



A comprehensive study on the leaching of metals from heated tobacco sticks and cigarettes in water and natural waters

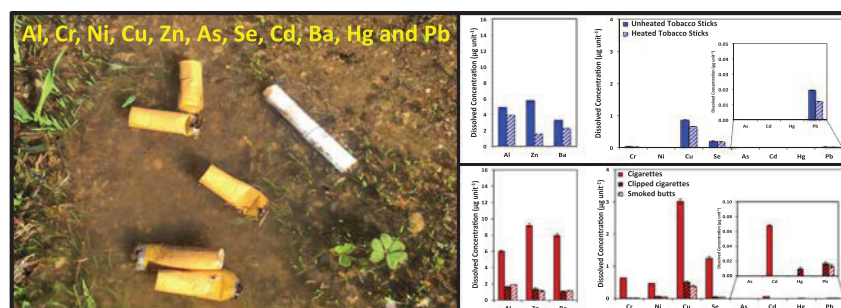
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HIGHLIGHTS

- Total metal concentrations in heated tobacco sticks are lower than that in unused cigarettes.
- The ash produced from conventional cigarettes retains a substantial amount of metals.
- Leaching of almost all metals from all types of tobacco products occurs.
- Tobacco is the major source of metal contamination.
- Varying the solution characteristics at environmentally relevant values did not affect metal leaching.

GRAPHICAL ABSTRACT



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ABSTRACT

The leaching behavior of Al, Cr, Ni, Cu, Zn, As, Se, Cd, Ba, Hg and Pb in water from two types of heat-not-burn tobacco sticks is presented here, and compared to that from conventional cigarettes. The total concentration of each metal in solid tobacco products was initially determined. Concentrations in used and unused tobacco sticks were similar and generally, lower than those in unused conventional cigarettes. Studies on the contribution of paper, filter and tobacco revealed that tobacco was the major source of metal contamination. Smoking conventional cigarettes reduced the total metal concentrations since a substantial amount of metals was retained in the ash; a post-consumption waste that is difficult to collect. Batch leaching tests were performed to determine dissolved concentrations as a function of time. With the exceptions of As and (in most cases) Hg that were not detected, metals were released at varying rates. At 24 h of soaking the percentage of metals leached ranged from 0.2–43%. The contribution of paper, filter and tobacco to the dissolved concentrations at 24 h of leaching was investigated and in almost all cases tobacco was the major source of metal contamination. The dissolved concentrations from ash were low as metals were strongly bound. Varying the pH, ionic strength and humic acids content at environmentally relevant values did not affect leaching of metals at 24 h of soaking. The use of river water, rain water and seawater as leachants was also not found to alter dissolved concentrations at 24 h compared to ultrapure water. The results presented here suggest that the consequences of improper disposal of tobacco products in the environment are two-sided and that next to the generation of plastic litter, discarded tobacco products can also act as point sources of metal contamination. Public education campaigns focusing on the environmental impact and best disposal practices are urgently needed.

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1. Introduction

Cigarette butts are the most commonly littered items in urban areas worldwide, accounting for 22–46% of visible litter (Novotny et al., 2009; Roder Green et al., 2014). Once disposed onto urban areas, cigarette butts move through the storm drains to streams, into the ocean, and back onto the beaches (Novotny et al., 2009). This makes cigarette butts the single most collected item in coastal environments each year, as reported by the Ocean Conservancy's International Coastal Cleanup (Ocean Conservancy (International Coastal Cleanup), 2019), and the second most found item on beaches in the European Union (European Commission, 2019). Thus, this type of litter cannot be considered as a local problem and the global economic and environmental implications should not be underestimated (Araújo and Costa, 2019).

Conventional cigarettes butts consist of remnant tobacco, the filter and the paper wrap. Although each component raises different environmental concerns, current attention focuses on the inability of discarded filters to biodegrade (Barnes, 2011; Novotny et al., 2009; Wallbank et al., 2017). To this end, tobacco product filters containing plastic were categorized as single-use plastic items in Europe (European Commission, 2019). Admittedly, there is markedly less awareness on the environmental impact of the toxic chemical components that may leach from cigarette butts and become bioavailable (Araújo and Costa, 2019; Booth et al., 2015; Lee and Lee, 2015; Micevska et al., 2006; Parker and Rayburn, 2017; Register, 2000; Slaughter et al., 2011). In this connection, cigarette butt leachates were found acutely toxic at concentrations ranging from 0.08 to 5 cigarette butt L^{-1} for different species such as water flea (*Daphnia magna*) (Register, 2000), marine bacteria (*Vibrio fischeri*) (Micevska et al., 2006), fish (Slaughter et al., 2011), snails (Booth et al., 2015) and fish and frog embryos (Lee and Lee, 2015; Parker and Rayburn, 2017). Moreover, the cytotoxic, genotoxic, and mutagenic effects on *Allium cepa* roots (Montalvão et al., 2019) and the potential for neurotoxic damage caused to mice (Cardoso et al., 2018) were recently reported.

A limited number of published studies attempted to identify and quantify the chemicals leaching from cigarette butts (Cardoso et al., 2018; Chevalier et al., 2018; Desideri et al., 2019; Dobaradaran et al., 2019, 2018, 2017; Moerman and Potts, 2011; Montalvão et al., 2019; Moriwiki et al., 2009). The studied chemicals mainly included metals (Cardoso et al., 2018; Moerman and Potts, 2011; Montalvão et al., 2019; Moriwiki et al., 2009), polycyclic aromatic hydrocarbons (Dobaradaran et al., 2019), nicotine (Roder Green et al., 2014), radionuclides (Desideri et al., 2019), or in one instance, focused on the leaching of nanoscale particles having selected metal species attached to them (Chevalier et al., 2018). Regarding metal species, Moriwiki et al. collected cigarette butts discarded on a roadside in Japan, measured metal concentrations (i.e., Cd, Cu, Pb, Cr, and As) in their leachates and confirmed the presence of arsenic (0.041 mg L^{-1}) after 2 h of leaching (Moriwiki et al., 2009). In a later work, the dissolved concentrations of Al, Ba, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sr, Ti and Zn from unsmoked conventional cigarettes and cigarette butts in aqueous solutions were determined over a range of soaking periods and pH values (Moerman and Potts, 2011). Almost all metals were detected after 1 day of soaking and the authors concluded that changes in pH within the range 4–6 did not affect the amount of metals leached. The presence of heavy metals was also confirmed in water with leached smoked cigarettes that was used to study the biological impact on mice (Cardoso et al., 2018) and toxicity in *Allium cepa* roots (Montalvão et al., 2019).

