2024-02

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Turner, A

10.1016/j.chemosphere.2023.140845
Chemosphere
Elsevier BV

Chemosphere 349 (2024) 140845

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Cigarette filter fibres as a source and sink of trace metals in coastal waters

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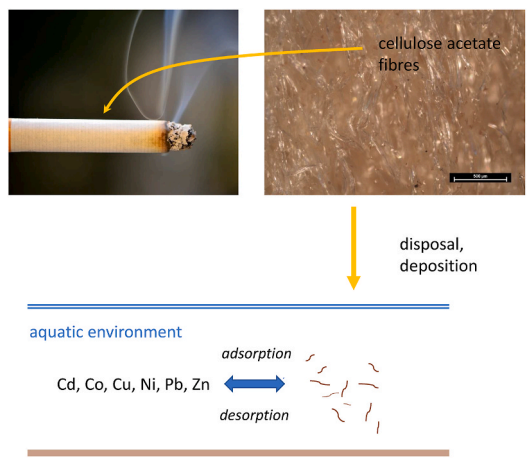
HIGHLIGHTS

- Smoked cigarette filters of cellulose acetate ground to fibres and suspended in coastal waters.
- Release of pre-existent trace metals range from ~40% (Pb) to ~90% (Cd, Co, Zn).
- Partitioning (K_D; L kg^{-1}) defining adsorption of added metals ranges from <10 (Co) to 1000 (Cu).
- Mean K_Ds exhibit significant correlation with published metal binding constants to humic acid.
- Findings are more generally appliable to anthropogenic cellulosic fibres.

GRAPHICAL ABSTRACT



ARTICLE INFO

Handling editor: Tamara S. Galloway

Keywords:
Estuary
Microplastics
Microfibres
Adsorption
Partition coefficient
Hydrophobic

ABSTRACT

Cellulose acetate fibres from cigarette filters represent a form of microplastic that has received little attention in the environment. In this study, a ground composite of spent, smoked filter material (FM) has been used to investigate the role of cellulose acetate fibres as a source and a sink of trace metals (Cd, Co, Cu, Ni, Pb and Zn) in coastal waters. FM suspended in river water and seawater and mixtures thereof representative of an estuarine gradient resulted in the leaching of pre-existent metals derived from the combustion of tobacco, with mean percentages of release ranging from about 40 for Pb to nearly 90 for Cd, Co and Zn. Addition of 40 μg L^{-1} of each metal to FM suspensions incubated for 48 h yielded mean partition coefficients (K_Ds) ranging from <10 L kg^{-1} for Co to > 100 L kg^{-1} for Cu, Pb and Zn, with Cu and Ni displaying a net increase in K_D with increasing salinity. Adsorption is interpreted in terms of hydrophobic interactions between metal-organic complexes and the cellulose acetate surface, and in support of this assertion K_Ds exhibited a significant, positive relationship with published metal-humic acid binding constants. The findings of this study improve our understanding of the role of cellulosic microfibres more generally in transporting trace metals in aquatic systems.

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https://doi.org/10.1016/j.chemosphere.2023.140845
Received 22 May 2023; Received in revised form 20 November 2023; Accepted 27 November 2023
Available online 1 December 2023

1. Introduction

Cigarette butts are one of the most common types of environmental litter (Rebischung et al., 2018). For example, the Local Environmental Quality Survey for England (Keep Britain Tidy, 2019) found that 79% of sites surveyed in 2018 had smoking-related litter present, representing a 6% increase from 2014. Without intervention, butts will end up in the coastal and marine environment where, in addition to directly discarded butts, they form a major constituent of beach litter (Munari et al., 2016; Araújo and Costa, 2019).

Cigarette butts are made up of a filter, ash, unburnt tobacco and paper. Filter material is normally constructed of fibres of the synthetic polymer, cellulose acetate, which is manufactured from cellulose through acetylation and has between two and three hydroxy groups esterified, and may contain functional additives like plasticisers, flame retardants, delustrants and softeners. The filter acts to remove volatile toxicants through adsorption (physisorption and chemisorption) and aerosols through entrapment (Branton et al., 2016). As a consequence of their filtration properties, butts, or more specifically, spent filters, act as a secondary source of chemicals from combusted tobacco and cigarette manufacturing to the environment through leaching. Chemicals identified in leachates include polycyclic aromatic hydrocarbons, pesticides, phthalates, pyridine, and heavy metals and metalloids (Moriwaki et al., 2009; Venugopal et al., 2021) which, individually or when combined, have been shown to be toxic to a range of aquatic organisms (Micevska et al., 2006; Green et al., 2020; Sandgaard et al., 2023).

Although cellulose is readily degraded by the cellulase enzyme, acetylation of the polymer and the addition of additives inhibit the biodegradation of cellulose acetate in the environment. Ultra-violet light can, however, break down cellulose acetate filters into smaller components but these can persist for more than a decade (Novotny et al., 2009; Torkashvand et al., 2020). During this period, individual fibres, or microplastics, are generated that are associated with a wide range of additional environmental problems. Among the impacts of microplastics is an ability to acquire (through adsorption), transport and transfer (to biota) other contaminants present in the water column, like persistent organic pollutants and heavy metals (Ashton et al., 2010; Bakir et al., 2012).

In the present study, we evaluate the importance of spent cigarette filter material as both a source and a sink of a range of toxic or potentially toxic trace metals. Specifically, and under carefully controlled laboratory conditions, we quantify metals released from a composite of ground, filter material into natural waters (river water, seawater and mixtures thereof representing an estuarine gradient), and determine the degree of adsorption to the material for metals added to natural waters. The results will improve our understanding of the role of cigarette filters as pollutants and adsorbents as well as the potential impacts of anthropogenic cellulosic fibres more generally.

