plastic container to prevent moistening caused by humidity in the laboratory.

Leaching procedure

Aqueous solutions were prepared by adding dilute analytical grade sulfuric acid and/or ammonium hydroxide dropwise to deionised water. The pH of the solutions (6.00, 5.00 and 4.00) was determined within ± 0.05 of the desired unit with a Vernier LabQuest pH probe (Beaverton, OR, USA). Aliquots (100 ml) were transferred to 125 ml high-density polyethylene (HDPE) phials. Leachates of smoked cigarette material were prepared by adding approximately 2.0 ± 0.2 g filter and 2.0 ± 0.2 g remnant tobacco to the phials of aqueous solution. Leachates of unsmoked cigarette material were prepared by adding 3.6 ± 0.1 g of unsmoked cigarettes (approximately four whole cigarettes) to the phials of aqueous solution. The cigarette material was allowed to soak in the aqueous solutions for 1 day, 7 days and 34 days. Individual phials designated for each soaking period were prepared to avoid changes in the volume of the leaching solution after successive analyses. This procedure is summarised in figure 1. Method blanks were prepared in the same manner as the leachate samples except no cigarette material was added.

Filtration and ICP-OES analysis

The leachates were extracted 1 day, 7 days and 34 days after sample addition using Luer-lock™ syringes. Nylon filter tips ($0.22 \mu\text{m}$) were attached to the syringes to allow direct filtration into test tubes for analysis. A new filter (conditioned by the sample leachate) was used for each sample. The concentration of each metal in the leachates was measured by ICP-OES. The operating conditions of the Jobin–Yvon Ultima ICP-OES (Edison, NJ, USA) are given in table S1, and the emission wavelengths of each metal are listed in table S2 (see Supplementary material).

RESULTS

Metals leached from cigarette material

All 12 of the metals selected for analysis were identified in quantifiable amounts in the leachates after 1 day of soaking with the exception of cadmium in the smoked cigarette leachates (tables 1 and 2). Detection limits, based on 2SD of the analytical

blank, ranged between $0.03 \mu\text{g/litre}$ (Ba) and $8 \mu\text{g/litre}$ (Al) and are given in table S2. The concentration of metal leached was converted to $\mu\text{g}_{\text{analyte}}/\text{g}_{\text{sample added}}$ to account for variation in sample mass added. Data that failed a 90% CI t-test were excluded from the data set, resulting in sample sets of varying sizes. The average concentration of metal leached varies from values below limits of detection (Cd, 1-day analysis, smoked material) to over $75 \mu\text{g/g}$ (Fe, 34-day analysis, unsmoked material).

Metal concentration and pH

Within the pH range studied, no identifiable trend emerged between pH of the aqueous leaching solution and metal concentration leached from the smoked cigarette material (figure 2). Analysis of variance (ANOVA) statistical tests were performed to determine whether the concentration of metal leached varied significantly with pH. The results of these tests indicate that in almost all cases, the difference in the metal concentration leached with pH is due to random error. Based on this conclusion, the concentration of metal leached for each soaking period presented in tables 1 and 2 incorporates samples from each pH group.

Metal concentration and soaking period

Variable relationships between soaking time and metal concentration leached from the smoked cigarette material were observed (figure 3). The concentration of Ba, Fe, Mn and Sr leached increased with soaking time, indicating an increase in metal contamination over time. The concentration of Ni, Pb, Ti and Zn did not change significantly after 1 day of soaking, suggesting all leachable Ni, Pb, Ti and Zn was released within 1 day. The concentration of Al, Cd, Cr and Cu leached was found to decrease at some point during the time study. The formation of insoluble compounds and complexes is likely responsible for the observed decrease since solids were removed from the leachates by filtration prior to analysis.

DISCUSSION

The sampling and leaching procedures used in this study were designed to simulate natural conditions as closely as possible. Littered cigarette butts found in the environment encompass a wide range of cigarette brands with varying amounts of tobacco left on the filters. In this study, smoked cigarette material was collected from actively used butt receptacles to provide a sample population representative of the local cigarette litter with respect to brand and amount of remnant tobacco. A disadvantage of this sampling technique is the introduction of additional variables, as previous work^{16–20} demonstrates that metal concentrations in cigarettes may vary between brands. The percentage relative standard deviation associated with the mean concentration of metal leached given in tables 1 and 2, however, is relatively low for most sample sets, demonstrating the reproducibility of this method. By collecting smoked samples from butt receptacles, the use of human subjects was also made unnecessary.

