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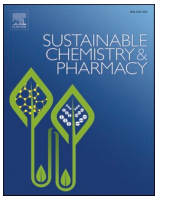

Microbeads from recycled polystyrene yogurt cups for the in-syringe micro solid-phase extraction of four opioids from environmental and biological samples

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A R T I C L E I N F O

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A B S T R A C T

A novel procedure for the extraction and determination of four opioids from environmental and biological fluids is presented. The main goal of this study is to introduce an innovative method for recycling plastic waste (i.e., polystyrene), aiming to achieve a consistent and dependable microstructure. Polystyrene microbeads, deposited on a rounded piece of paper, have been used as a sorbent material in an in-syringe extraction device. For the preparation of the polymeric sorbent, an emulsion solidification technique was optimized, achieving a regular micro material, obtained from second-hand regenerated polystyrene polymer from yogurt cups. This work presents, for the first time, the use of recycled polystyrene as micro-sorbent integrated into a paper-based support, combining waste valorization with effective analyte extraction. Under the optimum conditions, methadone, tramadol, codeine, and morphine were determined by direct injection mass spectrometry in environmental water as well as biofluids as saliva and urine. Limits of detection lower than 8 μg L^{-1} and precision better than 14.9 % have been obtained for all the analytes in saliva and environmental water samples. The interference of the endogenous compounds of urine prevents the determination of morphine and codeine in this matrix. The trueness, expressed as relative recovery (RR), ranged from 85 % to 114 %. The extraction device has proved to be a valid and sustainable alternative to traditional sorbents, offering good analytical standards and being transversal for the application to different matrices. The simplicity and environmental friendliness of this approach make it highly adaptable across various research and industrial domains.

1. Introduction

Polystyrene (PS) is an incredibly versatile polymer, finding nowadays applications in different fields, from packaging to electronic industry, consumer goods and construction (Maharana et al., 2007). Its widespread use due to its unique characteristics, such as low density, durability, low cost and easy processability, render it very attractive and easily applicable to a variety of industry processes

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(Thakur et al., 2018). Despite the growing demand of materials with such characteristics, plastic solid waste is becoming a global issue, limiting the production of newly synthetized polymers, and empowering the research for new recycling strategies of them.

Polystyrene is used in solid (i.e., coffee cups, trays) and expanded forms, both of which can be recycled. Most common strategies for PS recycling are the dissolution technique (Achilias et al., 2009; Cella et al., 2018), chemical recycling (Huang et al., 2022; Zhang et al., 1995), and thermochemical processes (Abdel-Raouf et al., 2013; Lettieri and Al-Salem, 2011), involving or not energy recovery. All these processes are well established for huge quantities of waste polymeric materials at an industrial scale. Otherwise, new procedures for polystyrene recycling, eventually returning applications of reconstituted materials in a lab scale dimension are demanded. Catalytical depolymerization (Marquez et al., 2023) and solvent dissolution represent the most common strategies, allowing to obtain different results, depending on the required final material. In the first case, the catalytic process returns styrene monomers and other aromatic hydrocarbons (as side products), to be reused in other industrial processes (Zhang et al., 1995). The second approach deals with the dissolution of the polymer itself, without touching the chemical structure of the waste material and giving back restored polystyrene (Mumbach et al., 2020).

Plastic waste managing with solvents involves several stages (Chaudhary et al., 2022). Initially, the polymeric materials are dissolved, establishing a procedure for the restoration of the polymeric material and for a proper solvent management. Filtration can effectively remove any insoluble contaminants, leaving the polymer clean for further processing. This dissolution process also enables the separation of plastics from other waste types and insoluble polymers based on their chemical properties, a method known as selective dissolution in recycling (García et al., 2009a, 2009b). Recently, a wide variety of green solvents have been proposed for the dissolution of polystyrene, among them terpenoids, ethyl acetate and supercritical CO_2 (Cella et al., 2018; García et al., 2008, 2009a; Hattori et al., 2008; Noguchi et al., 1998a, 1998b; Noguchi et al., 1998a, 1998b). All the reported experimental works and presented procedures offer recycling strategies involving foam polystyrene. Starting from an already reported micro-emulsion solidification method (Antonelli et al., 2024; De Cesaris et al., 2024), the first strategy for the preparation of micro and nano polystyrene spheres from solid polystyrene is here presented. This material is less soluble in classical solvents than the respective foam, and a lab made recycling strategy in dissolution mode has not been proposed yet.