2. Methodology

2.1. Materials

All plasticware and glassware was soaked in 10% HNO_3 and rinsed in Millipore Milli-Q water before being used. Chemical reagents were purchased from VWR and Fisher Scientific and were of analytical grade or equivalent, and trace metal standards (Cd, Co, Cu, Ni, Pb, Zn) were VWR Aristar-grade solutions (either 1000 mg L^{-1} or 10,000 mg L^{-1} in 2–5% HNO_3).

River water was sampled in a 2-L polyethylene bottle from the River Plym (pH 6.8), a small river draining protected moorland, in July 2022. In the laboratory, the sample was vacuum-filtered through a 0.45 μm Whatman cellulose nitrate membrane and stored in a clean bottle at 4 °C and in the dark. Seawater (salinity ~ 34; pH = 7.8) was available on tap in the laboratory and after online filtration through 0.6 μm having been collected in bulk from Plymouth Sound. A low acidity working stock solution of metals (1 mg L^{-1} of each metal) was prepared by serial dilution of standards in Milli-Q water and, subsequently, filtered River Plym water.

Spent cigarette filters employed in this study ($n \sim 50$) were supplied in polyethylene specimen bags from the same individual who smoked 'rollie' cigarettes consisting of Swan Extra Slim filters and Cutters Choice tobacco. Filters were separated from the butts and ground and homogenised to a fine composite in liquid nitrogen using a porcelain pestle and mortar. The resulting composite of spent filter material (FM) was transferred to a glass Petri dish and oven-dried at 40 °C overnight in order to remove any residual moisture. In addition, five new (unsmoked) filters were processed likewise.

2.2. Characterisation of filter material

About 10 mg of new and used FM were inspected under a NIKON SMZ800 stereomicroscope fitted with a 1× achromatic objective (and attaining a magnification up to 63×) that was connected to an Olympus SC30 camera operated by Olympus Stream software.

Both materials were also analysed by attenuated total reflectance Fourier-transform-infrared (ATR-FTIR) spectrometry using a Bruker Vertex 70. Here, offcuts of whole (unground) filters were clamped against the diamond crystal before spectra were acquired with 16 scans in the region 4000 to 400 cm^{-1} and at a resolution of 4 cm^{-1}. Sample spectra were compared with polymer spectra in various libraries.

2.3. Adsorption experiment and controls

An adsorption experiment simulating estuarine mixing was performed in 32 x 50 mL screw-capped polypropylene centrifuge tubes. To each tube, 25 mg of spent FM and 25 mL of river water, seawater or a precise river water-seawater mixture were added to obtain four reactors each of eight different salinities (0, 1, 3, 5, 10, 15, 20, 34 g kg^{-1}). Suspensions were conditioned for 24 h at room temperature before triplicates from each salinity were spiked with the working stock to concentrations of 40 μg L^{-1} of each trace metal (remaining tubes served as controls and allowed an evaluation of metal release from spent FM to be made). In a series of preliminary (isotherm) experiments, this concentration was the lowest at which adsorption of all metals to the FM could be detected. Centrifuge tubes were then agitated on a Stuart SSL1 orbital shaker at 150 RPM for 48 h before being vacuum-filtered through 0.45 μm Whatman membranes. Ten mL filtrates were transferred to a series of 15 mL screw-capped polyethylene centrifuge tubes before being acidified to pH < 2 with 1 mL of 1 M HNO_3.

Centrifuge tubes used as reactor vessels in the adsorption experiments were subsequently acid-extracted in 25 mL of 1 M HCl for 24 h on the orbital shaker. These tubes were then diluted to 50 mL with Milli-Q water pending analysis. Membrane filters arising from the adsorption experiment and controls were air-dried in petri-dishes for 24 h before being transferred to a series of 15 mL centrifuge tubes and digested in 10 mL of 1 M HCl for 24 h. In order to avoiding settled cellulose acetate fibres, the top 5 mL of each digest were pipetted into new centrifuge tubes pending analysis. In addition, this process was repeated in quadruplicate for five 25 mg portions of spent cigarette FM that had not been subject to the adsorption experiment.

2.4. ICP- MS analysis

Aqueous filtrates (or five-fold dilutions thereof in Milli-Q water where salinity was 10 g kg^{-1} or greater), triplicate samples of filtered river water and diluted seawater, acid extracts of the reactor vessels and digests of FM were analysed for Cd, Co, Cu, Ni, Pb and Zn by inductively coupled plasma-mass spectrometry (ICP-MS) using a Thermo Scientific iCAP TQ with a concentric glass nebuliser and cyclone spray chamber. The instrument was calibrated using blanks and mixed, matrix-matched standards up to 200 μg L^{-1}, while internal standardisation was achieved

by addition of 200 μg L^{-1} of ^{115}In and ^{192}Ir to all samples and standards. Instrument drift was monitored by standard checks after every ten samples, with reanalysis performed if deviation of more than 10% from the expected value occurred. Regular analysis of a diluted reference material (SCP Science *Enviro*MAT Drinking Water, low, EP-L) returned concentrations of each metal that were persistently within the respective tolerance intervals. Method limits of detection and limits of quantification (in μg L^{-1}), based on three and ten standard deviations arising from ten measurements of 1 M HCl blanks, respectively, were Cd = 0.015 and 0.051, Co = 0.007 and 0.025, Cu = 0.33 and 1.09, Ni = 0.27 and 0.91, Pb = 0.21 and 0.70, and Zn = 5.0 and 16.6.

3. Results

3.1. Characteristics of spent FM

Under the microscope (Fig. 1), spent and ground cigarette FM appeared to consist of clear or translucent fibres, with an orange tinge, of up to 400 μm in length and between about 30 and 50 μm in diameter. Material was contaminated by dark specks that presumably reflect the entrapment of combusted tobacco.