Recently, a novel 'heat-not-burn' tobacco product was introduced, which heats tobacco sticks using a specially designed holder at a temperature well below that required for initiating combustion. In the absence of combustion, the 'heat-not-burn' tobacco products do not produce ash during operation. The heated tobacco sticks contain tobacco, a polymer-film filter, a low-density cellulose acetate filter and a hollow acetate tube separating the tobacco and the polymer-film filter (Smith et al., 2016). Tobacco sticks and the heating system were

designed to reduce exposure to harmful and potentially harmful compounds and represent a new generation of tobacco products and a fast expanding market, daily gaining the attention of numerous consumers. Environmental studies on the 'heat-not-burn' tobacco product are limited to indoor air quality (Mitova et al., 2016), and the impact of discarding tobacco sticks in the environment and exposing them to natural waters is still unknown.

The present work presents for the first time, a comprehensive study on the leaching behavior of selected metals (Al, Cr, Ni, Cu, Zn, As, Se, Cd, Ba, Hg and Pb) from two types of marketed heated tobacco sticks (the non-aluminum (TS) and aluminum (TSAI) versions) and the results are compared to those obtained from conventional cigarettes (CC). Initially, the total concentration of each metal in used and unused solid tobacco products was determined. Then, batch leaching experiments were performed to determine dissolved concentrations and bioavailable fractions as a function of time. The contribution of the different parts of tobacco products (i.e., paper, filter, tobacco and ash for CC) to the total and dissolved concentrations was also investigated. At all times the results obtained for each used and unused tobacco product were thoroughly discussed and compared taking into account the literature data. The effect of different parameters (pH, salt and humic acids content) at environmentally relevant values on the leaching behavior of metals was also investigated. Finally, rainwater, river water and seawater were used as water matrices to leach metals from each used and unused tobacco product.

2. Material and methods

2.1. Chemicals, material and samples

Trace analysis grade HNO_3 (~68% v/v) was purchased from Fisher Scientific (Loughborough, UK) and NaOH ($\geq 98\%$, pellets) from Honeywell (Seelze, Germany). NaCl ($\geq 99.9\%$) was supplied by Penta (Radiova, Praha), and humic acids sodium salt by Fluka (Buchs, Switzerland). Milli-Q water was obtained from a water purification system (Barnstead EASYpure II) supplied by Thermo Scientific (Dubuque, USA).

Polypropylene 50 mL conical centrifuge tubes were used as sample containers. A Unimax 1010 shaker from Heidolph (Essex, UK) was used to agitate the samples in all cases. A Haraeus Labofuge 400 centrifuge from ThermoFisher Scientific (Waltham, USA) was used for phase separation after acid digestion. Mixed cellulose ester gridded membrane filters ($0.45 \mu\text{m}$ pore-size, 47 mm diameter) were purchased from Whatman (Dassel, Germany) and used during vacuum filtration of the water samples. A basic 20+ pH meter from Crison (Alella, Spain) was used to measure the pH.

River water was collected from Koiliaris River (Chania, Greece) and seawater from the Koum Kapi beach (Chania, Greece). Rain water was collected at the University campus (Chania, Greece) during rainy days by leaving open-air an amber glass bottle with a fitted plastic funnel. Each type of sample was collected in alternate days and in cleaned containers. Once in the laboratory, samples were filtered, stored in the dark at 4°C and used within a week for leaching. The composition of the three natural water types used here is given in Table A.1 in the Appendix.

2.2. Tobacco products

Two versions of marketed heated tobacco sticks (aluminum and non-aluminum versions) and one brand of CC were investigated here (Figs. 1 and A.1 in the Appendix). Philip Morris Products S.A is the only manufacturer of heated tobacco sticks and for this reason all tobacco products investigated here were from this manufacturer. Marlboro IQOS Regular Blue was the non-aluminum version (TS) of the tobacco sticks and HEETS Red Label was the aluminum (TSAI) one (Fig. 1). The only difference between the two versions was that in

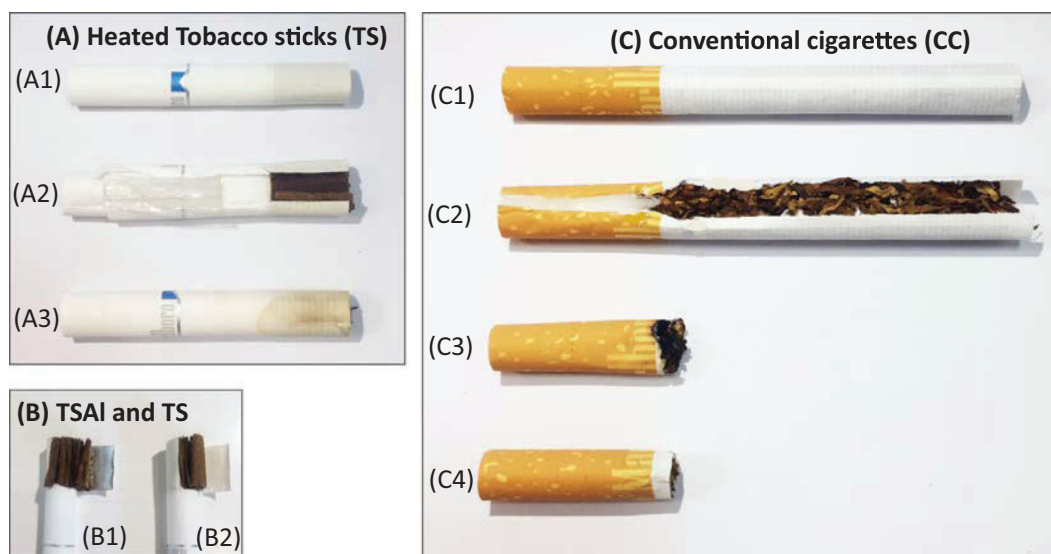


Fig. 1. Different representations of the tobacco products investigated here: (A) heated tobacco sticks (TS is only shown here for brevity; TSAI has similar representations): (A1) unused TS, (A2) open cut of a TS showing the three components investigated here (paper, filter and tobacco), and (A3) used TS (operated in a machine-smoking); (B) open cut of: (B1) TSAI showing the thin aluminum sheet under the paper over-wrap and (B2) TS; and (C) conventional cigarettes: (C1) unused CC, (C2) open cut of a CC showing the three components investigated here (paper, filter and tobacco), (C3) used CC (operated in a machine-smoking) and (C4) unused CC manually cut to the operated length (length of the filter plus 3 mm).

TSAI, the tobacco plug was wrapped in a thin aluminum sheet under the paper over-wrap. TSAI and CC (Marlboro Red Label) were purchased from the local distributor. The Marlboro IQOS Regular Blue tobacco sticks were supplied by Philip Morris Products S.A. (Neuchatel, Switzerland) since they were not available in Greece. When testing unused CC, two cigarette lengths were considered: (i) CC having the original length of unused cigarettes and (ii) CC cut to operated length (i.e. length of the filter plus approximately 3 mm of the tobacco plug) corresponding to the length of used CC after operating them with the machine-smoking.

