Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) Analysis of Trace Metals in Cigarette Litter collected at McNeese State University in Lake Charles, LA, United States

Liliya Snaychuk[†‡], Trey Vaughan[‡], Zachary Ullery[§], Chris Douvris[†], Derek D. Bussan[*§]

[†] Department of Biological and Chemical Sciences, New York Institute of Technology, Old Westbury, NY, United States;
[‡] Department of Chemistry, McNeese State University, Lake Charles, LA 70609, United States;
[§] Department of Chemistry, Eastern Kentucky University, Richmond, KY 40475, United States;
*e-mail: derek.bussan@eku.edu

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Cigarette smoking is the most commonly used form of tobacco in the world. It is practiced by a large portion of the population, especially young people. These people often ignore or disregard the harmful toxic impacts that cigarettes have on both themselves and the environment. The United States Center for Disease Control estimates that nearly 40 million U.S. adults still smoke cigarettes, with nearly 1600 U.S. youth starting cigarette smoking every day. Although it is well-known that smoking cigarettes is addictive and leads to a numerous health conditions including cancer, chronic pulmonary and heart disease, the effect of disposing the cigarette debris in the environment is not very well investigated. It is well known that tobacco smoke contains more than 7000 chemical components of which 250 of the components are harmful to human health. Therefore, there is a need to monitor the toxic elements in these residues, as it relates to the impact of cigarette smoking to the health of the smokers and the public health impact of society. Considering that college students are more likely to be smokers this study targeted a college campus in Southwest Louisiana, USA that still allows smoking on campus. The campus site chosen was McNeese State University with the typical younger college student population. Sample collection was done by distributing cigarette butt sample collection buckets throughout the campus for three weeks in March of 2018. The samples collected were then microwave digested with trace metal grade nitric acid, filtered with 0.45 μm filter and analyzed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) for the following trace elements As, Cd, Cr, Cu, Mn, Ni, Pb and Zn.

Keywords: inductively coupled plasma emission spectroscopy, cigarette butts, trace elements, college campus

Cigarettes are the most commonly used form of tobacco products in the world of which are known to be a source of environmentally toxic trace metals [1–3]. These trace metals are known to cause numerous health problems to the people who use them directly, as well as to those who are subjected to them indirectly [4]. Moreover, the waste byproducts specifically the cigarette butts are documented to be a point source for environmental pollution though accumulation on the ground [5]. Many harmful or potentially harmful constituents (HPHCs) are present in cigarettes. Many of them are known carcinogens, while others carcinogens are produced during combustion. Of importance are cardiovascular and reproductive toxic trace elements such as arsenic and lead [6–9], which are more readily released through the combustion of the cigarette. In addition, various carcinogen acting radioactive isotopes and other harmful trace elements such as manganese are contained in these products and can find their way into sediments and water resources, with manganese being linked to lower academic achievement in children [10].

As a result, it is imperative to monitor the fate of these chemicals originating from tobacco substances to the environment as these products tend to accumulate over time. Cigarette butts are the most common form of debris deposited from tobacco products and littered around in a wide variety of locations. Schneider et al. looked into the amount of money states and cities in the U.S. are spending on tobacco litter and found that millions of dollars are being spent on this project of which cigarette butt litter typically comprises between 22-36 % of all visible litter [11]. For example, it was reported in 2009 by the New York Times that the city of New York spent $11 million USD to remove cigarette litter [12].

As of November 2017, at least 2,082 U.S. colleges and universities have smoke-free policies so it was important to select a college/university that still permitted smoking [13] on-campus. It is important to note that a college campus is the place in which the student population spends most of their time. The reason is that students consume their time there in various activities, which include socializing, studying, participating in campus events, living in dormitories. As a result, the pollution of a campus directly relates to the health of its population. In this study we set out to investigate and report the concentrations of variety of trace elements in cigarette butts deposited around a campus that still allows smoking in designated areas. As the busiest time in terms of student's activities is the beginning of spring, we selected the month of March as the best time to perform our study. The campus selected was McNeese State University, located in the city of Lake Charles in Southwest Louisiana, USA. Using Inductively Coupled Plasma Emission Spectroscopy (ICP-OES) we determined Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Manganese (Mn), Nickel (Ni), Lead (Pb) and Zinc (Zn).

We chose ICP-OES as the technique for element analysis as it has the advantage of offering a cost- and time-effective method for analysis for a wide variety of trace elements when compared to other instrumental analysis techniques [14–17]. In addition, it is used regularly by both commercial and government agencies to test and ensure that metal toxins are within permissible limits. Overall, this study assesses the impact of littering cigarette butts as a point source for trace metals waste on a college campus.