Microextraction techniques have emerged in recent years as powerful tools in analytical chemistry, offering high efficiency with minimal solvent and sample consumption. Their ability to isolate target analytes from complex matrices while maintaining high selectivity and sensitivity makes them particularly suitable for trace-level analysis. These techniques, including solid-phase microextraction (SPME) (Amini et al., 2021), dispersive solid-phase extraction (dSPE) (Zarabi et al., 2021, Khiltash et al., 2021), and pipette-tip SPME (Millán-Santiago et al., 2024), are widely adopted in environmental, food, and biomedical analyses. The development of innovative sorbent materials has further enhanced their applicability, allowing for improved analyte recovery across a broad range of chemical polarities. In this context, integrating recycled materials into microextraction strategies represents a sustainable and cost-effective approach to sample preparation. Polystyrene microbeads have been reported as sorbent material for the extraction of contaminants from environmental, food and biological samples (Abdel-Rehim et al., 2005, 2007, 2008; Ali et al., 2016; Altun et al., 2006; Bekri-Abbes et al., 2006; Benedé et al., 2021; El-Beqqali et al., 2007; Hamdona et al., 2022; Li et al., 2018; Liu et al., 2023; Matin et al., 2022; Pautova et al., 2020; Shevchenko et al., 2020; Ullah et al., 2024; Vita et al., 2005; Wilton et al., 2018). In other cases, the application of polystyrene in other micro-formats for the extraction or remediation of contaminants from real complex matrices are disclosed, while polystyrene nanofibers have been described for adsorption purposes (Huang et al., 2015; Liu et al., 2023; Martins et al., 2022). A noteworthy study by Shin et al. (Shin and Chase, 2005) presented a method for producing nanofibers from waste expanded polystyrene, involving its dissolution in D-limonene, a green solvent. Paper supported PS has been reported (Benedé et al., 2021; Huang et al., 2015; Li et al., 2018; Matin et al., 2022) where the combined action of cellulose and polystyrene chains is underlined, in favour of an enhanced extraction ability against a broad polarity spectrum of analytes. The production and usage of recycled PS magnetic nanoparticles was recently presented by Ghambari et al. (2017) as an alternative device for microextraction in dispersive mode.

In this article, at the best of our knowledge, the first in-syringe device, using recycled polymeric material, for the extraction of analytes from real complex matrices is presented. The advantage of the in-syringe extraction, coupled with a one-time synthetic preparation of polystyrene microbeads from waste material, is the simplicity and reproducibility of the procedure. The synthetic process was scaled down to obtain the precise optimized quantity of polystyrene to be charged in a syringe device. Deposition of PS on paper, washing protocol of the synthetized material, adsorption, and desorption of analytes are all performed in the syringe body, sequentially. The extraction of four opioids was used as a control model to define the best operational parameters to maximize the figures of merit for the extraction of analytes. Polarity of the selected analytes are representative for the extraction of organic contaminants in a typical occurring range of logP values.

2. Experimental section

2.1. Materials and reagents

All reagents were of analytical grade or better. Methadone, codeine, morphine, tramadol, related internal standards (i.e., d_3-methadone, d_6-morphine, d_3-codeine), sodium chloride and ammonium fluoride were supplied by Sigma-Aldrich (Madrid, Spain). Stock standard solutions were prepared in methanol (MeOH, Panreac, Barcelona, Spain) at a concentration of 1 mg mL^{-1} and stored at 4 °C in the dark. Working solutions were prepared by dilution of the stock in methanol or Milli-Q water (Millipore Corp., Madrid, Spain), as required.

The whole optimization study was conducted with microspheres synthetized departing from commercially available PS in beads

(average molecular mass 192,000 u.m.a., Sigma-Aldrich, Madrid, Spain). The final material, used for the validation study and for the analysis of real samples, was prepared with PS from commercial yogurt cups, pooled. Ethyl acetate, acetonitrile, ethanol, ammonia and formic acid were purchased from Panreac.

2.2. Real samples

Saliva samples were collected by passive drooling from healthy volunteers, aged between 22 and 28 years, within our laboratory. A pool of blank saliva from the different donors (~50 mL) was then subsampled to be used for the method optimization and validation within the same day. The samples were centrifuged, and the solid residue eliminated. For analysis, saliva was diluted 1:4 (v/v) in MilliQ water.