Fig. 2 compares the infrared spectra of new and smoked cigarette FM. Both spectra were very similar, with no evidence of alteration effected by smoking, and were matched with cellulose acetate (CAS no. 9004-35-7).

Based on a representative fibre (as a regular cylinder) of 300 μm in length and 40 μm in diameter, and given the density of cellulose acetate (about 1.3 g cm^{-3}), we estimate that there are about 2×10^6 fibres per g of ground material, and that the geometric surface area of this material is 0.0821 m^2 g^{-1}.

3.2. Metal content of materials

Table 1 shows the ambient concentrations of trace metals in filtered river water and seawater and the original metal content of the ground, spent, cigarette FM. In Plym River water, mean concentrations range from <1 μg L^{-1} for Cd, Co, Ni and Pb to below 16.6 μg L^{-1} for Zn. In Plymouth Sound seawater, mean concentrations range from <1 μg L^{-1} for Cd, Co, Ni and Pb to about 18 μg L^{-1} for Zn. According to a series of paired *t*-tests, mean concentrations of Cd and Co are significantly higher ($p < 0.05$) in seawater than in river water. In the FM, mean metal concentrations range from <1 μg g^{-1} for Cd and Co to about 100 μg g^{-1} for Zn.

3.3. Metal desorption

The controls in the absence of added trace metal allowed an evaluation of metal release (or leaching) from the spent, ground FM to be made. Release was evident from an increase in aqueous metal concentrations in the controls relative to ambient river water and seawater but, because of detection constraints in the aqueous phase (see Table 1), was more readily calculated from the ratio of w/w metal concentrations in FM remaining after the 48-h exposure (C_{FM}, μg g^{-1}) relative to the corresponding metal concentration in the original, spent FM (C_{FM*}, μg g^{-1}; Table 1):

$$\text{desorption}, \% = 100\% \text{ x } (1 - C_{FM} / C_{FM*}) \quad (1)$$

Release calculated this way did not exhibit any clear relationship with salinity and mean values for each metal are, therefore, shown in Fig. 3. While the mean release of Cd, Co and Zn is close to 90% and exceeds 70% for Ni and Cu, mean release of Pb is less than 40%.

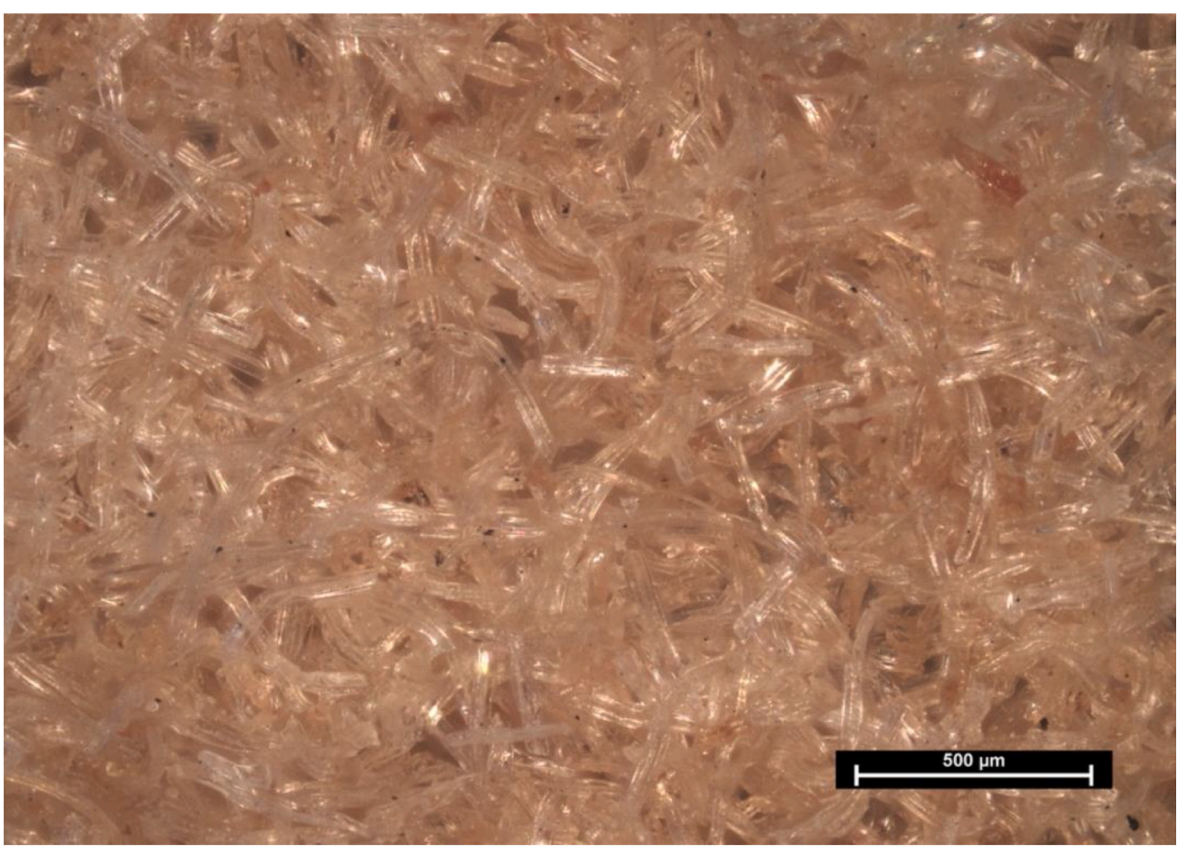

Fig. 1. Microscopic image of the spent and ground cigarette FM.