Materials and Methods

Sample collection. Samples were collected from eight different locations around the 121-acre campus of McNeese State University, which is in the heart of the city of Lake Charles in Southwest Louisiana. The samples were collected in buckets labeled "Discard cigarette butts here to be used in a chemistry project". Cigarette Brands were labelled the following designations included: "KH-1", "SUA-1", "UQ-1", "DC-1", "FH-1". We collected three samples for each site. Locations included outside the university library, the cafeteria, the dining hall, the science building, the engineering building etc. All locations are specified in the provided maps. Samples were collected over approximately three weeks during the month of March 2018. See Supplemental Information Table S1 and Figure S1 that lists the target locations which are labeled A, B, C, D, E, F, G, and H. These locations were selected based on how busy these were during a normal week during the regular academic semester in terms of social activity, table one lists the GPS coordinates of the sample locations.

Sample preparation. After the three-week collection process, all sample buckets were brought back to the laboratory and processed as follows. The individual samples were placed on acid washed clean watch glasses with the correct sample label. Next the samples were heated in an oven at 105 °C until a constant sample weight was obtained. After a constant weight was obtained the samples were taken out of the oven and placed in a desiccator until they cooled to room temperature. The samples were than placed in a freezer at -80 °C for a day and subsequently lyophilized for 7 days. The freeze-dried samples were stored in a freezer until further processing. Next the dried cigarette butts were ground with a mortar and pestle and subsequently passed through a 250 **μ**m sieve and stored in "Ziploc" bags for storage until they were digested via microwave digestion. For the microwave digestion portion of the analysis, three 0.500g aliquots of each sample were placed into 55 mL perfluoro-alkoxy alkane microwave digestion vessels. Sample digestion was carried out through the addition of 10mL of trace-metal grade Fisher Brand (69-70 %) nitric acid in each vessel and were digested according to EPA Method 3052. After digestion the samples were cooled to room temperature before removing them. The samples were then filtered through a 0.45 μm Whatman PTFE membrane filter and diluted to 50 mL with (> 18.2 MΩ deionized water. After dilution aliquots of each digested sample were pipetted into 15 mL polypropylene centrifuge tubes for sample analysis.

Instrumentation. The acid digestion portion of the analysis was done by a MARSXpress microwave from the CEM Corporation in Mathews, North Carolina. Concentrations of Cd, Cr, Cu, Mg, Mn, Ni, Pb, and Zn elements were determined by an Agilent 725 ICP-OES, Agilent Technologies, Santa Clara, California. The optical system to characterize the wavelengths of the elements consisted of an Echelle polychromator and a VistaChip II. VistaChip II is a custom charge coupled device detector that can detect wavelengths from 167 to 785 nm. The wavelengths chosen for analysis are listed in Table 1.

Table 1. Selected elements and corresponding wavelength values (nm).

Element λ (nm)	Wavelength
As	188.980
Cd	214.439
Cr	267.716
Cu	327.395
Mg	279.553
Mn	257.610
Ni	231.604
Pb	220.353
Zn	213.857

Quality control/quality assurance. Calibration curves consisted of a calibration blank and six calibration standards. The calibration standards consisted of solutions of 0.2, 0.5, 1.0, 5.0, 10.0 and 50.0 *μ*g/g concentrations for each element. For quality assurance and quality control a separate batch from a different multielement solution of the 5.0 *μ*g/g calibrator was used for instrument performance. Recoveries ranged from ± 15 %. This calibration check was reexamined every ten samples analyzed as a continuing calibration check. The limit of detection was found to be ~0.1 μg/g for all elements examined. The standard curve regression statistics above ≥ 0.9990 was deemed acceptable.

Calculations. The dry mass concentrations of the samples were calculated through the sample solution concentrations, which were determined instrumentally with the following equation: $C_{dm} = (C_s * V * D)/m$, where "C_{dm}" corresponds to the dry mass concentration of sample (mg/kg), "C_s" to the extract concentration (mg/L), "V" to the volume of extract (L), "D" to the dilution factor [volume of solution after dilution (L)/volume of digestion solution (L)], and "m" to the mass of sample digested (kg) [18].

Results and discussion

The sample selection site was McNeese State University, which is in the heart of Lake Charles, in Southwest Louisiana, USA and various cigarette brands were collected as the college allows smoking on campus. Smokers in college are mostly young people who expose not only their own health but put the environment in danger from littering cigarette waste on campus. A literature search revealed that this work is the first study of tobacco product pollution on a college campus. It is important to note that a college campus is a place of general activity among its students. That is, a variety of events are organized and students tend to spend a large part of their social life there. As a result, the any traces of toxic substances, including heavy metals on campus grounds could have an impact on the campus population. With this in mind, a college campus presented a logical test site for our study.

Using Inductively Coupled Plasma Emission Spectroscopy (ICP-OES) we determined As, Cd, Cr, Cu, Mn, Ni, Pb and Zn in samples consisting of tobacco cigarette butts collected around the McNeese campus. ICP-OES is one of the most important tools for detecting and determining the concentration of trace elements as an ICP-OES instrument costs half the price of an ICP-MS one, ICP-OES has good detection limits and it is relative sensitive [19]. The collection of the cigarette waste lasted approximately three weeks during the month of March, in which time designated labeled buckets, located next to trash cans were filled with waste by students who voluntarily participated and disposed cigarette butts after smoking cigarettes. As the collection buckets were open to the air, it is important to note that there is a likelihood that the concentrations of the reported elements may have been affected by other parameters, such as the environmental pollution of the area.