Similarly, blank urine samples were obtained from the same volunteers. They were pooled, subsampled (50 mL fractions) and stored in freezer until use. The samples were 1:1 (v/v) diluted in pure water before spiking with the analytes.

Environmental water was sampled via a 1-liter amber glass bottle, by filling it completely. The matrix spiking and analysis was performed within 1 week from the sampling and the water was stored at room temperature.

2.3. Preparation of PS microbeads modified paper (PS–P)

A 2.5 % (w/v) solution of PS (commercial or from waste material) in ethyl acetate was prepared, assisting the dissolution with a gentle magnetic stirring. 250 μL of this solution was transferred into a 10 mL glass vial (diameter: 2 cm) containing a magnetic bar. For the emulsion-solidification procedure two aqueous solutions, one saturated in NaCl and another containing 1 % (w/v) sodium dodecyl sulphate, were prepared and mixed (2:5, v/v), resulting in a homogeneous phase. This aqueous solution was added to the vial, according to a 7:1 volumetric ratio (1.75 mL). The formation of a biphasic system was the result of the salting-out effect. The two-phases system was magnetically stirred (1600 rpm) to form a microemulsion of organic polymeric droplets into the aqueous phase. To break down the emulsion and let PS precipitate in the shape of microbeads, 1.2 mL of absolute ethanol was added all at once, while the system is stirring. The PS microbeads dispersion was charged in a 5 mL syringe, equipped with a frit in polypropylene and a circular piece of paper that perfectly fits the internal diameter of the syringe. The syringe was then installed on a vacuum pump equipment, to

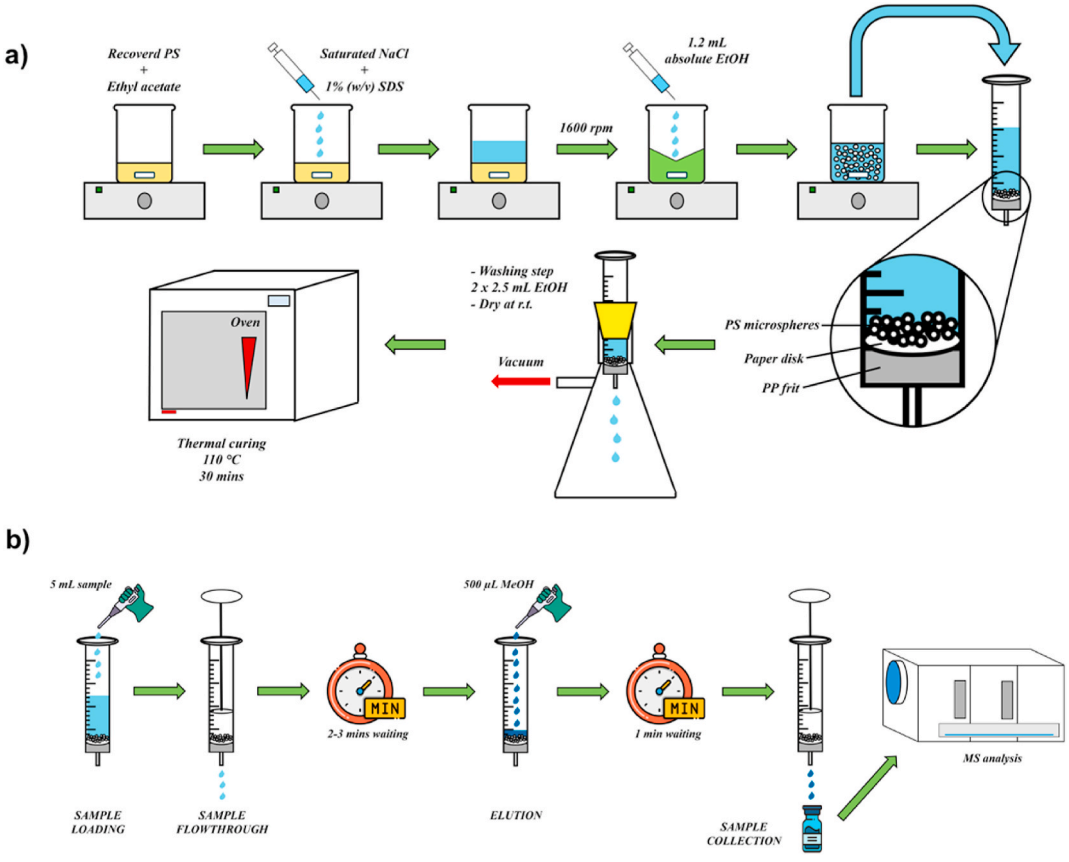

Fig. 1. Schematic representation of a) the synthetic route of the PS-P and b) the analytical procedure for the microextraction and MS analysis of the opioids.

