



The role of cigarette butts as vectors of metals in the marine environment: Could it cause bioaccumulation in oysters?

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ABSTRACT

Tobacco is a well-documented threat to human health. However, its environmental impact has only recently been considered. Metals can interact with cigarette butts (CBs) being transported in the marine environment and reaching organisms. To understand this mechanism, a series of metal(loid)s were analyzed in cigarette filters (virgin, artificially smoked, leached in seawater and aged in beach and harbour) as well as in artificially contaminated oyster tissues. Smoked filters showed higher levels of metals compared to the virgin ones showing enrichment factors up to 90, probably associated with tobacco metal content. Once the CBs are delivered to the environment, metals can be leached to seawater until reaching equilibrium, which may be dependent on initial metal levels in the water. Copper was the element with the highest percentage of desorption ($91 \pm 3\%$) while strontium showed the lowest percentage ($40 \pm 0\%$). CBs revealed a great capacity to accumulate metals from the environment when weathered in contaminated areas. A chemical impact derived from CBs contamination might exist as they serve as a carrier for metals in the marine environment. The release of metals from CBs or the ingestion of metal loaded CBs may pose a toxicological risk for marine organisms via accumulation in their tissues.

1. Introduction

Tobacco consumption is a well-known and documented threat to global health (World Health Organization, 2017). It kills more than 7 million people a year and is currently the world's single biggest cause of preventable death (World Health Organization, 2017). But their environmental associated problems were not an issue until relatively recently (see e.g. Araújo, Costa, 2019).

Cigarette filters were created in the 1950s to make filtered cigarettes a 'healthier' alternative to cigarettes without filters (Brandt, 2007). Cigarette filters are generally composed of more than 15,000 fibers strands made of cellulose acetate with plasticized additives (Belzagui et al., 2021). Cigarette butts (herein after CBs) which are the combination of the filter and the remnants of a smoked cigarette, contains more than 40 potentially hazardous chemical substances (Baker, 2006). Some researchers proposed the classification of CBs as hazardous waste (Barnes, 2011; Rebischung et al., 2018).

CBs are among the most common forms of litter (World Health Organization, 2017). Worldwide, approximately 4.95 trillion CBs are

estimated to be littered each year and they are usually found in the marine environment (Araújo, Costa, 2019). CBs represent an important share of beach litter being in the top 10 of items found on European beaches (Addamo et al., 2017). On the Atlantic coast of Europe, CBs represent 6% of litter monitored over 2016–2019 with densities ranging from 0 to 1032 CBs per 100 m of beach (André et al., 2020). It has been estimated that it could take 30 years for cigarette filters to degrade in certain conditions (Joly and Coulis, 2018). Once discarded into the environment, CBs can leach out chemicals such as nicotine, arsenic, polycyclic aromatic hydrocarbons (PAHs) and heavy metals (Baker, 2006) that can be acutely toxic to aquatic organisms (World Health Organization, 2017).

Despite awareness about the environmental problems that cigarette and their components could have in the environment has been raised in the latest years, previous research efforts on tobacco toxicity have been mainly focused on smoking-related diseases and their cure and treatment in humans (i.e. lung cancer). It has been well documented that cigarette companies responded to the 'lung-cancer scare' of the early 1950s by investing heavily in the design and marketing of filter-tipped

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cigarettes (Zipser, 1954). Despite that, a team of researchers from the USA and Japan asserted in 2010 that ‘the shift from nonfilter to filter cigarettes appears to have merely altered the most frequent type of lung cancer, from squamous cell carcinoma to adenocarcinoma’ (Novotny et al., 2009; Ito et al., 2011).

The tobacco industry has improved cigarette filters to retain most chemicals that would be potentially released once the CBs are disposed of in the environment (Harris, 2011). So, this improvement has probably conducted to an increase in CBs potential toxicity in the environment (Novotny and Slaughter, 2014). Understanding the environmental impact of CBs is important because they are by far the largest single type of litter by count (Novotny and Slaughter, 2014) representing a potential point source for environmental contamination.

In addition to their direct discard into the environment by smokers, water channelled by sewer systems and streams acts to accumulate CBs in localised areas. As stated before, they can leach their chemical components and substances adsorbed and generated as a result of the smoking into the environment (Novotny and Slaughter, 2014). A study performed by Moriwaki et al., (2009) found that arsenic, nicotine, polycyclic aromatic hydrocarbons and heavy metals are released into the environment by littered ‘roadside waste’ CBs. Most of these chemicals are not an original component of the filter; however, tend to accumulate on it as a result of smoking.

Among all the chemicals that might be introduced by CBs in the environment, metals constitute an important group (Moerman and Potts, 2011). Although a single CB would not inflict serious environmental damage, the cumulative effect of many CBs littered in a specific area may present a significant threat to local organisms (Araújo, Costa, 2019). In this sense, Quéméneur et al. (2020) demonstrated that the presence of CBs in marine sediments increased metal dissolved concentrations in the surrounding waters.

Considering this, it is likely that organisms such as bivalves will be exposed to butt released- metals. Given the gap of knowledge on metal adsorption-desorption by CBs, this investigation intended to shed light on these processes. In addition, the accumulation of metals leached from CBs was investigated in oysters. To this purpose, several field and laboratory experiments were carried out with the goal to understand the interaction between metals and CBs as well as their impacts on marine organisms.

The objectives of this study are; 1) to study the adsorption/

desorption kinetics of more than fifteen metal(oid)s and CBs in the marine environment and 2) to evaluate absorption and accumulation of metals released from CBs in oyster tissues.

2. Material and methods

2.1. Cigarette butts preparation

Three types of cigarette were selected for the study (A, B and C). Cigarette A was selected among the most sold manufactured cigarette types in France according to the French Observatory of Drugs and Drug Addiction (2019). The two others (B and C) were selected because of their contrasting characteristics in terms of ventilation and carbon monoxide and nicotine emission. The cigarettes characteristics are described in Table 1.

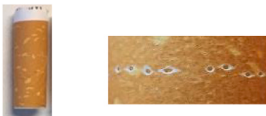


CBs were prepared in the laboratory by artificially smoking the cigarettes using a tool set up at the Centre of Documentation, Research and Experimentation on Accidental Water Pollution (CEDRE, Brest, France) consisting of a solid-phase extraction manifold connected to a vacuum pump and an airflow meter. A glass bottle containing osmosed water and a pipette filled with cotton was placed between the solid-phase extraction manifold and the vacuum pump to avoid clogging of the latter (Fig. 1). Artificial smoking conditions followed as much as possible the criteria set by ISO standard 3308:2012.

The protocol consisted of smoking 6 cigarettes simultaneously by making 8 puffs of 2 s while aspirating in each puff a volume of 35 mL per cigarette, interspersed with 45 s of pause. During aspiration phases, the total flow rate was set at 6 L/min, equivalent to 1 L/min per cigarette. After the smoking, the remaining tobacco was removed from CBs and the paper was cut close to the filter. Thus, in the present study, CBs consisted of a filter wrapped in paper with no tobacco remaining. Once smoked, CBs were stored individually at -20°C . These CBs were produced in sufficient quantity to run the 3 experiments considered in this study, i.e. weathering, leaching and oyster exposure.

2.2. Cigarette butts weathering

In February 2019, previously smoked CBs were placed at two different field locations. The first one was an artificial sandy beach owned by the (CEDRE, Brest, France) where 126 CBs (42 CBs of each

Table 1
Characteristics of the three cigarettes selected in the study.

Cigarette	Pictures of filter and ventilation holes ^c	Filter ventilation (%)	Tar emission (mg/cig)	Nicotine emission (mg/cig)	Carbon monoxide emission (mg/cig)	Cig total length/ filter length/ filter diameter (mm)
Allowed maximum ^d	–	–	10	1	10	–
A(light) ^a		80	1	0,1	2	83 / 27 / 7,8
B(medium) ^b		34	10	0,7	10	83 / 21 / 7,8
C(strong) ^e		22	10	1	10	84 / 25 / 7,9

^a Highly porous cigarette paper (to allow toxic chemicals to escape). Wide ventilation holes in the filter tip (to dilute smoke with air).

^b Porous cigarette paper. Narrow ventilation holes in the filter tip.

^c Not porous cigarette paper. Absence of ventilation holes in the filter tip.

^d According to the (French Agency for Food, 2019), Environmental and Occupational Health & Safety.

^e Ventilation holes: Holes in the sides of the filter that dilute the tobacco smoke with clean air.