The leaching procedure employed in this preliminary study simulates a closed system environment. Although an open system is likely more representative of natural conditions, a closed system was considered the most straightforward method of obtaining the maximum amount of leachable metal. For the investigation of how pH affects the leaching behaviour of the metals studied, a pH range of 6.00–4.00 was selected for the aqueous solutions because it represents the range of pH typically observed in natural rainwater.²¹ Indeed, the pH of

Figure 1 Schematic of leaching procedure for leachates derived from (A) smoked cigarette material and (B) unsmoked cigarettes.

Table 1 Concentration of metals leached from unsmoked cigarette material measured after specified period of soaking

	Unsmoked cigarette material, µg/g											
	Al	Ba	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Sr	Ti	Zn
1 day												
Mean value	5.94	6.45	0.130	0.326	3.74	13.8	46.4	0.480	1.36	14.1	0.603	11.1
Error*	±0.73	±0.46	±0.02	±0.019	±0.38	±1.8	±4.2	±0.07	±0.10	±1.7	±0.037	±1.1
Minimum value	5.13	5.76	0.105	0.306	3.23	12.0	41.8	0.387	1.24	11.7	0.559	9.9
Maximum value	7.49	7.05	0.166	0.360	4.38	17.9	54.8	0.585	1.54	15.6	0.671	13.1
RSD (%)	12	6.6	19	5.1	9.8	13	8.7	15	7.2	12	5.4	9.6
n	9	9	7	8	9	9	9	9	9	10	11	9
7 days												
Mean value	6.94	10.1	0.123	0.372	1.58	30.3	54.0	0.554	1.53	20.2	0.712	11.6
Error*	±0.36	±0.8	±0.010	±0.014	±0.18	±3.4	±3.4	±0.044	±0.06	±0.8	±0.027	±0.6
Minimum value	6.52	8.9	0.114	0.361	1.39	23.3	49.7	0.483	1.46	19.4	0.686	10.3
Maximum value	7.39	10.9	0.140	0.385	1.83	33.4	57.7	0.611	1.61	21.1	0.741	12.3
RSD (%)	4.3	6.9	8.0	2.5	11	11	5.6	7.5	3.0	2.7	2.6	4.8
n	7	8	5	11	9	9	10	8	11	9	9	9
34 days												
Mean value	6.90	15.3	0.132	0.283	0.67	75.3	59.6	0.404	1.79	32.8	0.729	9.68
Error*	±0.3	±1.3	±0.038	±0.105	±0.20	±5.7	±2.9	±0.231	±0.40	±1.5	±0.036	±0.71
Minimum value	6.59	13.8	0.092	0.197	0.48	69.2	55.8	0.171	1.34	31.8	0.689	8.82
Maximum value	7.27	18.2	0.176	0.429	1.12	84.7	62.2	0.755	2.55	35.2	0.775	10.7
RSD (%)	4.2	8.1	29	37	30	7.0	3.9	57	22	3.5	4.1	6.8
n	8	9	7	10	10	9	10	9	9	9	9	11

*Error represents square root of the sum of the squared relative errors of the mean concentration (1σ) and mass. RSD, relative standard deviation.

rainfall in the Chattanooga, Tennessee area in 2009 was approximately 4.8–5.0.²²

As illustrated in figure 2, the findings of this study suggest that differences in pH within the range typical of precipitation have no appreciable effect on the metal concentration leached from smoked cigarette material. This result implies that changes to the pH of precipitation within its natural range likely will not enhance or reduce the magnitude of metal contamination from cigarette litter. Further investigation, however, is required to determine the effect of pH values outside the natural range

of precipitation, such as those measured in areas with highly acidic rain.

Further, this study finds that the metals studied have different leaching behaviours over time (figure 3). The direct relationship between soaking period and the concentration of Ba, Fe, Mn and Sr leached indicates that a piece of cigarette litter is a point source of Ba, Fe, Mn and Sr contamination for at least a month and possibly longer. This result suggests that the longer cigarette litter remains in the environment, the greater the contamination of these metals will be. This finding supports the need for timely

Table 2 Concentration of metals leached from smoked cigarette material measured after specified period of soaking