let the supernatant gently flow through the paper and the frit, leaving the dispersed microspheres on the top of the paper. Two aliquots of 2.5 mL of ethanol were used to ensure the complete transference of the microparticles and eliminate the residual salt and surfactant. Finally, the PS-P was left to dry at room temperature under vacuum.

A thermal curing of the PS-P is performed by heating the whole syringe system in an oven for 30 min, at 110 °C. This temperature was chosen since it is slightly over the glass transition temperature of PS. This treatment ensures a low-level merging of the PS microspheres, which provides higher mechanical stability to the material without missing out the high surface area of the thin PS layer. The synthetic procedure for one device takes less than 3 min, considering emulsion solidification technique, filtration and washing step. The thermal curing step, lasting 30 min, can be performed simultaneously for a high number of devices, significantly increasing the throughput of the procedure. For this reason, more than 30 devices can be prepared in 1 h. The synthesis yield of the final material is higher than 90 % (in terms of weight of microbeads with respect to the weight of employed PS). Fig. 1a displays a scheme of the whole procedure.

2.4. Characterization of the PS modified paper device

PS microbeads were analysed after the synthesis and deposition on the paper by attenuated total reflection Fourier transformed infrared spectroscopy (ATR-FTIR) and scanning electron microscopy (SEM).

Thermogravimetric analysis (TGA) was carried out with a Mettler TG 50 thermobalance (Mettler Toledo, Columbus, USA). A weighted amount of sample was placed in the platinum crucible and the analysis was performed under nitrogen flow (20 mL min^{-1}), in the temperature range between 50 °C and 500 °C, with a heating rate of 10 °C min^{-1}. ATR-FTIR spectra were collected by using a Bruker LUMOS II FTIR micro-spectrometer (Bruker, Ettlingen, Germany), equipped with a germanium diamond ATR cell. Spectra were collected with a spectral window of 4000–550 cm^{-1}, coadding 2048 scans for each sample. Data collection and processing were made using the OPUS software package (Bruker, Ettlingen, Germany). The extraction devices were also analysed with a JEOL JSM 6300 model SEM (C entral Service for Research Support (SCAI) at the University of Córdoba) to investigate their sizes and morphology.

2.5. Optimization of the synthetic and extraction processes

The variables related with the synthesis of the polymeric microparticles as well as those affecting to the extraction procedure were investigated. Detailed information can be found in the Supplementary information (SI) file, see text and Table S1.

2.6. Analytical procedure

For the extraction, 5 mL of sample (i.e., saliva, urine, water with the appropriate dilution) containing the analyte at a concentration within the linear range were transferred to the syringe system. Pressure was applied with a syringe plunger, so that the sample flows through the paper supported microbeads. After the sample loading, the PS bed was left to dry for 2–3 min at room temperature. Analytes were then desorbed by adding 500 μL of methanol to the body of the syringe, which is left in contact for 1 min after which pressure is applied with the plunger and the eluate is collected in a MS vial. The entire extraction procedure takes less than 5 min, with the possibility of performing more than one extraction at the same time. The average throughput of the method amounts to 20–25 extractions in 1 h. The analytical procedure is displayed in Fig. 1b.

Analyses were performed by direct infusion-mass spectrometry (DI-MS/MS) on an Agilent 1260 Infinity HPLC system (Agilent, Palo Alto, CA, USA) equipped with a binary high-pressure pump for mobile phase delivery and an autosampler. The carrier consisted of an aqueous phase (water with 0.1 % ammonium fluoride) and acetonitrile in a 50:50 v/v ratio. The target analytes were quantified on an Agilent 6420 Triple Quadrupole MS with an electrospray source. The mass spectrometer settings were fixed to improve the multiple reaction monitoring (MRM) signals (Table S2). The flow rate and the temperature of the drying gas (N_2, 99 % purity) were 10 L min^{-1} and 300 °C, respectively. The nebulizer pressure was 18 psi and the capillary voltage was kept to 2000 V in positive mode for all the analytes. Agilent MassHunter Software (Version B.06.00) was used for qualitative and quantitative analyses.