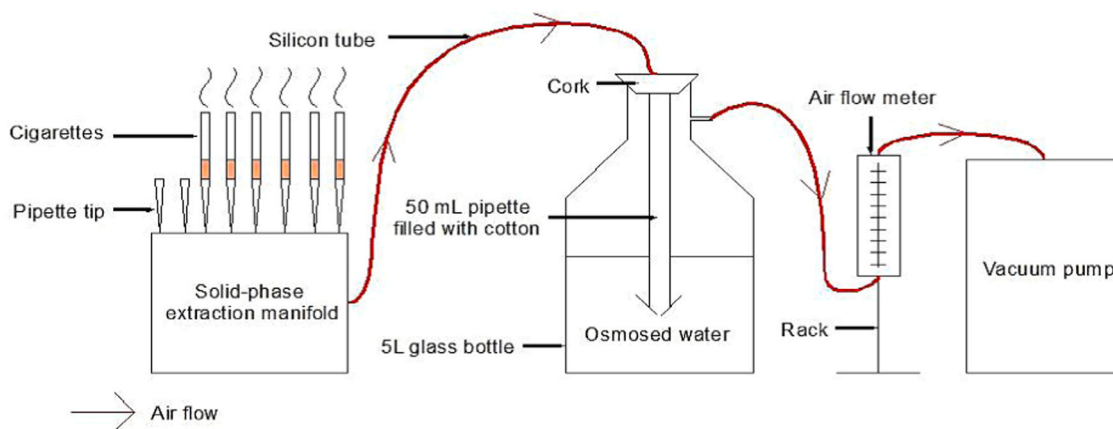


Fig. 1. Experimental tool used to artificially produce smoked cigarettes.

cigarettes type) were deposited for one year in contact with the sand and in the upper section of the beach inside a wooden frame and covered by a plastic net to avoid loss of material. The beach has limited access to people as it is placed in the CEDRE's domains. During the twelve months of the study, 3 CBs of each cigarette type were collected regularly (7, 14, 21, 28, 56, 85, 175, 273 days), to assess the evolution of metal contamination over time. Some samples were used to assess the loss of mass of the CBs and degradation status; others were used to study the evolution of metal contamination over time. The dates of sampling are detailed in the [supplementary material \(Supplementary Table 1\)](#).

The second location was the Brest Marina (Marina du Château, Brest, France). Two stainless steel (covered with epoxy paint) cages containing 7 plastic net pockets (pore size 2 cm) designed by CEDRE were manufactured. Each pocket is made up of 3 CBs of each type, i.e. 9 CBs per pocket. The pockets were numbered to identify the different CBs and the cages were then deposited on the seafloor of Brest Marina in March 2019. Two pockets (one for each cage) were taken regularly (70, 119, 182 and 267 days) and the CBs individually frozen in plastic zip-lock bags until analyses. In the same way, as CBs weathered in the beach, one group of CBs was used to assess the loss of mass and degradation status, while the other group was used to study the metal contamination over time. The dates of sampling are detailed in the [supplementary material \(Supplementary Table 2\)](#).

The degradation of CBs was studied by mass measurement, attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR) and visual observation. Metal analyses were carried out in some samples to study the evolution of chemical adsorption onto CBs over time. In the case of the exposure carried out on the sandy beach, these analyses were carried out in the CBs collected after 14, 28 and 85 days of weathering. Regarding the exposure on the harbour, the analyses were carried out in the CBs collected after 70 days of weathering.

2.3. Leaching experiment

The CBs leaching experiment was carried out in CEDRE's laboratory using the previously artificially smoked CBs (not weathered in the field). Natural filtered (0.4 μm) seawater collected offshore (salinity: 35.1; pH: 7.99) was used for the leaching experiments that were conducted at controlled temperature (20 °C). The water was collected from a boat and filtered online by pumping it through a filter cartridge previously acid cleaned to avoid contamination. Four leaching times were studied in triplicate for each cigarette type: 0, 6, 24 and 72 h. For the "0 h" condition, 3 CBs were stored directly after smoking at -20 °C in a plastic bag. For the rest of the leaching times, 1 cigarette butt was incubated, in triplicate, at room temperature in a glass bottle, filled with 125 mL of natural filtered seawater (concentration of 8 CBs/L) and placed on an orbital shaker at 160 rpm. Once leaching time was reached, CBs were

removed from the bottle and stored at -20 °C in a plastic bag (one bag per leaching time) and saved for further metal analyses.

2.4. Oyster's exposure

2.4.1. Organisms

One hundred and four triploid adult oysters (*Crassostrea gigas*) (size: 92 ± 7 mm) were supplied by an oyster farmer from Plouguerneau (Brittany, France) in March 2019. Once in the CEDRE laboratory (Brest, France), individuals were acclimated for 7 days in a 300 L tank continuously supplied with naturally filtered seawater (salinity: 35.1; pH: 7.99) at room temperature (20 °C). During this period, the water parameters were monitored every day, the faeces were removed and oysters were fed every two days with a dose of 162 $\mu\text{L}/\text{ind}$ of a concentrated microalgae solution (RGcomplete APBreed®). No oyster mortality was recorded during the acclimation period.

2.4.2. Stock solution preparation

Oysters were exposed to CBs 24 h-leachates by contaminating natural filtered seawater with a stock solution prepared from CBs leachate. The stock solution was prepared by incubating CBs in seawater at 160 rpm for 24 h at a concentration of 46 CBs/L. Then the leachate was filtered to remove CBs and derived particles, using a vacuum pump on a nitrocellulose filter (pore size 0.45 μm) before being stored in glass bottles in the dark at 4 °C.

2.4.3. Experimental set-up

Thirty-six individuals (18 per condition, 6 per tank) were exposed, in triplicate, for 7 days to the CBs 24 h-leachate obtained as explained above, in glass tanks containing 10 L of naturally filtered seawater and an aeration system. During the exposure, seawater, stock solution (leachate) and food were renewed every two days and the faeces were removed. Oysters were fed with a dose of 162 $\mu\text{L}/\text{ind}$ of a concentrated microalgae solution (972 μL per tank) and leachate (217 mL from the stock solution) was also added. A seawater control group (per triplicate) was processed at the same time.

After 7 days of exposure and 2 days after the last feeding, 3 fasting individuals of each tank (i.e. 9 individuals per condition and a total of 18 individuals) were sampled.

For each oyster, shells were opened and the body was weighed, then the gills and the digestive gland were dissected out using a metal scalpel before being weighed and stored individually in aluminium foil at -80 °C. After dissection, tanks were cleaned and filled with 10 L of non-contaminated natural filtered seawater.

The remaining oysters (18 individuals, 9 per condition) were left in clean seawater for an additional 7-day decontamination period. During this period, the seawater and the food were renewed every two days and

the faeces in the tanks were removed. Oysters were fed with a dose of 162 $\mu\text{L}/\text{ind}$ of a concentrated microalgae solution (486 μL per tank). After 7 days of decontamination and 2 days after the last feeding, the 3 remaining individuals of each condition (i.e. a total of 18 individuals) were sampled. For each oyster, shells were opened and the body was weighed, then the gills and the digestive gland were dissected using a metal scalpel before being weighed and stored individually in aluminium foil at -80°C . The oyster's exposure experiment is summarized in Fig. 2.

2.5. Cigarette filters characterization and degradation tracking

The CBs were characterized by attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR) in a SMART iTX NICOLET iS20 (Thermo Scientific). The cigarette filters were placed on the ATR crystal and FTIR absorption spectra were recorded as an average of 50 scans in the mid-infrared range $4000\text{--}525\text{ cm}^{-1}$. The polymer type was identified based on the absorption frequencies for specific chemical bond types present in the relevant polymer samples. Spectrum software was used to analyse recorded IR spectra and the material was identified by a spectrum search in commercial and customised polymer libraries (Omnic 9). These libraries contained spectra of all common polymers, natural and weathered materials with different uses and colours among others. To estimate the degradation status of cigarette filters (i.e. virgin, smoked, weathered in the beach sand and on the bottom of the harbour), FTIR absorption spectra were compared. According to several authors (Corcoran et al., 2009; Artham et al., 2009; Santos-Echeandía et al., 2020), as degradation and oxidation of the polymer surface increases, the highest peaks in the lower wave number spectrum and a broad peak around wave number 3400 cm^{-1} appear, which is consistent with the presence of hydroxyl functionality.

2.6. Weight loss

To evaluate the physical degradation of the CBs placed on the beach and in the harbour, CBs were dried at room temperature to a constant weight after collection. This dry mass was monitored over time and compared to the initial weight before the weathering process started.