The contribution of the different parts to the total and dissolved metal concentrations was also evaluated here. In these experiments, the paper, filter and tobacco parts of each tobacco product were separated and studied independently. For CC, the contribution from ash was also considered. Fig. A.1 shows a schematic representation of all tobacco products and their parts investigated here.

2.3. Machine-smoking regimens

All tobacco products were operated in a programmable single port machine-smoking from Burghart (Wedel, Germany). For TS and TSAI, the Health Canada Intense (HCI) smoking regime was used (Health Canada Official Method T-115, 1999), which included the following puffing parameters: 55 mL puff volume, 2 s puff duration, and 30 s puff interval. During machine operation, the IQOS™ 2.4 Plus heating device Philip Morris Products S.A. (Neuchatel, Switzerland), purchased from a local distributor, was employed to heat the sticks (Fig. A.1). The CC were ignited using a flameless lighter and smoking was programmed according to the puffing parameters set by ISO 3308 (ISO 3308, 2012): 35 mL puff volume, 2 s puff duration, and 60 s puff interval. The machine operation was performed until a predefined butt length (i.e., the length of the filter plus approximately 3 mm of the tobacco plug).

2.4. Determination of metal concentrations

The mean masses of unused TS and TSAI were 0.7607 and 0.7633 g respectively. After operation the tobacco stick units weighted 0.7007 and 0.7099 g respectively. Unused CC weighted in average 0.8386 g (whole product; total length) and 0.2159 g when cut to the operated length. After smoking, the mean mass of CC was reduced to 0.2561 g.

The average masses of all used and unused tobacco products and their parts are summarized in Table A.2. As seen, the three types of tobacco products and their corresponding parts had different masses. Moreover, after operation the mass of each CC unit (representing the discarded unit of these products) was significantly reduced. To allow direct comparison among the different tobacco products, metal concentrations were expressed as $\mu\text{g unit}^{-1}$ of solid tobacco product rather than $\mu\text{g g}^{-1}$.

2.4.1. Total metal concentrations

For the determination of the total concentrations of the selected metals, one unit of tobacco product was submerged and allowed to soak for three days in 9 mL of HNO_3 (~68% v/v). Each solid-liquid mixture was then diluted up to 45 mL with ultrapure water and allowed to soak for four extra days. Shaking at 180 rpm was applied at all times. After acid digestion, samples were centrifuged and the supernatants were collected for analysis. The contribution of the different parts of the tobacco products to the total concentration of each metal in unused and used tobacco products was carried out following the same procedure. The amount of paper, filter, tobacco and ash (in the case of CC) was adjusted to reach quantifiable metal concentrations. All experiments were run in triplicate.

2.4.2. Dissolved metal concentrations

For the determination of dissolved concentrations, tobacco products were submerged and allowed to soak in aqueous solutions at 180 rpm for a preset period of time. Unless otherwise stated in the text, tobacco products were soaked for 24 h in water. After soaking, the resulting solid-water mixture was immediately filtered and HNO_3 (~68% v/v) was added to the leachate. The acidified water extracts were stored in the dark at 4 °C until analysis.

A 10 L Kg^{-1} liquid-to-solid ratio (L/S) was used for all leaching experiments. This ratio corresponded to three TS or TSAI units soaked in 25 mL water solution, three unused CC units in 25 mL, six unused CC units at an operated length in 15 mL and six used CC units in 15 mL of aqueous phase. The contribution of the different parts of tobacco products to the dissolved concentrations was also investigated. For CC, the ash was also considered. In these experiments, the ash produced from 3 CC was soaked in 25 mL of water so as to allow direct comparison with the results obtained from unused CC. Table A.3 summarizes the number of units of TS, TSAI, CC and their parts, and the volume of

water used for the leaching experiments. The effects of pH, ionic strength and organic matter content on the dissolved metal concentrations were independently studied. The leaching solutions were adjusted to pH 4 and pH 8 using proper amounts of HNO_3 and NaOH (Moerman and Potts, 2011). All experiments were run in triplicate.

2.4.3. Inductively coupled plasma-mass spectrometry (ICP-MS) analysis

Total and dissolved metals concentrations were measured by ICP-MS using a 7500 cx ICP-MS coupled to an ASX-500 autosampler, both from Agilent Technologies. The system was controlled using the ICP-MS chemstation software. For the determination of metal concentrations, external calibration was applied. The limit of detection (LOD) and the limit of quantification (LOQ) of the calibration curves are shown in Table A.4 in the Supporting information. QA/QC procedures ensured that the system was operating within acceptable limits and that the method's performance was conforming. These procedures included the analysis of one calibration blank and one calibration standard after each group of 10 samples as a calibration check. In addition, recovery studies were carried out after every 18 samples by the fortification of a sample with all target metals at known concentrations (approximately two times the concentrations originally found in the fortified sample). Relative recoveries varied between 90 and 110% in all cases (data not shown).

3. Results and discussion

3.1. Total metal concentrations

The total metal concentrations, defined as the total amount of each metal sorbed to the solid tobacco products, were determined for used and unused tobacco products and the results are given in Fig. 2. As seen, in all tobacco products the highest total concentration values were recorded for Al, Zn and Ba, whereas the lowest were for Cd, Hg and Pb. Arsenic was the only metal that was not detected in all samples.

Direct comparison between the two versions of heated tobacco sticks, showed similar levels of total metal concentrations in all types tested (used and unused). The only exception was aluminum in both used and unused TSAI products, where concentrations were close to 20 times larger than the corresponding concentrations in TS, as a result of the thin aluminum sheet used to wrap the tobacco plug. Although not considered here, it is expected that a portion of metals was transferred to the aerosol generated during tobacco sticks operation. However, such concentrations were previously reported to be of the order of ng unit^{-1} (Schaller et al., 2016), explaining the similar levels of total metal concentrations found in used and unused heated tobacco sticks. All types of heated tobacco sticks tested here generally showed lower total metal concentrations than unused CC at the original length. The only exceptions were chromium and lead, where similar metal contents were recorded, and the expected higher aluminum content in TSAI. Fig. 2 also shows that the total metal concentrations in CC were generally reduced after use *i.e.* reduction in size. Past investigations reporting the chemical composition of mainstream smoke reported low metal concentrations of the order of ng cig^{-1} in smoke generated from CC during operation (Bernhard et al., 2005; Rustemeier et al., 2002). It was therefore assumed that smoked CC do not accumulate metals from the remainder cigarette during operation and that the ash retains a portion of the metal content. Indeed, comparison of the total concentration of each metal in used CC and unused CC at the operated length (*i.e.*, the length of the filter plus approximately 3 mm of the tobacco plug) showed similar results.