From Table 2, the highest trace element concentrations determined by our analysis were those of Zn, which ranged from 175-313 μg/g. While we didn't find a comparable study in the literature, the EPA has established a drinking water standard for zinc to be under 5 mg/L [20]. With Zn concentrations in this study being 35-65x higher than that permitted in drinking water there is the possibility of Zn leaching out into the environment from the cigarette waste that could potentially raise a city or counties drinking water levels above the permissible levels of Zn for drinking water. Other health effects involving zinc have linked zinc to be a pro-carcinogenic factor as well as affecting immune system function. Moreover, the reduction of Zn in the body has been linked to increased blood Cd concentration [21].

The concentrations for copper, Mn and Ni were in the ranges of 31.6-37.4 μg/g, 18.2-46.2 μg/g, and 31.6-45.4 μg/g respectively, with Cr below the detection limit. Mn has been known to cause psychiatric syndromes (hallucinations, emotional lability), which was first described in 1800 as Manganese Madness, today it is known as Parkinson-like syndrome [22]. It has been determined that nickel in a burning cigarette might form the volatile, gaseous compound, nickel tetracarbonyl, and thereby be introduced into the respiratory tract. Torjussen *et. al* concluded that inhaled nickel is probably the main source of the nickel exposure to the respiratory tract in these workers [23].

Table 2. Trace found in sample cigarette butt samples.

Sample ID	**Trace Element Concentrations in μg/g**							
	As	**Cd**	**Cr**	**Cu**	**Mn**	**Ni**	**V**	**Zn**
KH	2 ± 0.3	0.6 ± 0.1	BDL	31.6 ± 1.1	18.2 ± 0.8	31.6 ± 1.7	0.7 ± 0.2	293 ± 16.1
SUA	6.3 ± 0.5	1.1 ± 0.1	BDL	43.3 ± 1.0	30.1 ± 1.6	43.3 ± 2.1	1.6 ± 0.2	313 ± 13.8
UQ	6.3 ± 0.5	0.8 ± 0.1	BDL	42.7± 1.5	35.4 ± 1.7	42.7± 2.0	2.1 ± 0.1	269 ± 7.3
DC	4.4 ± 0.6	1.4 ± 0.4	BDL	45.4 ± 6.5	46.2 ± 3.0	45.4 ± 1.7	2.6 ± 0.1	216 ± 8.3
FH	BDL	0.8 ± 0.3	BDL	32.4 ± 8.7	36.3 ± 1.1	32.4 ± 1.5	1.6 ± 0.2	175 ± 25

Arsenic exerts its toxicity by inactivating up to 200 enzymes, especially those involved in cellular energy pathways and DNA synthesis and repair. Arsenic most often finds its way into cigarette smoke through some of the pesticides that are used in tobacco farming. In our analyses, the concentrations for arsenic were in the range of BDL to 6.3 μg/g. According to a report from the California Air Resources Board and the Department of Health Services, smokers breathe in roughly 0.8 to 2.4 μg of inorganic arsenic per pack of 20 cigarettes, with approximately 40 percent of it being placed in the respiratory tract [24].

It is known that chronic Cd inhalation may result in impairment of pulmonary function with obstructive changes. Cd toxicity may cause renal dysfunction with both tubular and glomerular damage with resultant proteinuria. This study found concentrations for Cd ranging from 0.6-1.1 μg/g. Inhaled Cd bio-accumulates in the lungs and is dispersed outside the lungs to other tissues [25].

Finally, we determined 0.7-2.6 μg/g concentrations of vanadium in our samples. It has been reported that inhalation of vanadium and V compounds has consequences and adverse effects on the respiratory system [26].

All the elements analyzed in this study can produce harmful effects on the user of tobacco as well as they can pollute the environment. Although numerous studies detail the effects of tobacco and smoke to the users, there much fewer that concentrate on how the cigarette litter can affect the environment. In this study the studied environment is the highly used college grounds, which tends to be very busy as students concentrate their activities on it. As a result, the metal concentrations determined in the cigarette litter are of high interest as they constitute pollution for the college population.

Conclusion

This study is novel in the fact that a college campus environment has never been used for the collection and analysis for trace metals of cigarette butts before. Our study reported the levels of As, Cd, Cr, Cu, Mn, Ni, Pb and Zn found in waste by-products of five different types of cigarette products. The periodic assessment of trace metals in cigarette butt waste is important as there are health and environmental risks associated with littering cigarette butts. Future studies could look at the same analysis on a different college campus to compare data. A follow-up assessment to this study could also be done to check to see if there are any changes in concentrations of cigarette butts as tobacco manufacturers can and do change where they obtain there tobacco from for the manufacturing of their products.

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