2.7. Metal analyses

A series of metals and metalloids: arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), lithium (Li), manganese (Mn), molybdenum (Mo), nickel (Ni), lead (Pb), antimony

(Sb), strontium (Sr), uranium (U), vanadium (V) and zinc (Zn) were analyzed both in CBs (virgin, artificially smoked, aged in beach or harbour and leached in seawater) and oyster tissues (gills and digestive glands). In the case of CBs, leachable metal concentrations in aqua regia were determined. For the latter, samples were placed in plastic centrifuge tubes containing a mixture of HNO_3 (3M) and HCl (2M) in a proportion of 1:3. Samples were subjected to orbital shaking for 24 h at 100 rpm. After that, samples were centrifugated for 10 min (3500 rpm) and filtered using syringe filters. Filtered samples were stored (-20°C) until analysis. Regarding oysters, total metal concentrations were determined in samples consisting of pooled gills or digestive glands from 3 individuals of each condition (1 per tank), equivalent to approx. 3 g of wet weight (ww) for the gills and approx. 2 g ww for the digestive glands. These samples were acid digested in Teflon pumps inside a microwave digester using 6 mL of HNO_3 (suprapur, Merck) and a temperature ramp of 75 min reaching a maximum of 180°C and were finally made up to 25 mL. And finally, analyses were carried out directly in the samples using an ICP-MS (7900 Agilent).

In order to have a quality control of the analysis, blanks and certified reference material (NIST-1566b, oyster tissue) were included within the samples. Recoveries for metals were ($n = 3$) $107 \pm 7\%$ (As), $104 \pm 8\%$ (Cd), $108 \pm 9\%$ (Co), $101 \pm 6\%$ (Cr), $104 \pm 4\%$ (Cu), $108 \pm 9\%$ (Fe), $97 \pm 2\%$ (Hg), $103 \pm 8\%$ (Mn), $101 \pm 14\%$ (Ni), $99 \pm 17\%$ (Pb), $98 \pm 14\%$ (Sb), $102 \pm 5\%$ (Sr), $111 \pm 11\%$ (U), $95 \pm 11\%$ (V) and $103 \pm 3\%$ (Zn).

2.8. Kinetic models equations and statistical analyses

To evaluate the nature and rates of interactions between metals and CBs, the data were modelled using the two types of kinetics generally used for the adsorption onto solids of compounds dissolved in a liquid phase: the pseudo-first order kinetics proposed by Lagergren (1898) (Eq. 1), and the pseudo-second order kinetics proposed by Ho and McKay (1999) (Eq. 2). We followed the procedure described by Sánchez and Cameselle (2017) to model the sorption of metals in CBs. Adsorption and desorption rate constants (forwards and reverse) and equilibrium constants were derived from Eqs. (1) and (2) by assuming that equilibrium concentrations were represented by the mean of the final measurements in the timecourse (Holmes et al., 2012).

$$q_t = q_e (1 - e^{-kt}) \quad (1)$$

where q_e is the adsorption capacity in equilibrium ($\text{ng metal mg}^{-1}\text{ CB}$), K is the first order adsorption rate constant (h^{-1}) and t is the time (h).

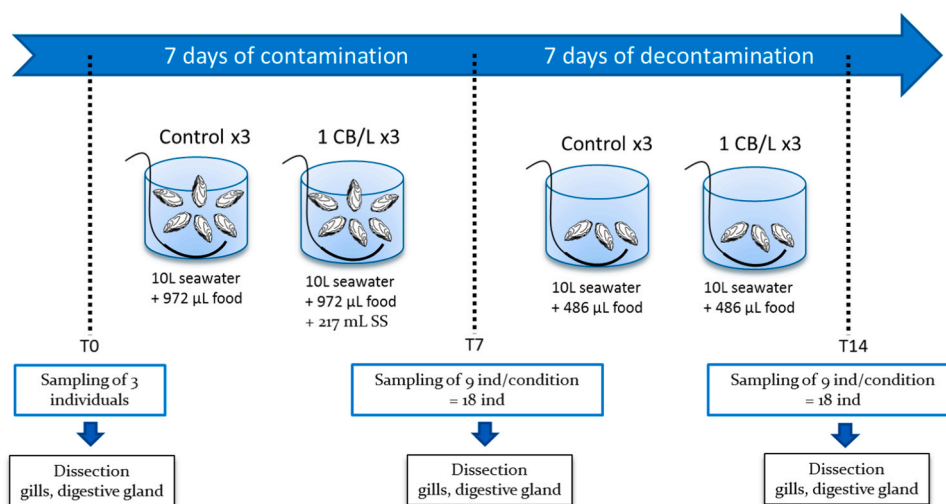


Fig. 2. Oyster's exposure experiment. SS= stock solution.

where q_t is the adsorption capacity (ng metal mg^{-1} CB) at a time t (h), K is the pseudo-second order adsorption rate constant ($mg\ ng^{-1}\ h^{-1}$), and q_e is the adsorption capacity in equilibrium.

Regarding the statistical treatment, three replicates of each measure were performed. An F -test was used to assess the homogeneity of variances. A t -test was run for mean difference and the p -values were calculated. When the p -value was lower or equal to 0.05, the difference was considered statistically significant.

3. Results

3.1. Metal concentration in virgin cigarette filters and “artificially smoked” cigarette butts

Leachable metal concentrations in virgin and artificially smoked CBs for the different brands are shown in Table 2. In the case of virgin CBs, iron was the element with the highest values measured (3.97–7.86 mg/kg) followed by Zn (0.470–0.900 mg/kg) and Cr (0.262–0.808 mg/kg) while the lowest values were measured for U (0.001–0.002 mg/kg) and Cd (0.001–0.003 mg/kg). Regarding smoked CBs, the highest levels were also measured for Fe (49.8–130 mg/kg) and Zn (3.05–5.26 mg/kg) while the lowest ones again for U (0.010–0.188 mg/kg) and Cd (0.002–0.037 mg/kg). Most of the elements showed a statistically significant increase ($p < 0.05$) in their levels for the smoked CBs (Cd, Co, Cu, Fe, Li, Mn, Sr, U, V and Zn). However, other elements significantly decreased ($p < 0.05$) their concentrations (As, Cr and Hg) or just showed no significant change in their levels ($p \geq 0.05$) after the cigarettes were smoked (Mo, Ni, Pb and Sb). The highest change before and after being smoked was observed for Sr, U and V with an enrichment factor up to 100 times, while the smallest change was observed for Mo, Ni or Sb which barely doubled their levels. Finally As, Cr, Hg or Sb reduced their levels by a quarter (see Fig. 3).

A closer look at each of the brands separately revealed a higher enrichment factor in brand C for metals such as As, Co, Fe, Pb, U or V. On the other hand, metals like Cd, Cr, Cu, Hg, Mn, Sr or Zn were enriched in brand A compared to the other two brands. Finally, Li, Mo, Ni or Sb, showed similar enrichment factors in all brands (Fig. 3).

3.2. Leaching of metals from the cigarette butts artificially smoked

The release of trace metals from CBs in naturally filtered seawater was monitored through time (6, 24 and 72 h) showing a logarithmic decrease in metal concentrations of the CBs. A sharp initial decrease that tends to a constant value with time was observed (Supplementary Fig. 1,

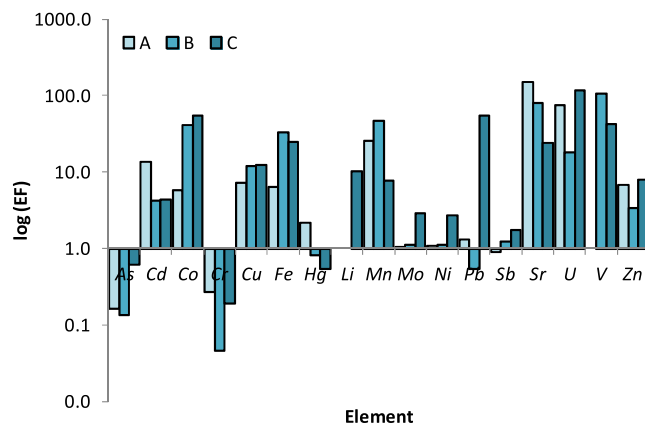


Fig. 3. Enrichment factor (in logarithmic scale) for all the elements in the butts, after being smoked, of the three different brands (A, B, C) considered in the present study.

the parameters for the kinetic model can be found in Supplementary Table 3). Except for Li, which was not released from the CBs (Supplementary Figure 1), all the elements showed a decrease in their concentrations in CBs. The percentage of desorption (24 h) for each metal and by cigarette brand is shown in Supplementary Table 4. Copper was the element with the highest percentage of desorption ($91 \pm 3\%$) followed by Mn ($89 \pm 3\%$) and Zn ($86 \pm 2\%$). On the other side, Mo ($86 \pm 2\%$), Pb ($39 \pm 52\%$) and Sr ($40 \pm 0\%$) showed the lowest desorption percentages.