Next, the contribution of the different parts to the total metal concentrations of each tobacco product was determined (results shown in Tables A.5, A.6 and A.7). The different parts studied were paper, filter and tobacco, and for CC, the ash was also considered. It is noted that the results on the whole tobacco products were obtained using units from different packs than those used for studying the contribution of

the different parts. This may have accounted for the small variability observed between the total metal concentrations in the whole tobacco products and the sum of the metal concentrations found in the different parts. Although these values were not substantially different, the discussion that follows focuses on the relative values obtained for the different parts rather than the direct comparison of their sum to the total metal concentrations found in the whole tobacco products. Based on the results, tobacco was the major source of most metals in both types of used and unused heated tobacco sticks (Tables A.5 and A.6). The only exceptions were recorded for aluminum (paper was the major or an important source), lead (similar contribution from paper and tobacco), chromium and mercury (filter and tobacco plug were contributing approximately to the same extent). According to Table A.7, tobacco was also the major metal source in unused CC at the total length. After CC operation, a substantial amount of metals was retained in the ash, confirming our previous assumption that smoked CC do not accumulate metals from the remainder cigarette during operation. The ability of ash to retain metals was regarded as critical in terms of environmental impact, since this type of post-consumption waste should be more difficult to collect than smoked cigarette butts.

The present results are in agreement with past investigations where tobacco was reported to be the major source of metal contamination in different brands of CC, and the reported concentrations ranges were similar to the ones found here (Chiba and Masironi, 1992; Eldridge et al., 2015; Fresquez et al., 2013; Journal, 2015; Moerman and Potts, 2011; Nada et al., 1999; Pinto et al., 2017). It is interesting to note that significantly higher metal concentrations were detected in tobacco counterfeit or illicit-trade tobacco products compared to the genuine equivalents (Stephens et al., 2005). In all reports, the high metal content in tobacco was attributed to the ability of tobacco plant to accumulate metals during growth and cultivation (Moerman and Potts, 2011; Tso, 1990). Current knowledge concludes that metals can be introduced in agricultural soils after the application of fertilizers, and there were case studies where the application of municipal sludge as a fertilizer was responsible for tobacco plant contamination from metals (Kazi et al., 2009; Moerman and Potts, 2011; Talhout, 2014). Further introduction of metals in tobacco may occur during cigarette manufacturing (*e.g.*, washing, drying and curing) and packing or storage processes after tobacco plant harvesting (Moerman and Potts, 2011; Talhout, 2014).

3.2. Leaching kinetic studies

Bioavailability and environmental risk objectives on metals sorbed on solids are typically based on dissolved concentrations (also called bioavailable or free concentrations) rather than the total concentrations, since there is evidence that metals complexed/sorbed on solids are less toxic to micro-organisms than the free metal ions present in solutions (Rieuwerts et al., 1998). A typical procedure for determining bioavailable concentrations is to perform leaching studies, and the final amount of a chemical desorbed depends on the properties of the solid matrix and target chemical as well as the composition of the water phase used for leaching.

To study the leaching kinetics of the selected metals, batch tests were performed with used and unused tobacco products soaked in ultrapure water for times ranging between 30 min to 6 days. Triplicates of fresh samples were soaked to ultrapure water for a preset leaching time and the entire leachate was used for analysis. Based on the results obtained, arsenic was not detected in the leachates from tobacco products whereas nickel, mercury, lead and cadmium were only detected in some leachates. The latter was attributed to differences between the tobacco stick and cigarette units used in the experiments but also to dissolved concentrations being present at trace levels, near to the limit of quantification of the method. Fig. 3 shows representative concentration-time profiles for Zn, Ba and Cu leached from used and unused TS and CC. The leaching curves for the remaining detected metals