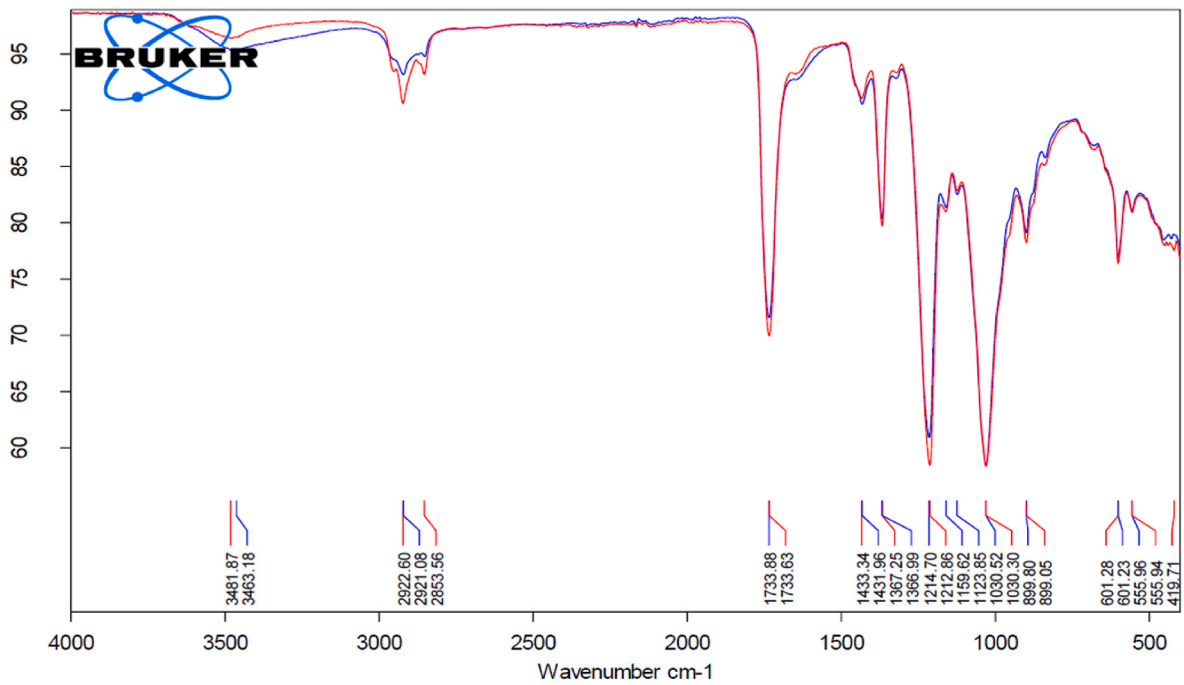

Fig. 2. FTIR spectra of unsmoked (red) and spent (blue) cigarette filters. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 1
Trace metal concentrations in filtered Plym River water, Plymouth Sound seawater and the ground, spent FM. The mean ± one standard deviation of *n* measurements is shown unless the metal was below the limit of quantification.

	n	Cd	Co	Cu	Ni	Pb	Zn
river water, μg L^{-1}	3	0.020 ± 0.006	0.061 ± 0.001	1.21 ± 0.12	<0.91	<0.70	<16.6
seawater, μg L^{-1}	3	0.12 ± 0.02	0.19 ± 0.03	1.71 ± 0.53	<0.91	<0.70	18.4 ± 1.82
spent FM, μg g^{-1}	4	0.97 ± 0.52	0.58 ± 0.15	7.21 ± 0.71	4.18 ± 0.31	2.11 ± 0.56	96.5 ± 15.8

3.4. Metal adsorption

The distribution of each trace metal measured in the adsorption experiment is shown as a function of salinity (created by mixing filtered River Plym water and Plymouth Sound seawater in different proportions) in Fig. 4. For all metals in each phase, concentrations were above the limits of quantification specified above. For Cd, Co and Ni, concentrations are greatest (~20–40 μg L^{-1}) in the aqueous phase, C_W (w/v), and exhibit a reduction with increasing salinity. For each metal, concentrations adsorbed to the spent FM, C_{FM} (w/v) and adsorbed to the interior of the polypropylene reactor vessel, C_{PP} (w/v), are similar and <10 μg L^{-1} throughout. Total concentrations, C_T:

$$C_T = C_W + C_{FM} + C_{PP} \quad (2)$$

average 38.8 ± 4.6 μg L^{-1} for Cd, 29.1 ± 3.0 μg L^{-1} for Co and 38.5 + 3.2 μg L^{-1} for Ni. Given the relatively low concentrations of these metals in the original materials (Table 1) and an added concentration of 40 μg L^{-1} in each case, these observations suggest that Cd and Ni are analytically accounted for. Regarding Co, however, there is a shortfall reflecting loss in the experiment that could be related to incomplete recovery from the cigarette FM or polypropylene reactor surface by 1 M HCl.

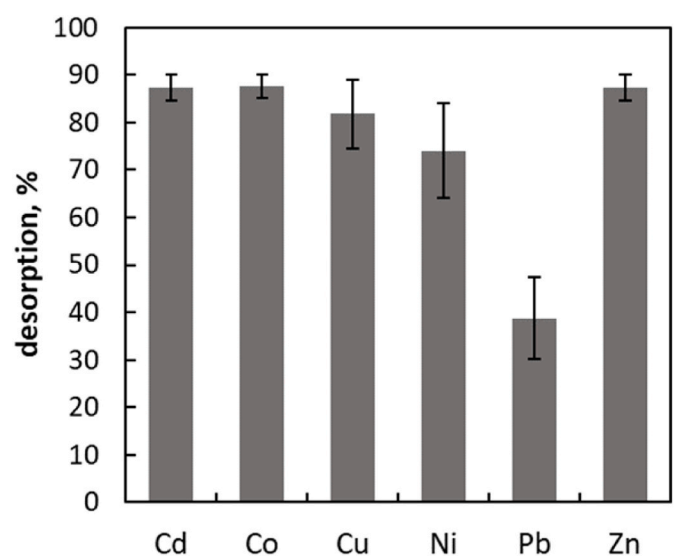

Fig. 3. Percentage of trace metal release after 48 h from the spent FM and calculated according to Equation (1). Errors are one standard deviation about the mean of eight measurements (made at different salinities).