3.3. Metal accumulation in smoked cigarette butts aged on the beach or the harbour

A statistically significant increase ($p < 0.05$) in metal concentrations in the CBs was observed with time (at 14, 28 and 85 days) after being placed both in the sandy beach and in the bottom of the harbour. In the case of the beach, most of the elements (except Mo and V), showed a logarithmic increase, that was sharp in the beginning and decreases with time tending to a constant value (Supplementary Fig. 2, the parameters for the kinetic model can be found in Supplementary Table 5). A similar kinetic is expected for the CBs aged in the harbour; however, these CBs were sampled only once (70 days). What is undoubtedly is that the increase of metals in the CBs aged on the harbour is significantly greater ($p < 0.05$) than the one observed for the sandy beach for most of the metals except for Cd, Mn, and Zn. This fact can be observed by having a

Table 2

Trace element concentrations (ppm) and standard deviation ($N = 3$) in virgin (A, B and C) and smoked (AF, BF, CF) butts.

Element	A	B	C	AF-1	BF-1	CF-1
As	0.153 ± 0.014	0.149 ± 0.015	0.131 ± 0.010	0.025 ± 0.007	0.020 ± 0.002	0.080 ± 0.008
Cd	0.003 ± 0.001	0.003 ± 0.001	0.001 ± 0.001	0.037 ± 0.003	0.014 ± 0.001	0.002 ± 0.001
Co	0.003 ± 0.001	0.001 ± 0.001	0.001 ± 0.001	0.017 ± 0.001	0.046 ± 0.004	0.076 ± 0.007
Cr	0.808 ± 0.073	0.430 ± 0.042	0.262 ± 0.020	0.215 ± 0.106	0.020 ± 0.002	0.050 ± 0.005
Cu	0.245 ± 0.022	0.055 ± 0.005	0.051 ± 0.004	1.78 ± 0.460	0.650 ± 0.059	0.630 ± 0.060
Fe	7.86 ± 0.707	3.97 ± 0.389	4.13 ± 0.318	49.8 ± 8.91	130 ± 11.8	104 ± 9.97
Hg ^a	2.46 ± 0.221	4.19 ± 0.411	7.18 ± 0.553	5.28 ± 0.300	3.45 ± 0.314	3.88 ± 0.372
Li	b.d.l.	b.d.l.	0.006 ± 0.001	0.085 ± 0.035	0.100 ± 0.009	0.060 ± 0.006
Mn	0.091 ± 0.008	0.056 ± 0.005	0.176 ± 0.014	2.33 ± 0.098	2.65 ± 0.241	1.35 ± 0.130
Mo	0.015 ± 0.001	0.012 ± 0.001	0.006 ± 0.001	0.016 ± 0.003	0.013 ± 0.001	0.016 ± 0.002
Ni	0.160 ± 0.140	0.140 ± 0.014	0.056 ± 0.004	0.175 ± 0.021	0.160 ± 0.015	0.150 ± 0.014
Pb	0.096 ± 0.009	0.151 ± 0.015	0.012 ± 0.001	0.125 ± 0.085	0.083 ± 0.008	0.684 ± 0.066
Sb	0.017 ± 0.001	0.014 ± 0.001	0.008 ± 0.001	0.015 ± 0.006	0.017 ± 0.002	0.014 ± 0.001
Sr	0.061 ± 0.005	0.066 ± 0.006	0.199 ± 0.015	9.25 ± 1.33	5.20 ± 0.473	4.80 ± 0.461
U	0.001 ± 0.001	0.001 ± 0.001	0.002 ± 0.001	0.057 ± 0.009	0.010 ± 0.001	0.188 ± 0.018
V	b.d.l.	0.005 ± 0.001	0.005 ± 0.001	0.145 ± 0.084	0.501 ± 0.046	0.208 ± 0.020
Zn	0.760 ± 0.068	0.900 ± 0.088	0.470 ± 0.036	5.26 ± 0.59	3.05 ± 0.278	3.80 ± 0.365

b.d.l. = below detection limit

^a ppb

look at the 70-days enrichment factor shown in Fig. 4. The highest enrichment factors in the harbour samples corresponds to Cr (60.000), followed by Mo (241) and Ni (233) while the lowest values were found for Mn (2), Cd and Hg (4). In the case of the sandy beach, the highest enrichment factors were observed for Cr (40), Cu (33) and Cd (24) and the lowest for Hg, Mo, U and V (2).

3.4. Cigarette butts degradation: ATR-FTIR measurements and weight loss

The characterization using the ATR-FTIR showed that the main component of the CBs was the cellulose triacetate (Supplementary Fig. 3). All the CBs analyzed showed a similar spectrum. The only change observed between spectra was the increase in height, area and broaden of a peak at around 3400–3500 cm^{-1} . As a general rule, this peak is higher and wider in the CBs weathered in the harbour than the ones weathered in the beach or the virgin cigarette filters (Supplementary Fig. 4).

The evolution of the dry mass overtime for the CBs weathered on the beach and in the harbour can be observed in Supplementary Fig. 5. The mean initial weight of the virgin filters was around 200 mg. The CBs showed a loss of mass with time, being more pronounced in the case of CBs weathered in the harbour (final weight after 350 days around 30 mg) than those placed on the beach (final weight after 350 days around 170 mg).

3.5. Metal concentrations in oysters

Trace metal concentrations in oyster tissues (gills and digestive gland) before the exposure to the leachate from the smoked CBs, after 7 days of exposure and after 7 days of decontamination are shown in Supplementary Table 6. The highest values among the elements were found for Zn (427–748 ng/mg) followed by Fe (52.4–103 ng/mg) and Pb (42.2–66.1 ng/mg). On the other side, the lowest values were found for Sb (0.005–0.017 ng/mg) and to a lesser extent for Co

(0.035–0.098 ng/mg), Hg (0.023–0.061 ng/mg), Li (0.049–0.091 ng/mg) and U (0.052–0.126 ng/mg).

If we differentiate by tissue, some elements showed higher concentrations in the gills (i.e. Hg, Li, Mn, Ni and Sr) while others in the digestive gland (i.e. As, Co, Cr, Fe, Mo, U and V). The third group of elements showed similar concentrations among tissues (i.e. Cd, Cu, Sb, Pb and Zn).

Finally, the accumulation factor (AF) has also been calculated for the sum of both tissues after the 7 days period of exposure by dividing metal concentration after seven days by initial metal concentration. The AF value for most of the elements was between 0.83 and 1.21. However, AF for Mn and Sr were above these figures being 1.29 for the former and 1.35 for the latter (Supplementary Table 6).

4. Discussion

4.1. Metal-Cigarette Butts interactions in the marine environment

In general, trace metal concentrations are higher in smoked CBs than in virgin CBs as already shown by Iskander (1985). Following this, in the present study the concentration of metals like Sr, U and V, and to a lesser extent Co, Fe, Li and Mn, showed a statistically significant ($p < 0.05$) increase in CBs after being smoked. Also, the cigarette brand with a lower percentage of filter ventilation was the one that significantly ($p < 0.05$) accumulated the higher quantities of metals among the three brands. This fact demonstrates that at least for metals, filters act as stoppers avoiding their inhalation via smoke at a certain degree. A feasible explanation for this may be related to trace metal concentration in tobacco leaves that would enrich CBs in metals after being smoked. Studies on the relative contribution of paper, filter and tobacco revealed that tobacco was the major source of metal contamination among these three parts of the cigarette (Koutela et al., 2020). Several works have already measured and compared trace metal content in tobacco and CBs (Kalcher et al., 1993; Alvarado and Cristiano., 1993; Pelit et al., 2013).