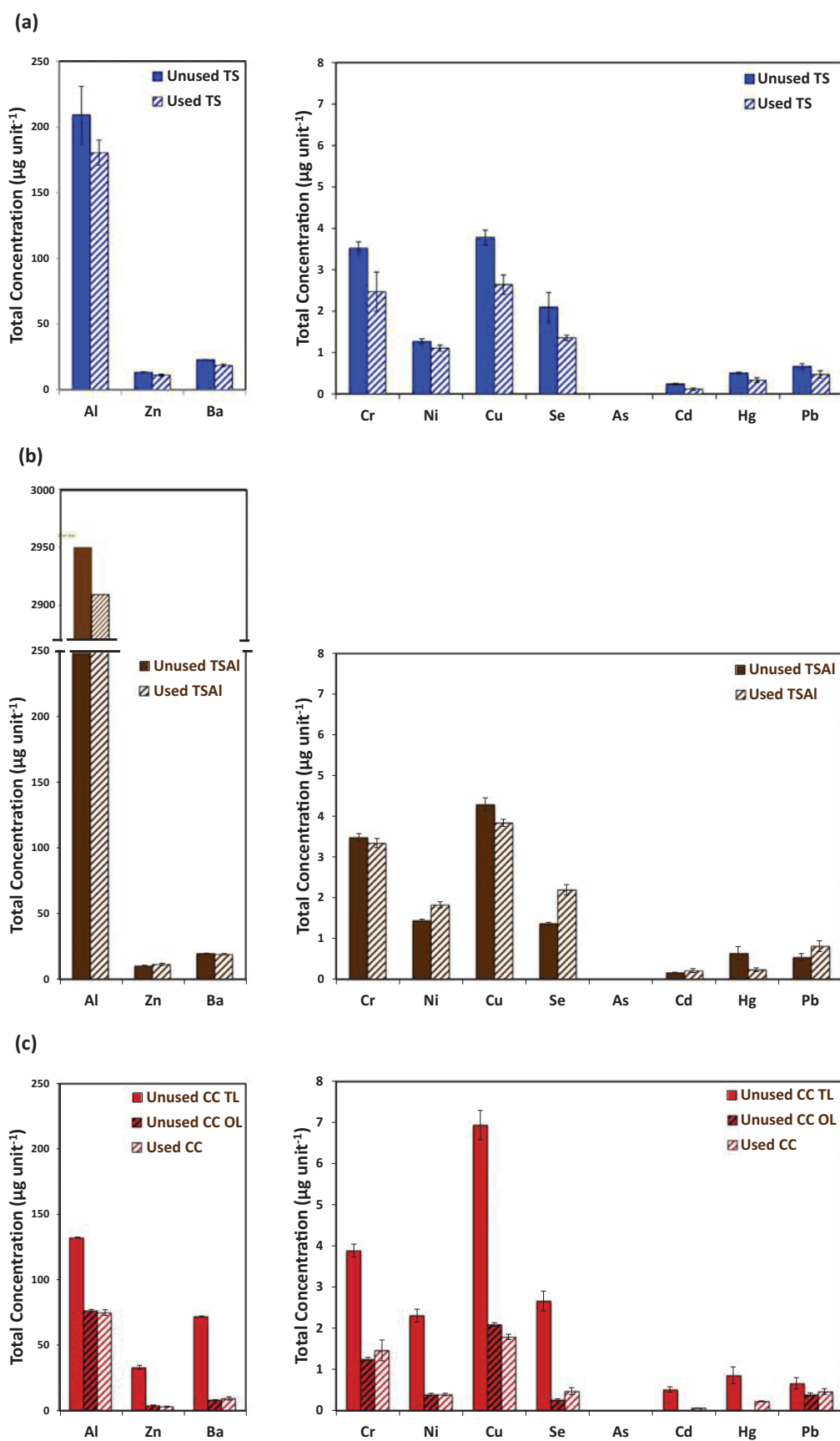


Fig. 2. Total metal concentrations in used and unused tobacco products for: (a) heated tobacco sticks non-aluminum version (TS); (b) heated tobacco sticks aluminum version (TSAI); and (c) conventional cigarettes (CC). For unused CC, total concentrations at total length (TL) and operated length (OL) are included. To facilitate comparison between graphs, a scale break is used in the y-axis of the Al, Zn and Ba concentrations in graph (b).

are given in Fig. A.2 (for TS), Fig. A.3 (for TSAI) and Fig. A.4 (for CC) in the Appendix. Mercury was only detected in some leachates from used CC at concentrations close to the limits of detection or quantification. For this reason, a representative leaching curve could not be constructed and included in Fig. A.4. The results showed that for all tobacco products, the majority of detected metals could be quantified in the leachate after just 30 min of soaking time.

Figs. 3 and A.2–A.4 show that three different leaching behaviors were recorded here. The first trend was observed for barium where dissolved concentrations increased with increasing soaking time and revealed a potential for increased metal release over time. The second trend was recorded for most target metals and showed no significant change in dissolved concentrations after 8 to 48 h of leaching (depending on the metal), i.e. equilibrium was reached. It is acknowledged however that in the present batch tests leaching occurred in a closed system, and these seemingly static concentrations throughout the study period may be due to dynamic equilibrium between the tobacco product samples and water soaking solution. In this connection, past reports suggested that in real case scenarios, greater amounts of these metals 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 (Desideri et al., 2019; Moerman and Potts, 2011). The third trend observed here was that of copper, where dissolved concentrations initially increased and after 24 to 48 h they decreased, most probably due to the formation of insoluble compounds and complexes (Moerman and Potts, 2011) that were eliminated during the filtration step prior to ICP-MS analysis. The described trend for copper was observed in the leachates prepared from all tobacco products except those from used TSAI and used CC. The variable relationships observed between metal concentrations leached from used CC and soaking time in aqueous solution were in good agreement with similar investigations studying leaching of Ba, Zn, Ni, Cr, Cd, Pb and Cu over time (Moerman and Potts, 2011). Although the leaching behavior of aluminum from unused cigarettes was similar to the one reported here, the dissolved concentration of aluminum in smoked cigarette leachates was reported to decrease with time (Moerman and Potts, 2011). It is noted however that in this report a 34-day study period was allowed, which is much longer than the 6-days study period used here.

The results obtained here showed that used TS and TSAI had faster equilibration times than unused sticks for the majority of the metals, suggesting that the heating process was affecting leaching kinetics. At the same time, the leaching curves from unused CC (operated length) and used CC were similar, suggesting that smoking did not affect the leaching behavior of metals in water. Finally, faster equilibration times were observed for all metals in unused CC (total length) compared to unused heated tobacco sticks. The differences in tobacco treatment for CC and heated tobacco sticks (Smith et al., 2016) were assumed to account for this observation.

Overall, under the present experimental conditions the majority of the metals reached concentrations at equilibrium or near-equilibrium conditions after 24 h of soaking. Taken that dissolved concentrations at 24 and 48 h were not markedly different, the 24 h soaking time was selected for all subsequent leaching experiments, also allowing comparison to past results on CC (Moerman and Potts, 2011).

3.3. Dissolved concentrations at 24 h soaking

The dissolved metal concentrations in used and unused tobacco products at 24 h of leaching time are given in Fig. 4. As discussed earlier, Ni, As, Hg, Pb and Cd were under the limit of detection of the analytical method in most of the leachates and when quantified, low concentrations (in the range 3–70 ng unit⁻¹) were recorded. Moreover, in accordance with the results presented during the determination of total metal concentrations, Al, Zn and Ba were the most abundant metals in all leachates.

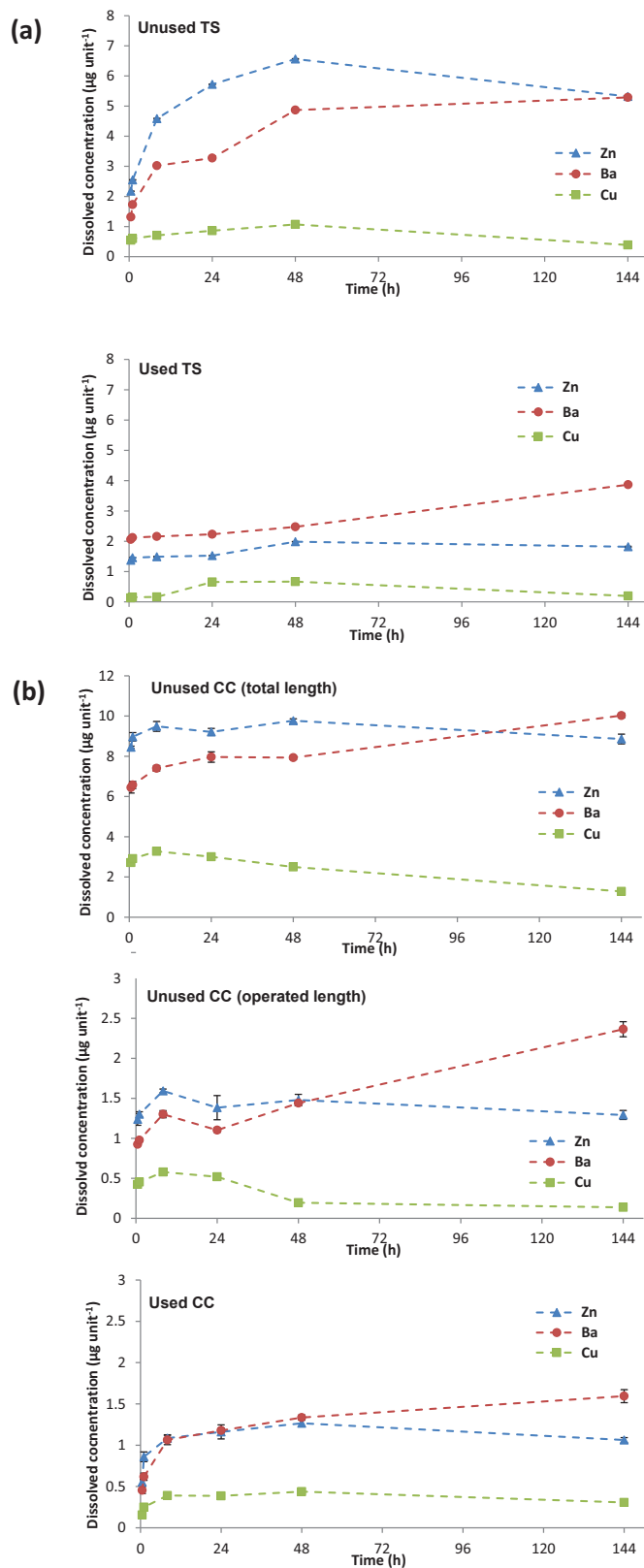


Fig. 3. Leaching kinetic curves of Zn, Ba and Cu obtained for used and unused (a) heated tobacco sticks non-aluminum version (TS); and (b) conventional cigarettes (CC).