3. Results and discussion

3.1. Optimization of synthetic parameters

The effect of four different procedural parameters, namely volume of the polymeric phase (mL), concentration of the PS in the organic phase (w/v %), ratio of the organic and aqueous phase (o:w) and ratio of the saturated NaCl and sodium dodecyl sulphate solutions in the aqueous phase (NaCl:SDS), influencing the synthesis of PS microbeads, have been studied together, selecting a reasonable range and relevant values for each of the considered variables. The detailed procedure is included in the Supplementary information. Three values were selected for each of these parameters (see Table S1), to monitor their influence in defining the final material. Qualitative evaluation of the final PS dispersion (yield of synthesis and visual assessment of the regularity of the obtained dispersed solid) was taken as the desirability parameter to discriminate between different experimental procedures. Best results were achieved with higher ratios of aqueous phase against organic polymeric phase and with low volumes and concentrations of the polymeric solution. At the end, the selected procedure comprises 0.25 mL of organic polymeric phase at a 2.5 % (w/v) concentration, keeping a 1:7 ratio o:w phases and 2:5 ratio of NaCl:SDS in the aqueous phase, which is the lowest consuming alternative that guarantees high throughput and desirable structured material.

3.2. Characterization of the PS-P

SEM analysis was performed on the final optimized PS-P prepared via in syringe physical deposition. The micrographs shown in Fig. 2 highlight the effect of the thermal curing on the final material. In Fig. 2a, the material has not been submitted to the curing step; microbeads of PS appear well separated and the surface area is at its highest. In Fig. 2b, the thermal curing is responsible for a partial merging of the micrometric structures, with a slight decreasing of the surface development. Anyway, the curing represents a technological advance, being accountable for the mechanical stability and durable deposition of the PS structures on the paper disk. The cured device maintains unchanged wettability levels, resisting the sample/eluent flowthrough. In Fig. 2c, a micrograph of the material obtained with the commercial recycled PS is displayed, where an almost complete correspondence with Fig. 2a is observed. In Fig. 2d, e, and f, micrographs at different magnifications of the thermal cured optimized PS-P are shown. Microparticles are regular in shape, but the diameters are dispersed in a quite wide range of sizes. Occurring microbeads can be grouped in fine particles with a diameter ranging from 0.1 to 2.5 μm as well as coarse particles with diameters within 2.5 and 10 μm.

TGA analysis was carried out on the analytical standard PS beads (3–5 mm, purchased from Goodfellow Cambridge Ltd., Huntingdon, UK), on powdered yogurt container material, and on the synthesized PS microspheres. Results are displayed in Fig. S1. In all three analyses conducted, a single degradation process was observed at 400–420 °C, aligning with the thermal degradation temperature of polystyrene reported in the literature (Faravelli et al., 2001). The slight temperature shift between standard and commercial polystyrene can be attributed to differences in the degree of polymerization and the average molecular weight of the polymer. Curve for PS from yogurt containers is completely overlapping with the one obtained for the PS microspheres, obtained with the optimized microemulsion solidification technique, confirming the stability of the polymeric support. The solid residue, thermally stable up to 500 °C, confirms the presence of plasticizers and other additives in the commercial PS.

ATR-FTIR was used also to confirm the actual conservation of the polymeric material after the synthetic process. For comparative purposes, PS-P as well as raw cellulose paper, PS microspheres and the original waste polymeric material have been analysed. Spectra are shown in Fig. S2 and bands are assigned and described in detail in SI. The spectra of the final PS-P display all the absorption bands of polystyrene, with the expected relative intensities. On the other hand, none of the absorption bands of cellulose are detectable in the spectrum of the extraction device. This can be explained with a complete and successful coverage of the cellulosic disk surface with the synthetized microspheres.

3.3. Optimization of extraction methodology

The variables affecting the extraction procedure were also submitted to an optimization study, i.e., volume and concentration of the sample solution loaded, quantity of deposited PS on the paper, pH, ionic strength, and chemistry of the desorption phase.