For Pb, C_W exhibits an increase with increasing salinity but is less than 25 μg L^{-1} throughout, and the sum of C_{FM} and C_{PP} is greater than or similar to C_W at each salinity. For Cu, C_W exhibits a net reduction with increasing salinity while C_{FM} exhibits a net increase and C_{PP} is relatively invariant. Total concentrations average 38.3 ± 3.4 μg L^{-1} for Pb and 44.2 ± 4.8 μg L^{-1} for Cu, with exceedance of the added concentration of 40 μg L^{-1} for the latter metal presumably related to the relatively high background concentrations in the original materials (Table 1).

Regarding Zn, C_{PP} is highly variable among replicates but mean concentrations are greater than either C_W or C_{FM} at each salinity. Total concentrations average 221.7 + 31.2 μg L^{-1} and exceed the added concentration by a factor of more than five. The sum of the added concentration and original concentrations in the cigarette filter material

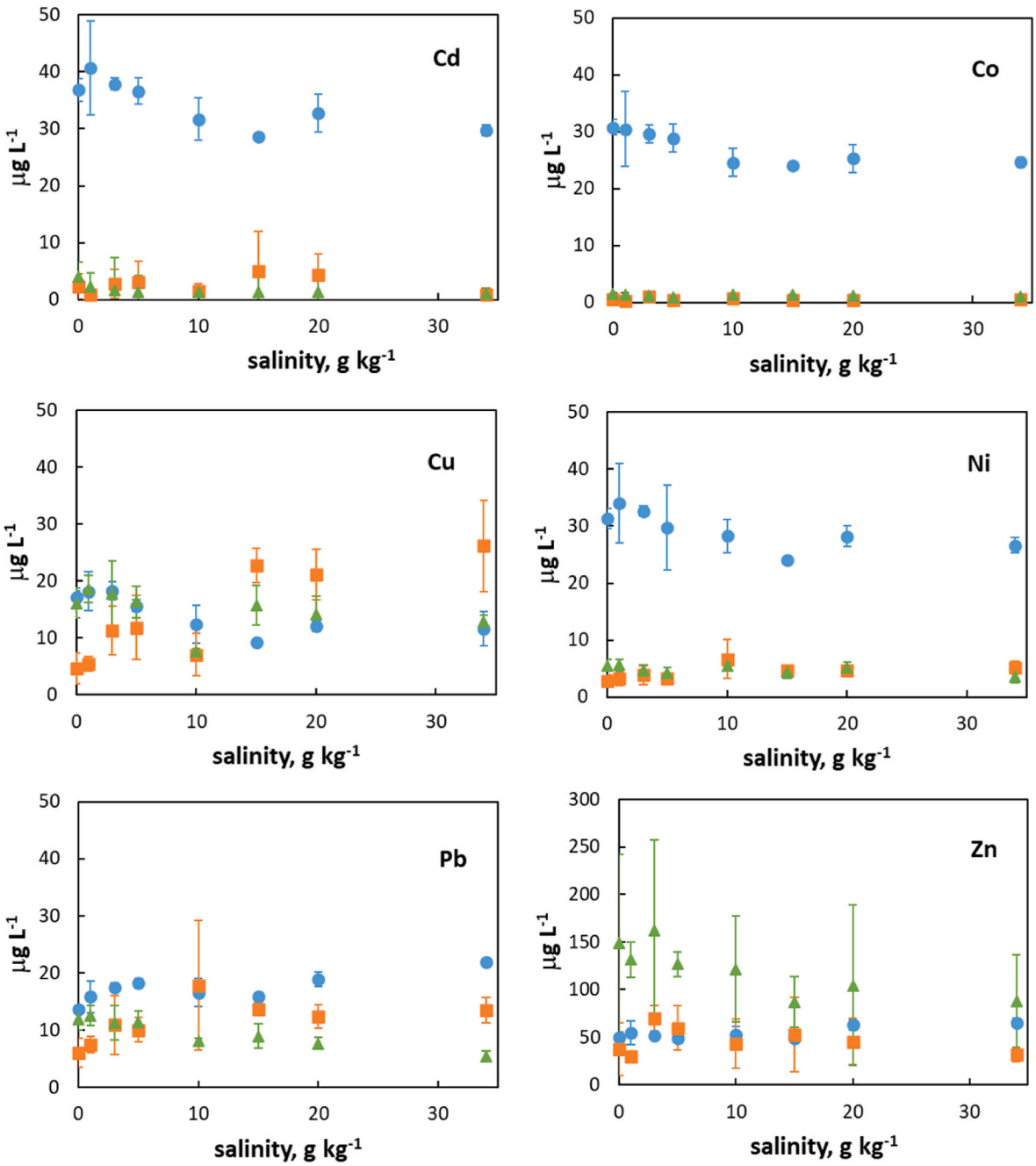

Fig. 4. Trace metal concentrations in the aqueous phase (C_W, blue circles), adsorbed to the spent FM (C_{FM}, orange squares) and adsorbed to the internal reactor vessel surface (C_{PP}, green triangles) as a function of salinity in the River Plym-seawater mixtures after a period of 48 h. Errors are one standard deviation about the mean of three experimental measurements. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

and river water or seawater is about 150–160 μg L^{-1} suggesting that Zn contamination arises externally (e.g., from the containers or reagents or during sample manipulation).