Direct comparison between the two types of heated tobacco sticks showed similar levels of dissolved concentrations for metals. The only exception was aluminum where as expected, higher concentrations were recorded for the aluminum-version of tobacco sticks. Comparable

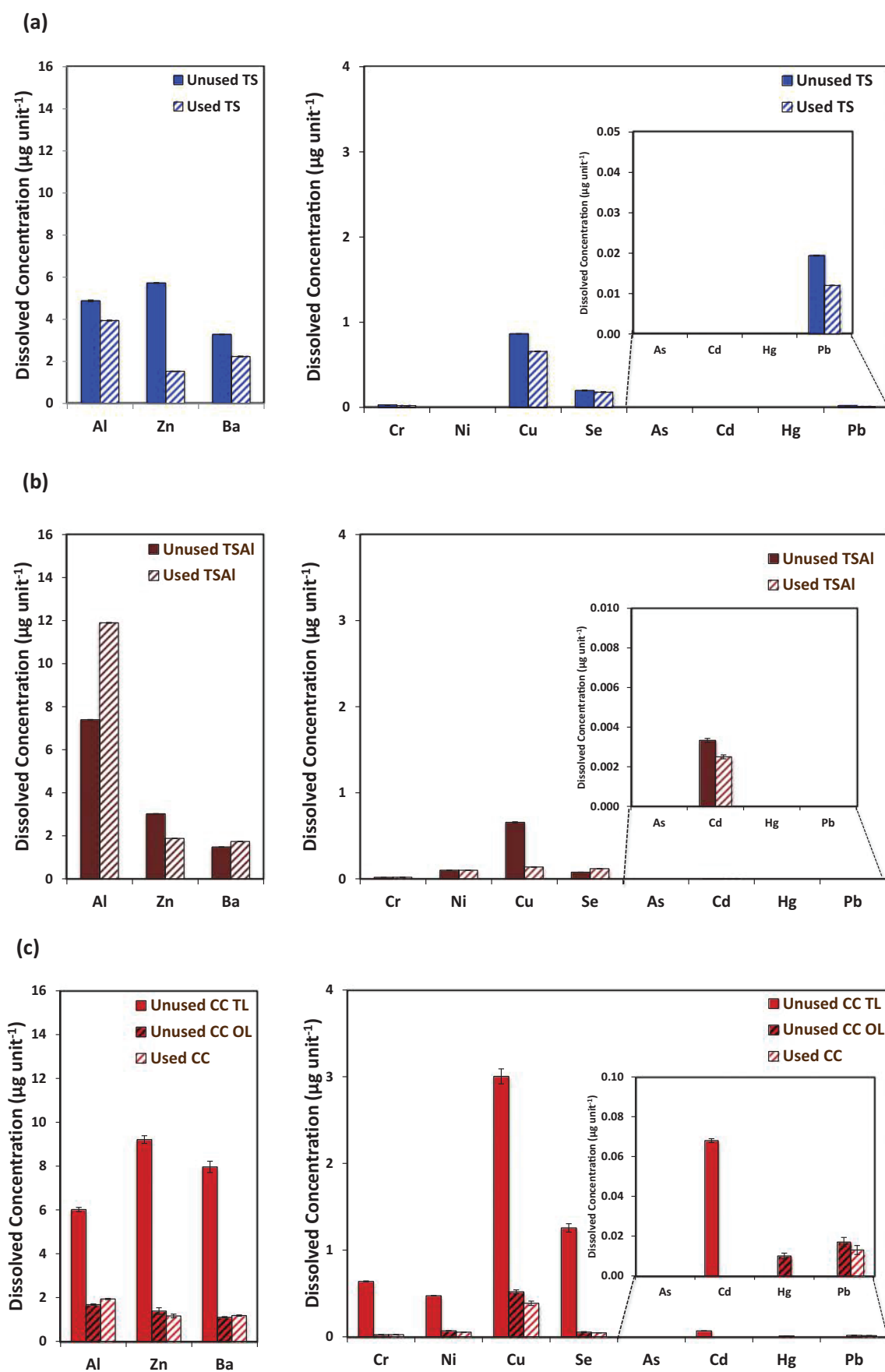


Fig. 4. Dissolved metal concentrations in used and unused tobacco products at 24 h for: (a) heated tobacco sticks non-aluminum version (TS); (b) heated tobacco sticks aluminum version (TSAI); and (c) conventional cigarettes (CC). For unused CC, dissolved concentrations from CC at total length (TL) and operated length (OL) are included.

concentrations were also found in the leachates of used and the corresponding unused heated tobacco sticks, with the exception of the lower levels of Zn and Cu obtained in the leachates of used TS and used TSAI respectively; an effect also shown in Fig. 3. More significant was the higher dissolved concentration of aluminum found in the leachate of used TSAI compared to the leachate of the unused product. Since the main source of this metal in TSAI was the thin aluminum sheet used to wrap the tobacco plug, it was assumed that the heating process affected the solid sheet and facilitated metal leachability. The higher dissolved concentrations of aluminum found in the leachates of used TSAI at all leaching times (Fig. A.3) compared to unused TSAI (Fig. A.2) further supported this assumption.

Leaching of metals from unused CC at operated length and used CC led to similar dissolved concentrations, whereas those found in the leachate of unused CC at the total length were higher reflecting the higher amount of tobacco in the original CC products. The dissolved concentrations of Al, Ba, Cd, Cr, Cu, Ni, Pb and Zn were similar to those obtained in a previous report investigating 24 h leachates from smoked and unsmoked cigarettes (comparison of data given in Table A.8) (Moerman and Potts, 2011). Compared to unused heated tobacco sticks, higher dissolved metal concentrations were leached from unused CC at the total length. On the contrary, for used CC, dissolved concentrations were lower than those from used TS and TSAI. Both observations reflected the differences in total metal content available for leaching in the initial solid tobacco products, and for used CC the reduction in tobacco (assumed at this point to be the major source of metals) after smoking.