	Smoked cigarette material, µg/g											
	Al	Ba	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Sr	Ti	Zn
1 day												
Mean value	7.83	3.81	—*	0.248	3.96	11.7	25.5	0.313	1.12	9.89	0.646	6.56
Error†	±1.06	±0.41	N/A	±0.025	±0.59	±1.3	±3.2	±0.079	±0.12	±1.29	±0.066	±0.69
Minimum value	7.02	3.56	—*	0.240	3.37	10.9	22.9	0.187	1.08	8.90	0.625	6.20
Maximum value	8.89	3.96	—*	0.257	4.55	12.5	28.2	0.431	1.17	11.1	0.665	6.82
RSD (%)	9.2	4.0	N/A	2.0	11	5.0	7.3	23	2.5	8.4	1.8	3.4
n	9	9	N/A	9	9	9	10	10	9	8	9	11
7 days												
Mean value	11.0	6.51	0.149	0.302	2.20	15.2	31.5	0.342	1.35	14.1	0.765	6.58
Error†	±1.3	±0.92	±0.044	±0.045	±0.6	±2.4	±4.4	±0.059	±0.16	±1.6	±0.082	±0.68
Minimum value	9.55	5.54	0.103	0.271	1.54	12.4	26.7	0.276	1.25	10.9	0.722	6.26
Maximum value	11.7	7.41	0.184	0.363	3.17	17.7	35.4	0.409	1.51	16.8	0.817	6.78
RSD (%)	6.5	10	28	11	26	12	9.8	14	6.9	5.2	4.0	2.5
n	8	9	3	10	11	8	9	8	11	9	11	10
34 days												
Mean value	8.92	10.4	0.142	0.236	1.22	45.3	40.1	0.298	1.42	23.4	0.755	5.87
Error†	±1.92	±3.0	±0.057	±0.109	±0.46	±9.7	±4.4	±0.223	±0.32	±2.5	±0.099	±0.96
Minimum value	12.1	7.2	0.079	0.128	0.63	30.3	37.7	0.072	1.10	19.3	0.681	5.06
Maximum value	6.52	15.6	0.221	0.460	1.68	59.0	43.5	0.721	2.06	27.3	0.902	6.92
RSD (%)	19	27	39	45	36	19	4.8	74	20	3.5	8.4	13
n	11	9	11	11	10	10	10	9	11	9	10	10

*Below detection limit.

†Error represents square root of the sum of the squared relative errors of the mean concentration (1σ) and mass. RSD, relative standard deviation.

Figure 2 Concentration of metals leached in aqueous solutions with varying pH after 7 days of soaking.

and continual litter cleanup to reduce the magnitude of metal contamination from improperly discarded cigarette butts. In contrast to the metals discussed above, the concentration of Ni, Pb, Ti and Zn remained relatively unchanged over the 34-day study period. One explanation for this observation is that all leachable metal is released from the cigarette butts after a single day of soaking. For local organisms sensitive to Ni, Pb, Ti and Zn, a rapid release of these metals may have implications for acute biological effects. Because leaching occurred in a closed system, however, these seemingly static concentrations throughout the study period may be due to dynamic equilibrium between the cigarette butt samples and aqueous soaking solution; if so, greater amounts of Ni, Pb, Ti and Zn may be leached by the continual removal of saturated aliquots of leachate and replacement with fresh water at a rate that exceeds that of equilibrium.

With respect to the metal concentrations previously measured in whole unsmoked American cigarettes,^{16, 23} more than half of Pb and Sr, one-quarter of Cu, and one-fifth of Ba, Mn and Zn

originally contained in cigarettes may potentially be leached into the environment (table 3). When placed in context of the estimated amount of cigarette butts littered annually (4.95 trillion),¹ the results of this study indicate that between 0.120 ± 0.048 kg (Cd) and 38.1 ± 8.2 kg (Fe) may enter the environment each year from cigarette litter alone.

Moriwaki *et al.*⁶ is thus far the only study known that has also investigated metals leached from cigarette butts. Moriwaki *et al.*⁶ studied four metals in common with this paper: Cd (0.24 ± 0.60 µg/g), Cr (1.8 ± 0.34 µg/g), Cu (21 ± 0.91 µg/g) and Pb (7.2 ± 0.70 µg/g). These values are approximately 2–7 times greater than those measured in this study, which is likely due to the difference in leaching methods employed. In this study, the metals were allowed to passively diffuse from the cigarette litter. Moriwaki *et al.*⁶ however, generated leachates by shaking suspensions of cigarette litter in 1 N HCl solutions for 2 h. The shaking action is likely responsible for the leaching of greater concentrations of metal from the cigarette litter.

Figure 3 Variable relationships observed between metal concentration leached from smoked cigarette material and soaking time in aqueous solution. A. Increase in metal concentration leached over time. Observed for Ba (shown), Fe, Mn and Sr. B. No significant change in metal concentration leached over time. Observed for Ni, Pb, Ti and Zn (shown). C. Decrease in metal concentration measured over time. Observed for Al, Cd, Cr and Cu (shown).