3.5. FM-water partition coefficients

Fig. 5 shows the partitioning of each metal between the spent FM and the aqueous phase. Partition coefficients on a filter mass basis, K_D (L kg^{-1}), were calculated as follows:

$$K_D = C_{FM} \text{ x } 1000 / C_W \quad (3)$$

where the units of C_{FM} are μg g^{-1}, while partition coefficients on a FM surface area basis, K_D^s (L m^{-2}), were calculated as follows:

$$K_D^s = (C_{FM} \text{ x } 1000) / (C_W \text{ x } 0.0821) \quad (4)$$

Here, the constant in the denominator is the calculated geometric surface area of fibres in m^2 per g of filter material. Partition coefficients are often assumed to represent equilibrium conditions but in the present context, strictly, they are specific to a 48-h period.

The magnitude of K_D or K_D^s gives a measure of the affinity of a metal (pre-existent and added) for the filter surface under the experimental conditions. Overall, coefficients are greatest for Cu, Pb and Zn and lowest for Co, with Cu and Ni exhibiting a net increase over the salinity gradient.

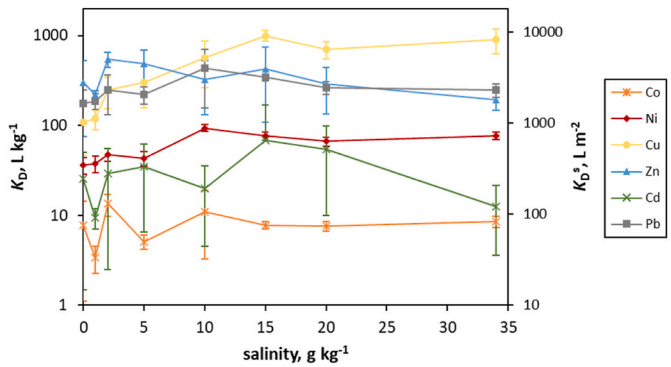

Fig. 5. FM-water partition coefficients of trace metals on a mass basis, K_D, and on a surface area basis, K_D^S, as a function of salinity in the River Plym-seawater mixtures and calculated according to Equations (3) and (4). Errors are one standard deviation about the mean of three experimental measurements.

4. Discussion

An important observation of the present study is that external contamination and metal adsorption to containers can be problematic in any approach where interactions between the adsorbent and adsorbate are limited. This highlights the requirements for careful experimental design and robust analytical considerations in studies involving trace metals and microplastics. In particular, adsorbed concentrations should never rely on mass balance (the difference between added and measured aqueous concentrations) as this could lead to a serious overestimation of adsorption to the targeted plastic (e.g., Almeida et al., 2020; Yu et al., 2021; Lim et al., 2022).

With these potential artefacts minimised, this study has shown that spent (smoked) cigarette FM can act as both a source and sink of trace metals in the aquatic environment (and specifically, in rivers, estuaries and coastal waters). Metals in the spent FM are reaction residues and contaminants in the original cellulose acetate and contaminants derived from the burning of tobacco and tipping paper that are retained on filtration, with concentrations close to the detection limit in unsmoked material suggesting the latter source is more important. Metal concentrations in Table 1 are similar in magnitude and sequence to those recently reported for filter materials from other spent cigarettes (Dinh et al., 2021; Snaychuk et al., 2022). Here, particulate metals are captured by the cellulose acetate matrix during smoking, with Dinh et al. (2021) suggesting the retention is related to metal density.

With the exception of Pb, and perhaps because of its relatively high density, these metals are readily released in natural waters, presumably through desorption or solubilisation from combusted particles remaining in the ground composite. Significant metal release has also been shown in independent studies using whole cigarettes sourced from litter or artificially smoked cigarette suspended in or exposed to deionised water, tap water and seawater (Moerman and Potts, 2011; Koutela et al., 2020; Akhbarizadeh et al., 2021; Santos-Echeandía et al., 2021). The present study did not establish any dependence of release on salinity, while Moerman and Potts (2011) found no relationship between release and pH (between 4 and 6), suggesting that water chemistry (within environmental limits) is not a significant factor. Overall, and despite cigarette butts being one of the most important forms of litter, impacts arising from metal release are likely to be greatest in aquatic systems on a localised scale and for intact, spent filters (where a high density of fibres remain); for example, in interstitial waters if butts become buried in sediment, or for animals that inadvertently ingest and digest material.

Although environmental release of particulate and combusted trace metals acquired from smoking takes place, adsorption also occurs when the cellulose acetate is exposed to metals in the environment. Adsorption has been demonstrated in long-term (up to several months) deployments of filters in the coastal environment, including on the sediment surface itself (Dobaradaran et al., 2017; Santos-Echeandía et al., 2021). However, in these studies, and because whole filters were used, it is possible that metals had also been acquired through entrapment of contaminated sediment particles within the filter matrix. In the present study, adsorption (without entrapment) was measured on to ground filter material that represents cellulose acetate after fragmentation (as individual fibres) and during suspension in the water column. Adsorption to this material is variable among the metals studied, with 48-h partition coefficients on a mass basis (K_D) ranging from <10 L kg^{-1} for Co to up to about 1000 L kg^{-1} for Cu, and a net increase in K_D with increasing salinity for Cu and Ni but no clear trends in other cases.