The percentage of each metal leached at 24 h of soaking was then calculated as the percentage ratio of the dissolved concentration over the total concentration and the results are shown in Table A.9 in the Appendix. For used CC, the unused product at operated length was used as reference. As can be seen, the percentage of metals leached ranged from 0.2 to 43%, with the lowest values being recorded for Al, Cr and Pb. In general, for each metal the percentages leached from used and the corresponding unused tobacco product were similar and any variations were generally assumed to be due to the inherent differences in the initial solid tobacco product units used for leaching or the low concentrations in the leachates. The obtained results suggested that although operating the tobacco products affected the leaching kinetics, the amount released at equilibrium or near-equilibrium conditions remained more or less the same.

The contribution of the different parts of each tobacco product to the dissolved metal concentrations was then assessed and the results are shown in Tables A.10, A.11 and A.12 in the Appendix. The different parts studied were paper, filter and tobacco, and for CC, the ash was also considered. Similarly to the studies on total metal concentrations, some variability was observed when comparing the dissolved metal concentration from the whole tobacco products compared to the sum of the dissolved metal concentrations for the different parts, due to units originating from different packs. As expected, tobacco was the major source of dissolved metal concentrations in the majority of cases. The only exception was for aluminum where in TSAI, the paper was the main aluminum source and in TS and CC tobacco and paper seemed to contribute equally to the aluminum content. Among the different metals targeted here, Cu, Zn, Se and Ba were the only metals that were quantified in the leachate prepared from ash. Although the results on the total metal concentrations in ash showed that a substantial amount of metals was retained during smoking, only a small fraction of them was released into the aqueous phase under the present experimental conditions.

3.4. The effects of pH, salt and humic acids and leaching in natural waters

The pH is considered as one of the most important factors affecting the leaching of metals from solid wastes, since it is directly related to their solubility and stability in the aqueous phase, as well as to the

formation and precipitation of insoluble species (Saikia et al., 2018). In this context, past knowledge points that the pH of the aqueous leachant solution may lead to high variations in the quantities of contaminants that may be released into the environment (Quina et al., 2009). Nonetheless, previous publications reported that pH values ranging from 4 to 6 (Moerman and Potts, 2011) and from 4 to 8 (Desideri et al., 2019) had no effect on the metal and radionuclide concentrations leached from unsmoked cigarettes (Moerman and Potts, 2011) and cigarette butts (Desideri et al., 2019; Moerman and Potts, 2011). Only stronger acidic conditions (pH = 2.5) were reported to promote the leachability of radionuclides (^{210}Po) (Desideri et al., 2019). During the present investigations the pH of the leachant varied from 4 to 8. Table 1 shows the results on used and unused TS and CC. In the Appendix, the corresponding results on TSAI and unused CC at an operated length are given in Tables A.13 and A.14 respectively. In each Table, the results with ultrapure water as leachant are also given for comparison. The pH in leachates obtained with ultrapure water varied from 6.6–6.9 for all types of tobacco sticks and unused CC at the full length, and from 7.1–7.2 for used CC and unused at operated length. As seen, the present results confirmed past conclusions, and changing the pH of the aqueous solution within this range showed no significant changes in dissolved metal concentrations of the target metals.

In the presence of complexing agents, metals that would otherwise not be soluble under the conditions in the leachant, can be mobilized and reach concentrations far exceeding the equilibrium concentrations existing in the phase system (van der Sloot et al., 1997). To this end, past publications have reported that leaching of metals from solid samples is highly associated to the presence of NaCl in the aqueous solution (Kim and Osako, 2003; Luo et al., 2019). At the same time, humic acids can provide important sources of dissolved organic ligands with a high affinity towards metals and were also found to adsorb on the surface of particles and alter its properties (Kim and Osako, 2003; Liu and Gonzalez, 1999; Luo et al., 2019). The leaching of metals in the presence of humic acids can be considered as a complex process whose final effects will depend on the interplay of several factors such as metal and solid properties, dissolved organic matter and metal concentrations, the presence of coexisting metals, water pH and ionic strength (Klučáková et al., 2018; Liu and Gonzalez, 1999; Luo et al., 2019; van der Sloot et al., 1997; Zhao et al., 2017). To investigate the effects of salt and humic acids, two independent experiments were run where the salt content of the leachant was set at 3.5% w/v NaCl (representing the seawater matrix) and the humic acids content was set at 2.5 mg L⁻¹ (representing an environmentally relevant value for natural organic matter). The results are given in Table 1 (used and unused TS and CC), Table A.13 (TSAI) and Table A.14 (unused CC at an operated length). For comparison, the results with ultrapure water are also given representing the cases of 0% w/v NaCl and 0 mg L⁻¹ humic acids. As seen, such changes in ionic strength and organic matter content of the soaking solution did not affect considerably the leaching of metals from used and unused tobacco products. To the best of our knowledge, there are no past reports investigating the effect of NaCl and humic acids on the leaching of metals from tobacco products. Nevertheless, past reports dealing with the release of metals from different solid wastes reported an increase in dissolved metal concentrations in the presence of NaCl and dissolved organic matter, but such effects were observed at considerably higher concentrations than those studied here, namely 15–30% for NaCl (Ruşen et al., 2008; Turan et al., 2004; Weibel et al., 2018) and 15.2–213.1 mg L⁻¹ for humic acids (Luo et al., 2019; Potysz et al., 2017).

To investigate the leaching behavior in natural water, river water, rain water and seawater were then used to leach metals from used and unused tobacco products. The results for TS, TSAI and CC are given in Tables A.15, A.16 and A.17 respectively. As can be observed, for all tobacco products, the dissolved metal concentrations in natural water

Table 1
Effect of pH, NaCl and humic acids content on the leaching of metals from unused and used TS and CC at 24 h soaking time. The concentrations of metals in ultrapure water are also given. In the Appendix, Table A.13 shows the corresponding results for TSAI and Table A.14 shows the results for unused total length CCs. All concentrations are in $\mu\text{g units}^{-1}$. Error values correspond to the standard deviation of three replicated analysis.