First of all, the effect of the PS functionalization on paper was studied, to confirm and test the actual benefit of using PS microspheres as an additive of cellulosic paper for extraction purposes. For this reason, the performances of the raw paper disk as well as PS-P have been studied and compared by carrying out the extraction procedure inside the syringe device at the same conditions. For this

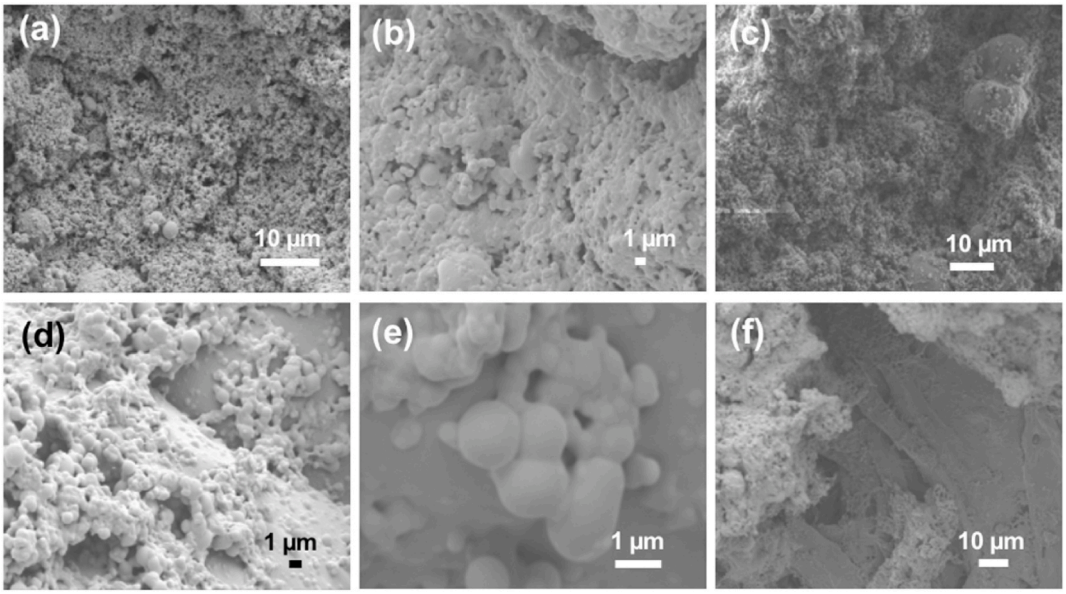

Fig. 2. SEM images of the optimized polystyrene on-paper adsorbent material. The reported images are related to different materials; (a): non cured polystyrene microsphere from reference polymer; (b, d, e, f): cured polystyrene microsphere after thermal curing, from reference polymer; (c): non cured polystyrene microspheres from commercial recycled polymer. The micrograms are collected at the following magnifications: 2000× (**a**), 3000 X (**b**), 1500 X (**c**) 4000 X (**d**), 16000 X (**e**) and 1000 X (**f**).

purpose, 5 mL of aqueous spiked solution, at a concentration of 500 μg L^{-1} of each analyte adjusted to pH 9 have been loaded, the elution being carried out with 300 μL of MeOH. The final extract has been analysed in triplicate at the optimized instrumental conditions and the results are displayed in Fig. S3 of the Supplementary Material. As shown, functionalization with PS significantly enhances recoveries compared to raw paper, with a minimum increase of approximately 14-fold for methadone and a maximum boost of around 74-fold for morphine. This clearly highlights the crucial role of PS in the extraction of the target analytes. As described in literature (Stelmaszczyk et al., 2024), the presence of hydrophobic benzene rings in PS may promote π-π interactions between the polymeric microbeads and the aromatic moieties of analytes, in addition to van der Waals interactions between them.

Response Surface Methodology (RSM) was utilized to evaluate the correlation between variables directly involved in the extraction procedure of analytes and contributing to the definition of the extraction yields of the protocol. As explain in detail in the SI, a