Trace metal adsorption studies in estuaries of typical pH values and involving suspended sediments (and including the Plym Estuary) often report a reduction in K_D with increasing salinity (Turner and Millward, 2002). This is because metal adsorption usually involves the free ion (and in the present study, bivalent ions) interacting with negatively charged regions of the particle surface, and the concentration and activity of this species decrease with increasing salinity (Tipping et al., 1998; Moermond et al., 2001). With respect to cellulose acetate, its unmodified surface is unlikely to attract or bind with the free ion to a significant extent and other species must be involved in any interactions. Kiso et al. (1999) report that cyclic organic compounds adsorb to cellulose acetate through hydrophobic bonding and we suspect that weak (and possibly hydrophobic) interactions between the cellulose acetate surface and organic complexes of metals take place; an increase in adsorption with increasing salinity observed for some metals would then reflect the salting out (through electrostriction) of these complexes (Turner et al., 2002). We did not measure the dissolved organic matter content of the river and seawater end-members but previous studies have indicated concentrations of around 1.5–2 mg L^{-1} (Turner et al., 2004). Metal-organic complexation may take place in the aqueous phase prior to interactions with cellulose acetate, or on the cellulose acetate surface itself after the sorption of aqueous organic molecules during sample conditioning. In support of this assertion, a statistically significant relationship was found between the average log K_D for each metal (combining all salinities) and intrinsic equilibrium constants for metal binding with humic acids, pK_{MHA}, that have been derived from the

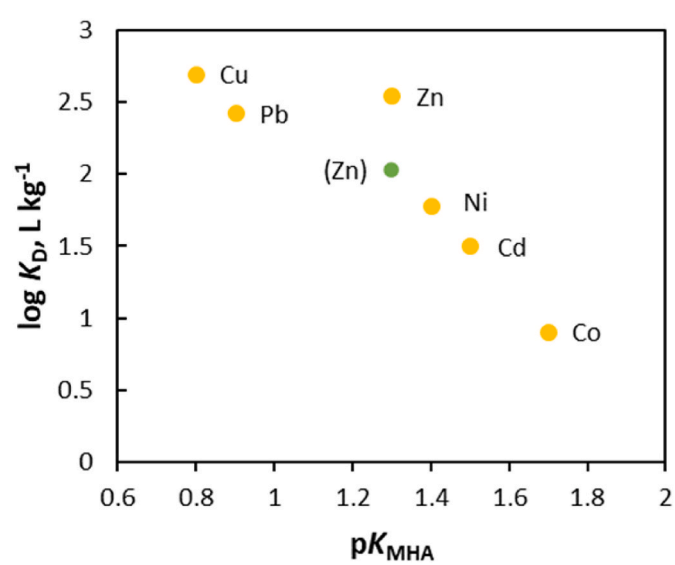

Fig. 6. Mean log K_D, defining spent FM (cellulose acetate) - aqueous partitioning for each trace metal, versus intrinsic metal binding constants for humic acid reported by Tipping et al. (1998). Note that a reduction in pK_{MHA} is associated with an increase in metal binding. For all data, $r = 0.882$ ($p = 0.019$), but by replacing Zn with a control-corrected K_D (in green), $r = 0.972$ ($p = 0.001$). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

literature (as averages) and used to model organic complexation in estuaries by Tipping et al. (1998) (Fig. 6). Note that Zn, as an outlier, has a relatively high K_D, because this measure includes pre-existing metal as a significant contaminant of the original and spent FM. Correcting K_D by subtracting an average concentration determined in the control (all salinities) of 13.0 μg g^{-1} results in a better relationship with greater statistical significance.

Overall, values of K_D defining trace metal adsorption to cigarette filter material are small compared with corresponding values for other, natural solids measured under comparable conditions. For example, in the River Plym, radiotracer experiments have returned values of K_D for Cd, Ni and Zn of 67,000 L kg^{-1}, 5800 L kg^{-1} and 53,000 L kg^{-1}, respectively (Turner and Millward, 2002). On this basis, therefore, cigarette FM would be expected to play a minor role in the transport and retention of metals in rivers and estuaries. However, it is possible that metal adsorption to FM is enhanced as the cellulose acetate degrades through photooxidation. For example, an increase in surface area, porosity and density of anionic functional (binding) groups has been observed on degradation of cellulose triacetate membranes (Wang et al., 2014) and modification or functional group grafting on cellulose acetate is known to facilitate metal binding through complexation (Tian et al., 2011).

In summary, once in the aquatic environment cigarette filters are likely to act as a localised source of trace metals as contaminated combusted particles are mobilised or broken down and partially solubilised, and as a sink of metals through adsorption of organic-metal complexes to the cellulose acetate surface. The latter interaction likely becomes more widespread and significant as fibrous FM disintegrates and cellulose acetate degrades and acquires functional groups and is predicted to be greatest for metals with a higher affinity for natural organic ligands (e.g., Cu and Pb). These characteristics might be more generally applicable to other semi-synthetic cellulosic fibres, including those derived from clothing like rayon, but further studies would be required to confirm this.

CRediT authorship contribution statement

Andrew Turner: Conceptualization, Data curation, Investigation, Project administration, Supervision, Writing – original draft, Writing – review & editing. **Abigail Louise Cundell:** Data curation, Formal analysis, Investigation, Methodology, 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.

Data availability

Data will be made available on request.

Acknowledgements

We are grateful to Billy Simmonds and Rob Clough (University of Plymouth) for technical assistance.

References

Akhbarizadeh, R., Dobaradaran, S., Parhizgar, G., Schmidt, T.C., Mallaki, R., 2021. Potentially toxic elements leachates from cigarette butts into different types of water: a threat for aquatic environments and ecosystems? Environ. Res. 202, 111706.

Almeida, C.M.R., Manjate, E., Ramos, S., 2020. Adsorption of Cd and Cu to different types of microplastics in estuarine salt marsh medium. Mar. Pollut. Bull. 151, 110797.