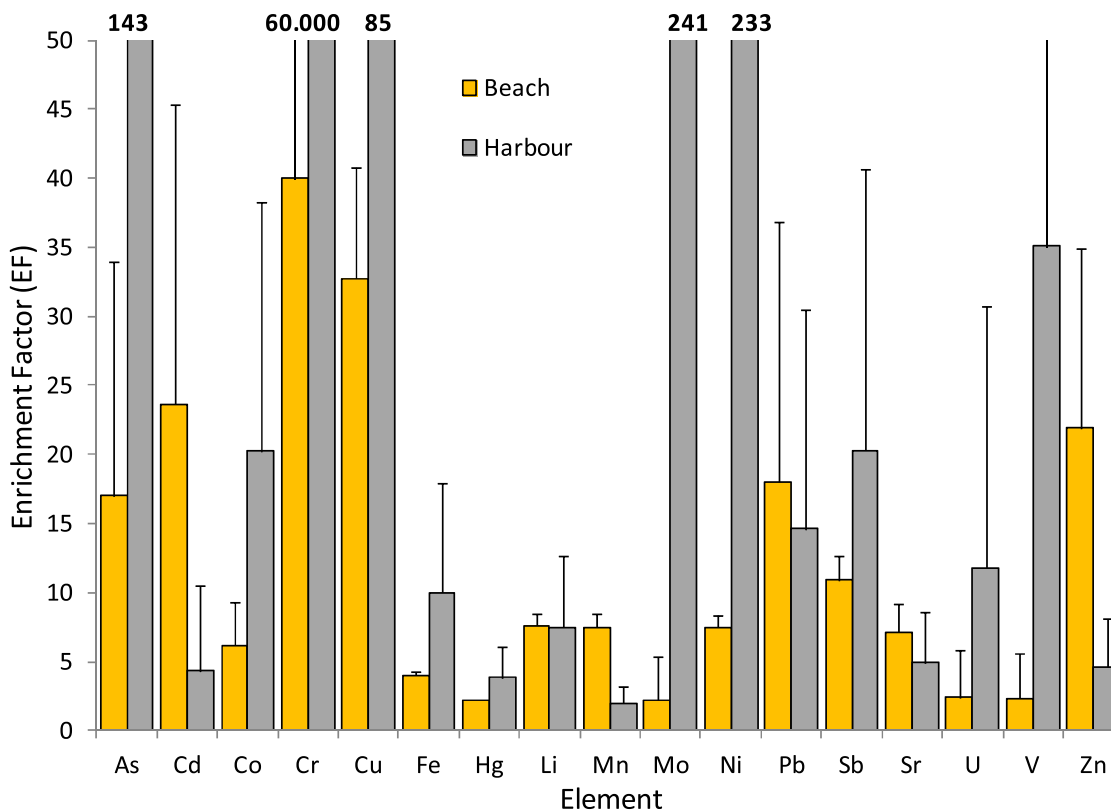


Fig. 4. Enrichment factor (mean and standard deviation) of the different elements by weathering area in the CBs.

Kalcher et al. (1993) showed that Cd and Pb concentrations in tobacco were up to 2 orders of magnitude higher than in the CBs. In the same way, Alvarado and Cristiano (1993) showed that Cd, Co and Fe concentrations in tobacco were up to 100 times higher than their levels in the CBs. However, these authors showed that the levels of Ni or Pb were similar or lower in tobacco than in the CBs. Finally, Pelit et al. (2013) measured higher concentrations of Cd, Cu, Mn and Zn in tobacco samples than in the CBs forming the same cigarette. These results are in line with the findings of the present study where a great enrichment in the levels of Co, Fe and Mn was observed while Ni was enriched to a lower extent.

The fact that CBs are not enriched in the same proportion for all the elements after being smoked suggests that not only the metal concentration or the additives included by the manufacturer in the paper and tobacco may be determinant, but the chemistry of each element is also going to play a role. This is the case of volatile elements (i.e. As and Hg). Although their concentrations are higher in the tobacco than in the filter, As and Hg are not enriched in the filter after smoking because a great part of them may be volatilized during the smoking action due to the high temperatures reached. The As or Hg levels are reduced in CBs after being smoked (Fig. 3).

The CBs are discarded into the environment after being smoked reaching, on most occasions the sea. The results obtained from the leaching experiment presented in this work, carried out with coastal clean waters, confirm that all the elements but Li, are released from the CBs to seawater in different percentages of desorption, ranging from 35% for Mo to 91% for Cu (Supplementary Table 4). The release consists of a first quick desorption period (around 5 h) followed by a slow release in time reaching a roughly constant value. Similar desorption kinetics have been previously reported for a series of metals in microplastics (Nakashima et al., 2012; Fernández et al., 2020) and in CBs (Moerman and Potts, 2011; Koutela et al., 2020). In the work of Moerman and Potts (2011), leaching experiments were conducted in deionized water. These authors observed net desorption for all the metals studied in the smoked CBs. However, the desorption percentage was lower than our study ranging from 1% for Ti and 59% for Sr or Pb. Koutela et al. (2020) carried out the leaching experiments in different solutions (i.e. deionized water and seawater) showing net desorption of metals (mainly Zn, Ba, Cu) in all the different treatments. The desorption percentages were similar to the ones found by Moerman and Potts (2011) varying between 0.2% and 43% for the metals considered. As observed in the present study, Cu and Zn showed the highest desorption percentages. The metal leaching from the CBs, increased dissolved metal concentration (Fe, Mn and Zn) in seawater samples as recently demonstrated in a field study (Quéméneur et al., 2020) This fact can have negative consequences as potentially toxic elements (i.e. metals) are being desorbed to water after CBs disposal in the environment and increasing their concentrations above reference or natural values.

Nevertheless, metal desorption in the marine environment is not the only mechanisms that will occur between the CBs and the metals, as CBs can adsorb metals once in the marine environment. This would depend on the metals levels present in the waters where CBs are disposed of. In the present work, it has been demonstrated that CBs are enriched in metals after being weathered in different marine environments (i.e. sandy beach, water bottom of a harbour). Except for Cr, whose concentrations increased in 6 orders of magnitude ($p < 0.05$), the rest of the elements showed increases up to 200 times ($p < 0.05$) the original levels measured in smoked CBs after 85 days in the harbour. In the same line, Dobaradaran et al. (2017) indicated adsorption of trace metals onto CBs in the environment. These authors showed that levels approximately duplicated the original values after 10 days in the marine environment. The adsorption is very quick in the first days (15–20 days) but the rate decreases with time to reach an almost constant value after 60–70 days depending on the metal under study. Compared to the desorption kinetics, the adsorption is slower. In this way, Fernández et al. (2020) proved that the desorption kinetics of Hg from microplastics was also

slower than the adsorption under natural environmental conditions.

For most of the elements considered in the present study, the enrichment factor is significantly higher ($p < 0.05$) in the CBs deposited in the harbour only Cd, Mn and Zn showed significantly higher concentrations ($p < 0.05$) in the CBs aged on the sandy beach. Several factors can drive these differences. The first one would be the metal composition or concentration of the matrices in contact with the CBs (i.e. sand in the case of the beach and sediments/water in the harbour). Metals will move between the different matrices until equilibrium is reached. In general, harbour sediments and waters display higher concentration of metals than other natural coastal environments due to the anthropogenic activities carried out in them (see e.g. Prego et al., 2008). This fact would facilitate the adsorption of great quantities of different metals to CBs as observed in CBs aged on the harbour in the present study.

Another important factor regarding the accumulation of metals is the degradation status of the CBs. Previous works (see e.g. Ashton et al., 2010; Acosta-Coley et al., 2019; Santos-Echeandía et al., 2020) have already demonstrated that microplastics tend to accumulate metals once they are being degraded in the environment. The cigarette filters, made of compressed, plasticized cellulose acetate wrapped in a paper layer (Bonanomi et al., 2015) are not an exception. Recent research shows that CBs do not biodegrade under most circumstances because of their compressed makeup and the presence of acetyl molecules (see review by Costa, 2019). However, under specific circumstances (with sunlight and moisture), the cigarette filters may break into smaller plastic pieces (Belzagui et al., 2021). Light-induced oxidation is usually several orders of magnitude greater than the other types of degradation (Andrady, 2011). In particular, ultraviolet (UV) light is responsible for the initiation of photooxidative degradation, a very effective process for positively buoyant particles or particles deposited on the beach (i.e. CBs). Photo-oxidation is followed by thermal degradation or thermo-oxidation (Murata et al., 2004; Anderson et al., 2016).

As previously shown in Supplementary Figs. 4 and 5, after being weathered for 70–80 days the degradation status is higher in the CBs located in the harbour than in the beach, and even higher with respect to a virgin butt. This fact is indicated by the presence and increase of a broad peak around 3450 cm^{-1} that corresponds to a hydroxyl group as previously observed for other polymers apart from the cellulose acetate weathered in beaches (Corcoran et al., 2009; Santos-Echeandía et al., 2020). Regarding our specific case (cellulose acetate) Wang et al. (2014) also observed a wide peak around 3450 cm^{-1} and an additional increase in the 2900 cm^{-1} peak, corresponding to a C-H group after degradation in a methanol-water solution. Cellulose acetate degradation creates a higher specific surface and porosity related to the increase of polarity and anionic active sites by the creation of new functional groups such as acetate, carboxyl, ether and hydroxyl (Wang et al., 2014) and once in seawater, chlorinate groups (Nguyen et al., 2017). All of these functional groups can bind metals as confirmed in the present study. The presence of fouling as hydrous metal oxides (Ashton et al., 2010; Holmes et al., 2012) or the incorporation of organic matter into the CBs surface (Artham et al., 2009) would also favour the metal binding to CBs in the marine environment. The higher degradation status in the harbour observed using the absorbance spectra is confirmed if we attend to the mass loss of CBs with time (Supplementary Fig. 5).