Heated tobacco sticks non-aluminium version (TS)									
Unused					Used				
Ultrapure	pH = 4	pH = 8	Humic acids	NaCl	Ultrapure	pH = 4	pH = 8	Humic acids	NaCl
Al	4.88 ± 0.04	6.27 ± 0.07	8.9 ± 0.4	11.9 ± 0.1	3.94 ± 0.02	7.3 ± 0.3	5.3 ± 0.2	7.78 ± 0.02	8.38 ± 0.03
Cr	0.0293 ± 0.0001	0.070 ± 0.001	0.019 ± 0.001	0.052 ± 0.001	0.02093 ± 0.00001	0.0111 ± 0.0005	0.0070 ± 0.0001	0.017 ± 0.001	0.0083 ± 0.0001
Ni	<LOD	0.148 ± 0.002	0.188 ± 0.004	0.123 ± 0.003	<LOD	0.129 ± 0.003	0.092 ± 0.003	0.032 ± 0.004	0.0075 ± 0.0001
Cu	0.863 ± 0.002	1.07 ± 0.01	1.15 ± 0.01	1.03 ± 0.02	0.657 ± 0.004	0.182 ± 0.002	0.203 ± 0.003	0.081 ± 0.001	0.347 ± 0.002
Zn	5.72 ± 0.01	4.49 ± 0.08	4.94 ± 0.07	3.81 ± 0.02	1.527 ± 0.005	2.58 ± 0.05	1.48 ± 0.01	1.25 ± 0.03	0.903 ± 0.003
As	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Se	0.197 ± 0.004	0.163 ± 0.003	0.40 ± 0.01	0.102 ± 0.005	0.178 ± 0.003	0.65 ± 0.01	0.42 ± 0.01	0.069 ± 0.001	0.079 ± 0.003
Cd	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Ba	3.27 ± 0.01	2.75 ± 0.04	2.30 ± 0.09	1.695 ± 0.004	2.23 ± 0.02	3.96 ± 0.02	2.20 ± 0.03	1.84 ± 0.05	4.10 ± 0.01
Hg	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Pb	0.0194 ± 0.0001	0.010 ± 0.001	<LOD	<LOD	0.01200 ± 0.00002	<LOD	<LOD	<LOD	<LOD
Conventional cigarettes (CC)									
Unused (total length)					Used				
Ultrapure	pH = 4	pH = 8	Humic acids	NaCl	Ultrapure	pH = 4	pH = 8	Humic acids	NaCl
Al	6.01 ± 0.09	4.03 ± 0.08	3.59 ± 0.09	4.18 ± 0.01	1.94 ± 0.03	1.62 ± 0.02	2.564 ± 0.008	3.508 ± 0.008	2.48 ± 0.01
Cr	0.639 ± 0.006	0.092 ± 0.004	0.073 ± 0.006	0.055 ± 0.001	0.0248 ± 0.0010	0.0053 ± 0.0006	0.0075 ± 0.0004	0.016 ± 0.001	0.0046 ± 0.0009
Ni	0.474 ± 0.002	0.381 ± 0.01	0.333 ± 0.005	0.221 ± 0.007	0.0533 ± 0.0015	0.0137 ± 0.0003	0.024 ± 0.001	0.035 ± 0.003	0.0060 ± 0.0003
Cu	3.00 ± 0.09	2.84 ± 0.02	2.8 ± 0.2	2.29 ± 0.03	0.39 ± 0.03	0.20 ± 0.01	0.250 ± 0.002	0.31 ± 0.02	0.208 ± 0.009
Zn	9.21 ± 0.17	9.1 ± 0.3	10.3 ± 0.1	6.36 ± 0.08	1.16 ± 0.08	0.71 ± 0.01	0.838 ± 0.005	1.3 ± 0.2	0.589 ± 0.005
As	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Se	1.26 ± 0.05	0.471 ± 0.006	0.410 ± 0.009	0.325 ± 0.003	0.0453 ± 0.0014	0.044 ± 0.001	0.056 ± 0.001	0.029 ± 0.001	0.0615 ± 0.0004
Cd	0.0681 ± 0.0010	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Ba	8.0 ± 0.3	5.71 ± 0.07	5.48 ± 0.04	4.14 ± 0.02	1.18 ± 0.03	0.559 ± 0.004	0.637 ± 0.009	0.796 ± 0.004	1.619 ± 0.007
Hg	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Pb	<LOD	0.022 ± 0.001	0.02004 ± 0.00004	<LOD-<LOD	0.013 ± 0.002	<LOD	<LOD	<LOD	<LOD

samples were comparable to those obtained with ultrapure water, suggesting that the composition of natural water was not affecting the leaching behavior of metals.

3.5. Implications

The leaching of metals from heated tobacco sticks, a novel tobacco product category, has been thoroughly investigated, discussed, and compared to that of conventional cigarettes. The results suggest that tobacco products improperly discarded in the environment, can act as point sources of prolonged metal contamination. Tobacco was found in almost all cases to act as the major source of metal contamination. This conclusion also brings in the spotlight the issue of counterfeit (or illicit-trade) tobacco products where literature data report significantly higher metal concentrations than the genuine equivalents (Stephens et al., 2005). Single batch leaching tests were performed here and it is acknowledged that the use of column percolation tests, which represent a better approximation to leaching process under natural conditions, may lead out a larger amount of metals (Desideri et al., 2019; Moerman and Potts, 2011). Although a tobacco product unit does not pose a serious threat to the environment, the cumulative effect of large quantities of discarded tobacco products in localized areas may amplify the problem (Booth et al., 2015). In the case of conventional cigarettes an additional concern exists: the ash produced during smoking retains a substantial amount of metals, and this type of post-consumption waste should be difficult to collect compared to smoked cigarette butts.

The EU Directive 2019/904 on the reduction of the impact of certain plastic products on the environment identified tobacco products with filters containing plastic as single-use plastics, and acknowledged the huge environmental impact caused by post-consumption waste of these products when discarded directly into the environment (European Commission, 2019). The same Directive established extended producer responsibility schemes and awareness-raising requirements, and advised EU Member States to promote measures to reduce litter from post-consumption waste, such as appropriate waste receptacles in common litter hotspots. The results presented here demonstrate that the negative consequences of improper tobacco product waste disposal are two-sided, and that next to the generation of plastic waste, discarded tobacco products can also act as point sources of metal contamination. The negative environmental impact of tobacco products waste is therefore, not due to the presence of filters alone, but to the tobacco product as a whole.

Public education campaigns and raising of public awareness are urgently needed to communicate best disposal practices and emphasize that discarded tobacco products are not just litter within the frame of single-use plastics, but can also act as point sources for metal contamination. Although, tobacco product waste seems to steadily receive the attention it deserves, this type of waste still remains largely unnoticed most probably because of its small size. It is interesting to note that a dichotomy was reported on the public attitude on discarded conventional cigarettes and this waste was not always recognized as a litter and an environmental problem (Rath et al., 2012). The false perception that discarded tobacco products are the end point of a life cycle, points that there is still a way to go in addressing responsible disposal and post-consumer waste cleanup, so as to minimize the environmental hazards of discarded tobacco products.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: this research was funded by an Investigator-Initiated Study award by Philip Morris Products SA (IIS.PMI.2017.30). The study protocol was written by Professor E. Psillakis who was also the principal investigator of the study. Philip Morris Products SA had no involvement in the study conduct, data analysis and writing of the manuscript.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2020.136700>.

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