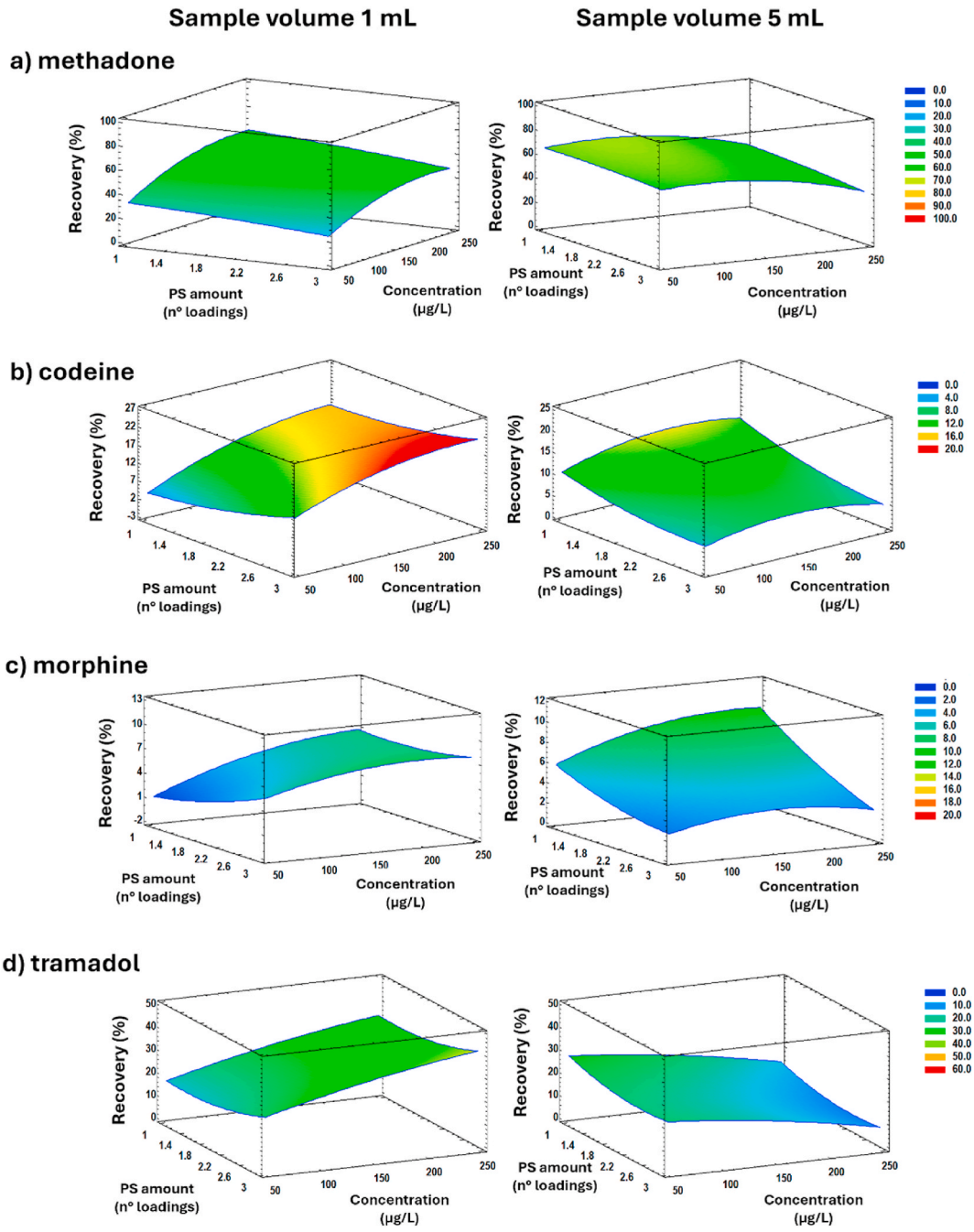

Fig. 3. Response surface plots of the recoveries obtained for the four analytes, i.e., (a) methadone, (b) codeine, (c) morphine and (d) tramadol, showing the interaction of analyte concentration and PS amount at a fixed sample volume (1 and 5 mL).

Box–Behnken design methodology was employed. For all the analytes the loading volume is a crucial parameter for the definition of performances. High volumes are responsible for the saturation of the material, even with high loading amounts of PS. For the same reason, desirability becomes worse for higher values of concentration of the initial loading phase. By plotting the surface responses of the design for different fixed volume values, it is possible to estimate a maximum load quantity for each analyte before the saturation (coinciding with a decrease in the desirability). In Fig. 3, surface responses for each analyte at two different loading volume values (i.e., 1 and 5 mL) are plotted. At a volume of 1 mL, recovery increases while improving the amount of PS on the paper, while by increasing the volume up to 5 mL, the influence is less marked, or even it worsen in some cases. In addition, from a visual point of view, it can be observed that the thermal curing is not effective for higher quantities of PS, observing in the case of 2 and 3 loadings of the synthetized microbeads a partial leaching of the material during the desorption step. Thus, one loading of PS microbeads was selected for further studies, since it is also simpler, faster and requires less reagents and material.