4.2. Bioaccumulation of metals leached out from cigarette butts in oyster tissues

Once proved that metals can be adsorbed and desorbed from the CBs in the marine environment depending on the metal concentration of the surrounding matrices (i.e. water or sand), one of the aims of this study was to evaluate if the metals leached from the CBs could increase baseline metal values in oyster tissues. The evolution with time of metal levels in the two tissues considered for the study (gills and digestive gland) can be observed in Fig. 5. In this figure control vs exposed treatments are compared. Different behaviours were observed among

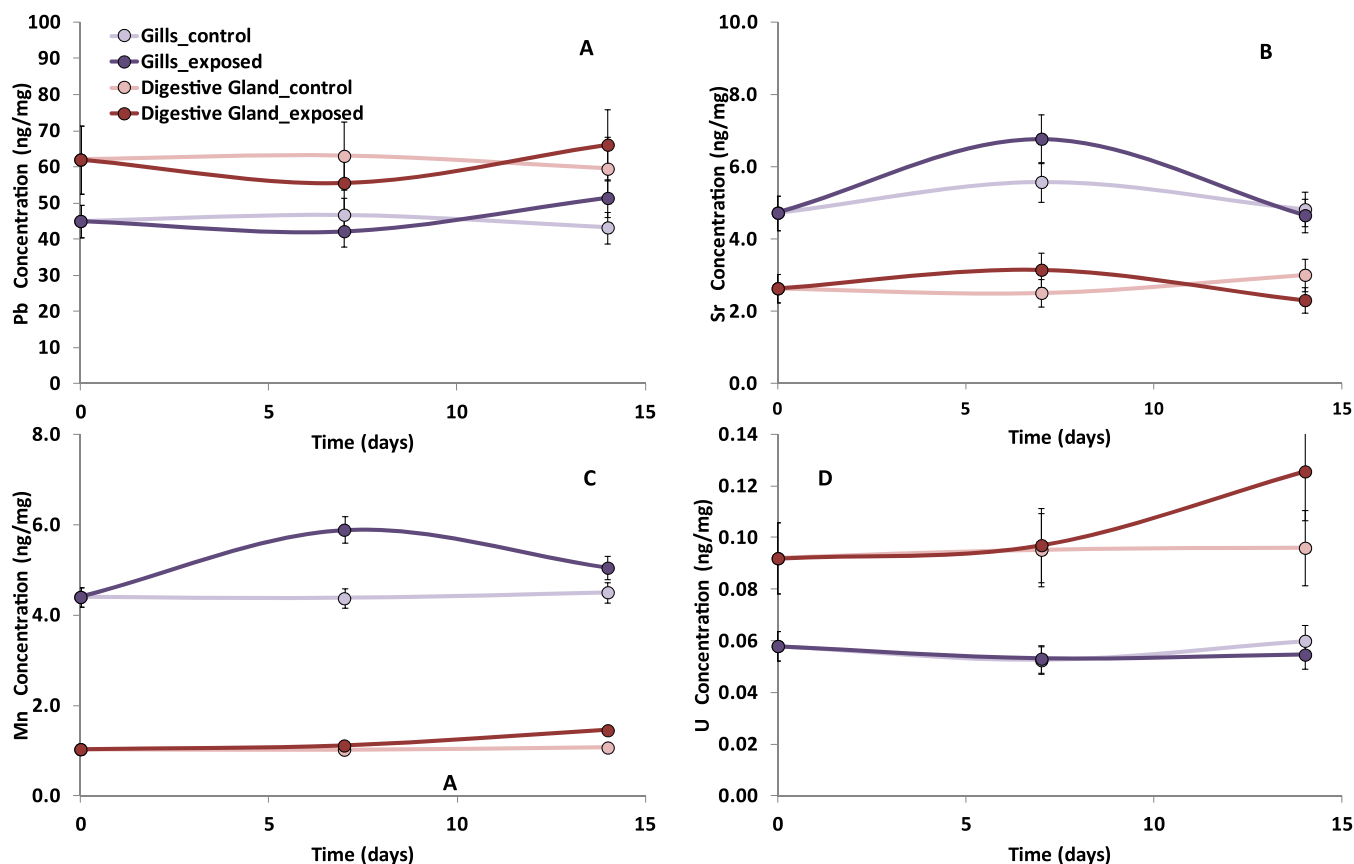


Fig. 5. Metal concentrations (ng/mg) with time in oyster tissues: gills in purple and digestive gland in red for the control (light colour) and exposition (dark colour) treatments.

the different elements. In most of the cases, no significant changes ($p \geq 0.05$) were observed with time and among treatments. This was the case for Pb (Fig. 5A), As, Cd, Co, Li, Ni and V. For other metals like Sr (Fig. 5B), an increase was observed in both tissues after 7-days exposure to the CBs leachate. However, only the increase observed in the gills was statistically significant ($p \geq 0.05$). A significant decrease ($p < 0.05$) after the 7-days of decontamination was observed in both tissues. In the case of Mn (Fig. 5C), levels significantly increased ($p < 0.05$) after 7 days in the gills and decreased after the decontamination time. Although the mean value was lower after decontamination, the decrease was not statistically significant ($p \geq 0.05$). In the digestive gland, Mn levels increase significantly ($p < 0.05$) after the decontamination time. Finally, an important number of the elements (U (Fig. 5D), Cr, Fe, Cu, Mo, Sb and Zn) showed no significant increase ($p \geq 0.05$) in gills after the exposure time but a net increase in the digestive gland after the decontamination time. However, the increase was statistically significant ($p < 0.05$) only for U and Sb. This agrees with previous studies (e.g. Rivera-Hernández et al., 2019) that have shown a net translocation among tissues with time (from the gills to the digestive gland) before metals are being egested. Gills are the first tissue that gets in contact with the dissolved contaminant, which is transferred to the digestive gland after some days.

Except for Sr and Mn, and to a lesser extent Sb and U, metal concentration in oyster tissues after exposure to CBs leachates did not show a significant increase ($p \geq 0.05$). Marine organisms in general and marine bivalves in particular, use some of these elements (i.e. Co, Cu, Fe, Zn, Mo, V) for their metabolic functions, which make them essential for their survival. Consequently, they tend to accumulate these elements in their tissues to use them as micronutrients. Suami et al. (2019) analyzed trace metals in oysters from the Atlantic Ocean finding concentrations up to 2 $\mu\text{g/g}$ for Co, 16 $\mu\text{g/g}$ for Cu, 460 $\mu\text{g/g}$ for Fe and 113 $\mu\text{g/g}$ for Zn.

These values are very similar to the ones found in the present study (Table 3). In addition to the high natural values present for these elements in oyster tissues, the potential accumulation of the metals derived from the CBs is relatively low. Taking into account the metal content in the CBs, the percentage of desorption, the total volume added to the experimental tanks where the oysters were placed, the volume of these tanks, the number of oysters and the mean weight of each tissue (gills and digestive gland) the maximum concentration that could be accumulated in the oysters' tissues are shown in Table 3. Considering these values, only Fe, Mn, Sb or Sr could increase their concentration in the tissues with respect to the natural values. All these elements showed moderately increased concentrations in oyster gills and/or digestive gland after being exposed to CBs leachate (Fig. 5). This could lead to the misconception that metals released from the CBs do not increase their levels in oysters' tissues.

Dobaradaran et al. (2017) observed that once in the environment, CBs accumulate more metals than after being smoked. This process has been confirmed in the present study, both for the CBs weathered on the beach and in the harbour. If these CBs reached clean waters, the metals could be released to reach equilibrium and thus be potentially available for marine organisms. The accumulation of these elements is more feasible in oysters, as being filter-feeding animals; they filter high quantities of water accumulating all the elements. Oysters may have more chances to accumulate a higher concentration of metals released from weathered CBs than from non weathered ones (Table 3). Not only higher concentrations for the metals but also more elements (i.e. As, Cr, Cu, Ni, Pb, U or V) could potentially increase their concentrations in oyster tissues under this new scenario.

Finally, the potential risk of these metal-loaded CBs being ingested by marine organisms should not be ignored. Under digestive acidic conditions, metals can be desorbed from the CBs and accumulate in

Table 3

Natural metal concentrations (ng/mg) in oyster tissues compared to the potential bioaccumulation of these elements leached from smoked butts, butts aged on the beach or in the harbour.