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.

Ashton, K., Holmes, L., Turner, A., 2010. Association of metals with plastic production pellets in the marine environment. Mar. Pollut. Bull. 60, 2050–2055.

Bakir, A., Rowland, S.J., Thompson, R.C., 2012. Competitive sorption of persistent organic pollutants onto microplastics in the marine environment. Mar. Pollut. Bull. 64, 2782–2789.

Branton, P., Leistner, M., Wöllner, M., Kaskel, S., 2016. An innovative technique for rapid screening of cigarette filter adsorbents. Chem. Eng. Technol. 40, 71–75.

Dinh, Q.P., Norvisa, R., Jeong, H., Nugraha, W.C., Addai-Arhin, S., Viet, P.H., Tominaga, N., Ishibashi, Y., Arizono, K., 2021. Mercury, cadmium, and lead in cigarettes from international market: concentrations, distributions and absorption ability of filters. J. Toxicol. Sci. 46, 401–411.

Dobaradaran, S., Nabipour, I., Saeedi, R., Ostovar, A., Khorsand, M., Khajeahmadi, N., Hayati, R., Keshtkar, M., 2017. Association of metals (Cd, Fe, As, Ni, Cu, Zn and Mn) with cigarette butts in northern part of the Persian Gulf. Tobac. Control 26, 461–463.

Green, D.S., Kregting, L., Boots, B., 2020. Smoked cigarette butt leachate impacts survival and behaviour of freshwater invertebrates. Environ. Pollut. 266, 115286.

Keep Britain Tidy, 2019. Litter in England: the Local Environmental Quality Survey of England 2017/18. Wigan, UK.

Kiso, Y., Kitao, T., Nishimura, K., 1999. Adsorption properties of cyclic compounds on cellulose acetate. J. Appl. Polym. Sci. 71, 1657–1663.

Koutela, N., Fernandez, 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.

Lim, C., Kim, N., Lee, J., Yoon, Y., 2022. Potential adsorption of diverse environmental contaminants onto microplastics. Water 14, 4086.

Micevska, T., Warne, M. St J., Pablo, F., Patra, R., 2006. Variation in, and causes of, toxicity of cigarette butts to a Cladoceran and microtox. Arch. Environ. Contam. Toxicol. 50, 205–212.

Moerman, J.W., Potts, G.E., 2011. Analysis of metals leached from smoked cigarette litter. Tobac. Control 20, i30–i35.

Moermond, C.T.A., Tijink, J., van Wezel, A.P., Koelmans, A.A., 2001. Distribution, speciation, and bioavailability of lanthanides in the Rhine-Meuse estuary, The Netherlands. Environ. Toxicol. Chem. 20, 1916–1926.

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, 1192–1197.

Munari, C., Corbau, C., Simeoni, U., Mistri, M., 2016. Marine litter on Mediterranean shores: analysis of composition, spatial distribution and sources in north-western Adriatic beaches. Waste Manag. 49, 483–490.

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. Publ. Health 6. https://doi.org/10.3390/ijerph6051691.

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.

Sandgaard, M.H., Syberg, K., Grønlund, S.N., Riisgaard, E.K., Rishøj, C., Palmqvist, A., 2023. Small butt harmful: individual- and population-level impacts of cigarette filter particles on the deposit-feeding polychaete *Capitella teleta*. Environ. Sci. Technol. 57, 3218–3227.

Santos-Echeandía, J., Zéler, A., Gago, J., Lacroix, C., 2021. The role of cigarette butts as vectors of metals in the marine environment: could it cause bioaccumulation in oysters? J. Hazard Mater. 416, 125816.

Snaychuk, L., Vaughan, T., Ullery, Z., Douvris, C., Bussan, D.D., 2022. Inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis of trace metals in cigarette litter collected at McNeese State University in Lake Charles, LA, United States. Methods and Objects of Chem. Anal. 17, 5–9.

Tian, Y., Wu, M., Liu, R., Li, Y., Wang, D., Tan, J., Wu, R., Huang, Y., 2011. Electrospun membrane of cellulose acetate for heavy metal ion adsorption in water treatment. Carbohydr. Polym. 83, 743–748.

Tipping, E., Lofts, S., Lawlor, A.J., 1998. Modelling the chemical speciation of trace metals in the surface waters of the Humber system, 210/211 Sci. Total Environ. 63–77.

Torkashvand, J., Farzadkia, M., Sobhi, H.R., Esrafili, A., 2020. Littered cigarette butt as a well-known hazardous waste: a comprehensive systematic review. J. Hazard Mater. 383, 121242.

Turner, A., Martino, M., Le Roux, S.M., 2002. Trace metal distribution coefficients in the Mersey Estuary, UK: evidence for salting out of metal complexes. Environ. Sci. Technol. 36, 4578–4584.

Turner, A., Le Roux, S.M., Millward, G.E., 2004. Speciation and partitioning of cadmium and zinc in two contrasting estuaries: the role of hydrophobic organic matter. Limnol. Oceanogr. 49, 11–19.

Turner, A., Millward, G.E., 2002. Suspended particles: their role in estuarine biogeochemical cycles. Estuar. Coast Shelf Sci. 55, 857–883.

Venugopal, P.D., Hanna, S.K., Gagliano, G.G., Chang, H.W., 2021. No butts on the beach: aquatic toxicity of cigarette butt leachate chemicals. Tobacco Regulatory Sci. 7, 17–30.

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.

Yu, A., Sun, X., Tang, S., Zhang, Y., Li, M., Wang, X., 2021. Adsorption mechanism of cadmium on polystyrene microplastics containing hexabromocyclododecane. Environ. Technol. Innovat. 24, 102036.