Table 3 Percentage of metal leached from cigarette butts with respect to concentration in whole American cigarettes and annual amount of metal leached from cigarette butts littered worldwide

Metal	Concentration in whole cigarette, µg/g	Percentage leached	Amount leached worldwide,* kg/year
Al	950 ± 354^{16}	1.2 ± 0.5	9.26 ± 1.99
Ba	48.7 ± 11.2^{16}	21 ± 8	8.76 ± 2.52
Cd	0.99 ± 0.49^{23}	14 ± 9	0.120 ± 0.048
Cr	1.78 ± 2.37^{16}	17 ± 23	0.254 ± 0.117
Cu	11 ± 0.5^{23}	36 ± 6	3.33 ± 1.25
Fe	394 ± 13^{23}	11 ± 3	38.1 ± 8.2
Mn	178 ± 8^{23}	23 ± 3	33.8 ± 3.7
Ni	2.75 ± 0.31^{23}	12 ± 3	0.288 ± 0.215
Pb	2.39 ± 0.32^{23}	59 ± 15	1.20 ± 0.27
Sr	39.6 ± 14.0^{16}	59 ± 22	19.7 ± 2.1
Ti	106 ± 61^{16}	0.7 ± 0.4	0.644 ± 0.084
Zn	35.3 ± 0.7^{23}	19 ± 2	5.54 ± 0.91

*Calculated using highest mean metal concentration leached and estimated amount of cigarette butts littered annually.¹

What this paper adds

- The constituents leached from cigarette butts have been identified and quantified by only a few studies. This paper investigates the amount and behaviour of selected trace metals leached from cigarette butts in aqueous solution over a range of soaking periods and pH.
- All metals were detected in the leachates after 7 days of soaking. The results indicate that some metals may be rapidly released into the environment whereas others are leached more gradually from littered cigarette butts.
- This study also finds that the amount of metal leached from cigarette butts does not significantly vary with pH within the range typical of rainfall.

Leachates of unsmoked cigarettes were investigated in this study to provide background concentrations of the metals of interest and to identify possible instances of contamination. In general, the metal concentrations of the leachates prepared from unsmoked cigarettes were greater than those measured in the leachates prepared from smoked cigarette butts. This result is likely due to the loss of metals in smoke or ash during cigarette combustion, as cigarette smoke and ash are known to contain metals.^{24–26} This trend was observed for all metals except Al, Cu and Ti. These exceptions to the trend introduce the possibility of metal contamination prior to sample collection.

Sand and cigarette ash in the butt receptacles were investigated as potential sources of contamination, since they may have adhered to the cigarette wrapping prior to sampling. X-ray diffraction analyses, however, indicate that these materials do not contain minerals bearing the metals studied. Non-crystalline compounds were also detected in the cigarette ash, but their composition could not be identified. Therefore, the adherence of additional ash to the cigarette wrapping cannot be ruled out as a potential contamination source. Sunscreen or lip balm transferred to the cigarette wrapping during smoking is another possible contamination source, as these products have been found to contain many of the studied metals, including Al, Cu and Ti.^{27, 28} Contamination from these sources, however, is not necessarily problematic since cigarette ash, sunscreen and lip balm are often on littered cigarette butts. Another explanation for the higher concentrations of Al, Cu and Ti in the leachates of smoked cigarette material is that these metals are in a more mobile phase in the cigarette filter than in the tobacco. Greater mobility would likely yield greater concentrations leached. Further investigation, however, is required to determine the mobility of metals in filters versus tobacco.

The finding that greater concentrations of metals were in general leached from unsmoked cigarettes than smoked cigarette materials implies that cigarette litter with more remnant tobacco likely causes greater contamination than butts with little or no remnant tobacco. This result calls into question a practice of some environmentally conscious smokers, who scatter remnant tobacco into the environment but keep the filter until it can be deposited into a waste container.

Conclusions

The results of this research suggest that littered cigarette butts are point sources for prolonged metal contamination. Furthermore, the apparent rapid release of multiple metals from littered

cigarette butts increases the potential for acute harm to local organisms. Given the varying responses of organisms to metal contamination, knowledge of the leaching behaviour of metals from cigarette butts is necessary to assess the effect littered cigarette butts have on local biota and the environment in general. With a better understanding of the toxicity of cigarette butts^{3–5} and how contaminants are leached from them (see Micevka *et al.*³ Moriawaki *et al.*⁶ and this paper), the environmental hazards posed by littered cigarette butts may no longer be a subject of debate.

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