Element	Baseline value		Potential accumulation Smoked butts		Beach aged		Harbour aged	
	Gill (ng/mg)	Digestive Gland (ng/mg)	Gill (ng/mg)	Digestive Gland (ng/mg)	Gill (ng/mg)	Digestive Gland (ng/mg)	Gill (ng/mg)	Digestive Gland (ng/mg)
As	4.68	8.29	–	–	0.027	0.043	0.205	0.328
Cd	0.691	0.621	–	–	0.007	0.011	–	–
Co	0.037	0.079	–	–	0.025	0.040	0.070	0.111
Cr	0.162	0.23	0.013	0.021	0.048	0.077	51.9	82.8
Cu	16.3	14.0	0.103	0.164	1.67	2.67	3.95	6.30
Fe	57.0	84.0	3.65	5.83	32.6	51.9	75.2	120
Hg	0.062	0.053	–	–	–	–	–	–
Li	0.088	0.049	–	–	–	–	–	–
Mn	4.40	1.03	0.600	0.740	1.07	1.71	0.292	0.465
Mo	0.081	0.251	–	–	–	–	0.095	0.151
Ni	0.608	0.170	0.009	0.015	0.052	0.083	1.61	2.56
Pb	45.0	62.0	–	–	0.244	0.389	0.052	0.084
Sb	0.009	0.009	0.001	0.002	0.012	0.019	0.022	0.035
Sr	4.73	2.64	1.16	1.32	1.15	1.833	0.874	1.39
U	0.054	0.09	–	–	0.006	0.009	0.011	0.017
V	0.170	0.579	0.012	0.019	0.088	0.140	0.804	1.28
Zn	508	427	0.394	0.629	4.07	6.49	1.11	1.77

different tissues as previously shown for Hg after desorption from microplastics in mussels (Rivera-Hernandez et al., 2019).

5. Conclusions and future directions

Several previous works have focused on the interaction between metals and microplastics but to date, this is the first study addressing metal leaching and accumulation process in CBs under real environmental conditions. Cigarette filters concentrate metals while tobacco is smoked. The accumulation of metals is inversely related to filter ventilation. Trying to avoid cancer lung and other diseases derived from the inhalation of smoked tobacco filters have been improved with to retain more toxic substances. This was an advance from the point of view of human health but not in terms of environmental protection, as CBs could act as vectors of toxic substances (i.e. metals) into the environment if not disposed of correctly.

A variety of interventions can help to prevent, reduce, and mitigate the environmental impacts of CBs. These measures include; applying additional litter fees on tobacco products to pay for clean-up and anti-tobacco product waste educational and advocacy programmes; levying and enforcing fines for littering that specifically include CBs or labelling cigarette filters as hazardous waste (World Health Organization, 2017). Also, other strategies could be explored like improving recycling solutions to promote the recovery of CBs (Marinello et al., 2020).

When smoked CBs reach the marine environment in a non polluted area, all the metals adsorbed to them are released in different quantities, being copper the element with the highest desorption percentage (91%) and molybdenum (35%) the one with the lowest. However, CBs can also accumulate metals from the environment when reaching contaminated waters (e.g. harbour areas). The adsorption of metals is directly related to the degradation of the CBs. The creation of free radicals in the CBs favours the binding of metals to the cellulose triacetate, the main component of the CBs. In this way, CBs may serve as a vector for metals in the marine environment when ending up in areas with lower metal concentrations.

Once desorbed from the CBs, metals may bioaccumulate in marine organisms. The present study has shown the increase in concentrations of some metals (Sr, Mn, U, Cr, Fe, Cu, Mo, Sb and Zn) in different tissues of oysters (i.e. gills and digestive gland) after exposure to leachates of CBs. Consequently, the high amount of metals adsorbed onto CBs weathered in the marine environment (beach or harbour), may derive in

an increase of metal concentration in oyster tissues. However, our results do not point to a risk of bioaccumulation as after decontamination, most of the metals are eliminated from the tissues. Nevertheless, potential bioaccumulation may happen if oysters are exposed for a longer time to waters contaminated with metals leached from the CBs.

Besides the visual contamination and physical effects on marine organisms (i.e. ingestion and suffocation), CBs could pose a chemical risk due to the toxic substances that they accumulate. Further research should be conducted for a better understanding of the interaction between metals and CBs under different environmental conditions and their potential bioaccumulation and toxicological effects in marine organisms.

CRediT authorship contribution statement

Juan Santos-Echeandía: Metal analysis, Writing - original draft. **Aurore Zeler:** Conceptual design of the experiments and field work. **Jesús Gago:** Writing - original draft. **Camille Lacroix:** Conceptual design of the experiment, Writing - original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jhazmat.2021.125816](https://doi.org/10.1016/j.jhazmat.2021.125816).

References

- A., Zipser, 1954. Cigarette Industry Convalescing; Filter Prescription Seems to HELP: Cigarette Output Survives a Crisis. *New York Time*, 3 Oct. Principio del formulario.
- Acosta-Coley, I., Mendez-Cuadro, D., Rodríguez-Cavallo, E., de la Rosa, J., Olivero-Verbel, J., 2019. Trace elements in microplastics in Cartagena: a hotspot for plastic pollution at the Caribbean. *Mar. Pollut. Bull.* 139, 402–411. <https://doi.org/10.1016/j.marpolbul.2018.12.016>.
- Addamo, A., Laroche, P., Hanke, G., 2017. Technical report of the Top marine litter items in Europe. *Publ. Off. Eur. Union*. <https://doi.org/10.2760/496717>.
- Alvarado, J., Cristiano, A., 1993. Determination of cadmium, cobalt, iron, nickel and lead in Venezuelan cigarettes by electrothermal atomic absorption spectrometry. *J. Anal. Spectrochim.* 8 (2), 253–259. <https://doi.org/10.1039/ja9930800253>.
- Anderson, J.C., Park, B.J., Palace, V.P., 2016. Microplastics in aquatic environments: implications for Canadian ecosystems. *Environ. Pollut.* 218, 269–280. <https://doi.org/10.1016/j.envpol.2016.06.074>.
- Andrady, A.L., 2011. Microplastics in the marine environment. *Mar. Pollut. Bull.* 62, 1596–1605. <https://doi.org/10.1016/j.marpolbul.2011.05.030>.
- André, S., Regional characterisation of marine litter in the Atlantic area. *CleanAtlantic Interreg project*. (<http://www.cleanatlantic.eu/marine-litter-in-the-atlantic-area/>).
- Araújo, M.C.B., Costa, M.F., 2019. A critical review of the issue of cigarette butt pollution in coastal environments. *Environ. Res.* 172, 137–149. <https://doi.org/10.1016/j.envres.2019.02.005>.
- Artham, T., Sudhakar, M., Venkatesan, R., Madhavan Nair, C., Murty, K.V.G.K., Doble, M., 2009. Biofouling and stability of synthetic polymers in sea water. *Int. Biodeterior. Biodegrad.* 63, 884–890. <https://doi.org/10.1016/j.ibiod.2009.03.003>.
- Ashton, K., Holmes, L., Turner, A., 2010. Association of metals with plastic production pellets in the marine environment. *Mar. Pollut. Bull.* 60, 2050–2055. <https://doi.org/10.1016/j.marpolbul.2010.07.014>.
- Baker, R.R., 2006. Smoke generation inside a burning cigarette: modifying combustion to develop cigarettes that may be less hazardous to health. *Prog. Energy Combust. Sci.* 32, 373–385. <https://doi.org/10.1016/j.pecs.2006.01.001>.
- Barnes, R.L., 2011. Regulating the disposal of cigarette butts as toxic hazardous waste. *Tob. Control* 20 (1), 45–48. <https://doi.org/10.1136/tc.2010.041301>.
- Belzagui, F., Buscio, V., Gutiérrez-Bouzán, C., Vilaseca, M., 2021. Cigarette butts as a microfiber source with a microplastic level of concern (<https://doi.org/10.1016/j.scitotenv.2020.144165>). *Sci. Total Environ.* 762, 144165. <https://doi.org/10.1016/j.scitotenv.2020.144165>.
- Bonomi, G., Incerti, G., Cesarano, G., Gaglione, S.A., Lanzotti, V., 2015. Cigarette butt decomposition and associated chemical changes assessed by ¹³C cpmas NMR (<https://doi.org/10.1371/journal.pone.0117393>). *PLoS One* 10 (1), e0117393. <https://doi.org/10.1371/journal.pone.0117393>.
- Brandt, A.M., 2007. *The Cigarette Century: the Rise, Fall, and Deadly Persistence of the Product That Defined America*. Basic Books, New York.
- Corcoran, P.L., Biesinger, M.C., Grifi, M., 2009. Plastics and beaches: a degrading relationship. *Mar. Pollut. Bull.* 58 (1), 80–84. <https://doi.org/10.1016/j.marpolbul.2008.08.022>.
- Dobaradaran, S., Nabipour, I., Saeedi, R., Ostovar, A., Khorsand, M., Khajehmadi, N., Hayati, R., Keshkar, M., 2017. Association of metals (Cd, Fe, As, Ni, Cu, Zn and Mn) with cigarette butts in northern part of the Persian Gulf. *Tob. Control* 26, 461–463. <https://doi.org/10.1136/tobaccocontrol-2016-052931>.
- Fernández, B., Santos-Echeandía, J., Rivera-Hernandez, J.R., Garrido, S., Albentosa, M., 2020. Mercury interactions with algal and plastic microparticles: comparative role as vectors of metals for the mussel, *Mytilus galloprovincialis*. *J. Hazard. Mater.* 396, 122739 <https://doi.org/10.1016/j.jhazmat.2020.122739>.
- French Agency for Food, (2019). Environmental and Occupational Health & Safety. *Liste FR Cigarette of 01/05/2019*, (www.anses.fr).
- Harris, B., 2011. The intractable cigarette “filter problem”. *Tob. Control* 20 (1), 10–16 [doi:10.1136/tc.2010.040113](https://doi.org/10.1136/tc.2010.040113).
- Ho, Y., McKay, J., 1999. Pseudo-second order model for sorption processes. *Process Biochem.* 34 (1999), 451–465. [https://doi.org/10.1016/S0032-9592\(98\)00112-5](https://doi.org/10.1016/S0032-9592(98)00112-5).
- Holmes, L.A., Turner, A., Thompson, R.C., 2012. Adsorption of trace metals to plastic resin pellets in the marine environment. *Environ. Pollut.* 160 (1), 42–48. <https://doi.org/10.1016/j.envpol.2011.08.052>.
- Iskander, F.Y., 1985. Egyptian and foreign cigarettes - I. Determination of trace elements in cigarette filter before and after smoking. *J. Radioanal. Nucl.* 91 (1), 191–196. <https://doi.org/10.1007/BF02036326>.
- Ito, H., Matsuo, K., Tanaka, H., Koestler, D.C., Ombao, H., Fulton, J., Shibata, A., Fujita, M., Sugiyama, H., Soda, M., Sobue, T., Mor, V., 2011. Nonfilter and filter cigarette consumption and the incidence of lung cancer by histological type in Japan and the United States: analysis of 30-year data from population-based cancer registries. *Int. J. Cancer* 128 (8), 1918–1928. <https://doi.org/10.1002/ijc.25531>.
- Joly, F.-X., Coulis, M., 2018. Comparison of cellulose vs. plastic cigarette filter decomposition under distinct disposal environments (<https://doi.org/10.1016/j.wasman.2017.11.023>). *Waste Manag.* 72, 349–353. <https://doi.org/10.1016/j.wasman.2017.11.023>.
- Kalcher, K., Kern, W., Pietsch, R., 1993. Cadmium and lead in the smoke of a filter cigarette. *Sci. Total Environ.* 128, 21–35 [https://doi.org/10.1016/0048-9697\(93\)90177-8](https://doi.org/10.1016/0048-9697(93)90177-8).
- Koutela, N., Fernández, E., Saru, M.-L., Psillakis, E., 2020. A comprehensive study on the leaching of metals from heated tobacco sticks and cigarettes in water and natural waters. *Sci. Total Environ.* 714, 136700 <https://doi.org/10.1016/j.scitotenv.2020.136700>.
- Lagergren, S., 1898. Zur theorie der sogenannten adsorption gelöster stoffe. *Kungliga Svenska Vetenskapsakademiens Handlingar* 24 (4), 1–39. (<https://doi.org/10.1007/BF01501332>).
- Marinello, S., Lolli, F., Gamberini, R., Rimini, B., 2020. A second life for cigarette butts? A review of recycling solutions. *J. Hazard. Mater.* 384, 121245 <https://doi.org/10.1016/j.jhazmat.2019.121245>.
- Moerman, J.W., Potts, G.E., 2011. Analysis of metals leached from smoked cigarette litter. *Tob. Control* 20 (1), 30–35. <https://doi.org/10.1136/tc.2010.040196> (Principio del formulario).
- Moriwaki, H., Kitajima, S., Katahira, K., 2009. Waste on the roadside, ‘poi-sute’ waste: its distribution and elution potential of pollutants into environment. *Waste Manag.* 29 (3), 1192–1197. <https://doi.org/10.1016/j.wasman.2008.08.017>.
- Murata, K., Sato, K., Sakata, Y., 2004. Effect of pressure on thermal degradation of polyethylene. *J. Anal. Appl. Pyrol.* 71 (2), 569–589. <https://doi.org/10.1016/j.jaap.2003.08.010>.
- Nakashima, E., Isobe, A., Kako, S., Imai, T., Takahashi, S., 2012. Quantification of toxic metals derived from macroplastic litter on Ookushi Beach, Japan. *Environ. Sci. Technol.* 46, 10099–10105. <https://doi.org/10.1021/es301362g>.
- Nguyen, T.P.N., Jun, B.M., Kwon, Y.N., 2017. The chlorination mechanism of integrally asymmetric cellulose triacetate (CTA)-based and thin film composite polyamide-based forward osmosis membrane. *J. Membr. Sci.* 523 (1), 111–121. <https://doi.org/10.1016/j.memsci.2016.09.020>.
- Novotny, T.E., Slaughter, E., 2014. Tobacco product waste: an environmental approach to reduce tobacco consumption. *Curr. Environ. Health Rep.* 1 (3), 208–216. <https://doi.org/10.1007/s40572-014-0016-x>.
- Novotny, T.E., Lum, K., Smith, E., Wang, V., Barnes, R., 2009. Cigarettes butts and the case for an environmental policy on hazardous cigarette waste. *Int. J. Environ. Res. Public Health* 6 (5), 1691–1705. <https://doi.org/10.3390/ijerph6051691>.
- Pelit, F.O., Demirdogen, R.E., Henden, E., 2013. Investigation of heavy metal content of Turkish tobacco leaves, cigarette butt, ash, and smoke. *Environ. Monit. Assess.* 185 (11), 9471–9479. <https://doi.org/10.1007/s10661-013-3266-4>.
- Prego, R., Filgueiras, A.V., Santos-Echeandía, J., 2008. Temporal and spatial changes of total and labile metal concentration in the surface sediments of the Vigo Ria (NW Iberian Peninsula): Influence of anthropogenic sources. *Mar. Pollut. Bull.* 56 (5), 1031–1042. <https://doi.org/10.1016/j.marpolbul.2008.01.036>.
- Quéméneur, M., CHifflet, S., Akrouf, F., Bellaaj-Zouari, A., Belhassen, M., 2020. Impact of cigarette butts on microbial diversity and dissolved trace metals in coastal marine sediment. *Estuar. Coast. Shelf Sci.* 240, 106785 <https://doi.org/10.1016/j.ecss.2020.106785>.
- Rebischung, F., Chabot, L., Biaudet, H., Pandard, P., 2018. Cigarette butts: a small but hazardous waste, according to European regulation. *Waste Manag.* 82, 9–14. <https://doi.org/10.1016/j.wasman.2018.09.038>.
- Rivera-Hernández, J.R., Fernández, B., Santos-Echeandía, J., Garrido, S., Morante, M., Santos, P., Albentosa, M., 2019. Biodynamics of mercury in mussel tissues as a function of exposure pathway: natural vs microplastic routes. *Sci. Total Environ.* 674, 412–423. <https://doi.org/10.1016/j.scitotenv.2019.04.175>.
- Sánchez, J., Camelelle, C., 2017. Biosorción de mercurio (Hg²⁺) usando materiales sólidos residuales como adsorbentes. *Afinidad: Revista de química teórica y aplicada* 74 (577), 18–25.
- Santos-Echeandía, J., Rivera-Hernández, J.R., Rodrigues, J.P., Moltó, V., 2020. Interaction of mercury with beached plastics with special attention to zonation, degradation status and polymer type. *Mar. Chem.* 222, 103788 <https://doi.org/10.1016/j.marchem.2020.103788>.
- Suami, R.B., Al Salah, D.M.M., Kabala, C.D., Otamonga, J.P., Mulaji, C.K., Mpiana, P.T., Poté, J.W., 2019. Assessment of metal concentrations in oysters and shrimp from Atlantic Coast of the Democratic Republic of the Congo. *Heliyon* 5 (12), e03049. <https://doi.org/10.1016/j.heliyon.2019.e03049>.
- Wang, D.K., Zhang, X., da Costa, J.C.D., 2014. Claisen-type degradation mechanism of cellulose triacetate membranes in ethanol-water mixtures. *J. Membr. Sci.* 454, 119–125. <https://doi.org/10.1016/j.memsci.2013.12.010>.
- World Health Organization, 2017. Tobacco and its environmental impact: an overview. Licence: CC BY-NC-SA 3.0 IGO.