Regarding concentration, whether in the case of 1 mL no saturation of the adsorption capacity of the sorbent phase is observed for any of the analytes, thus an increase in the recovery values is observed upon increasing the concentration, by increasing the volume to 5 mL, especially for methadone and tramadol, a decrease in recovery is observed, which is related to saturation of the sorption sites. Therefore, a volume of 5 mL of sample, which is the maximum sample allowed to be simultaneously loaded by the capacity of the syringe, was selected for further studies, so that improved recoveries are obtained. Taking into account the saturation observed for certain analytes at concentrations above 100 μg L^{-1}, a concentration of 50 μg L^{-1} was selected for the studies of the influence of the next variables.

Once defined the conditions for further studies, the extraction procedure was optimized in terms of pH and ionic strength of the loaded sample by using aqueous standards. The pH of the sample defines the ionization form of the analytes, which are basic substances (pKa in the range from 8.2 to 9.2), cationic at physiological and environmental conditions. As shown in Fig. 4a, the extraction of the analytes is favoured at intermediate pH values. The pH of the sample without pH adjustment is around 8.3, and the use of internal standard within the samples would compensate possible fluctuations in the pH of the sample, thus, no pH adjustment of the sample was selected for further studies. On the other hand, ionic strength has not a relevant influence on the extraction yields of the selected analytes. The analyses were conducted without correcting the solution with acidic or basic additives, operating at uncontrolled pH (~ 8.7). The results (Fig. 4b) show a decrease of the extraction performances for conductance values higher than 40 mMHO (corresponding to NaCl concentrations higher than 0.25 %). This evidence may be ascribed to an increase of viscosity of the loaded sample, that has an adverse effect on the wettability and permeability of the adsorbent. For simplicity, the ionic strength of the sample was not adjusted before extraction, as already commented in the case of pH, the use of an internal standard minimizes and corrects the effect of ionic strength, avoiding the strict control of this parameter.

Last investigated parameters were those related to the elution conditions, i.e., both the nature and volume of the eluent phase. First of all, three different eluents have been tested, namely pure methanol and with the addition of acidic (1 % v/v of formic acid) or basic (1 % v/v of ammonia) modifiers. As it can be seen in Fig. 5a, analytes recoveries are only slightly influenced by the addition of pH modifiers. For this reason, pure methanol was chosen as the eluent phase.

Eluent phase volume was studied in the range 200–500 μL (Fig. 5b). At higher volume there is an increase in the recovery, allowing a better contact of the eluent with the sorbent and a more effective elution of the analytes, while an improvement in precision was also observed. Higher volumes were not evaluated, since the improvement as regards 400 μL was not high and to prevent further dilution of the extract. Thus, 500 μL was selected as the eluent volume for the subsequent validation protocol.

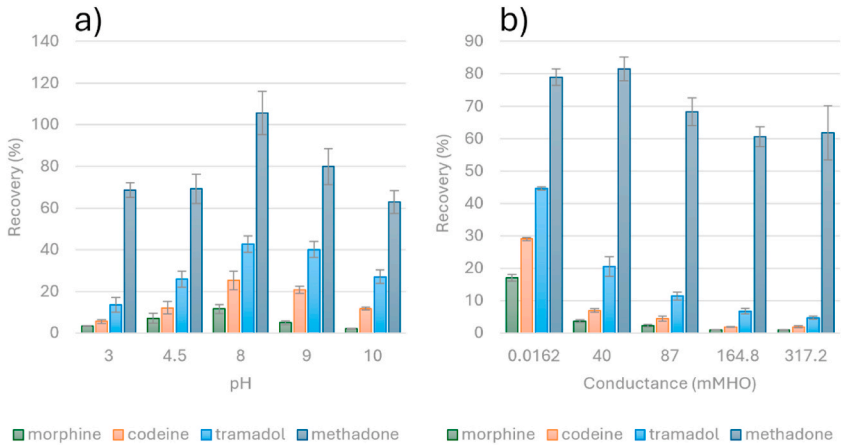

Fig. 4. Effect of pH and ionic strength expressed as conductance of aqueous solutions containing different amounts of NaCl on the recovery (%) obtained for the target analytes. Studies performed on MilliQ water spiked at a fixed concentration of 50 μg L^{-1} for each analyte. For ionic strength evaluation no pH adjustment was carried out.

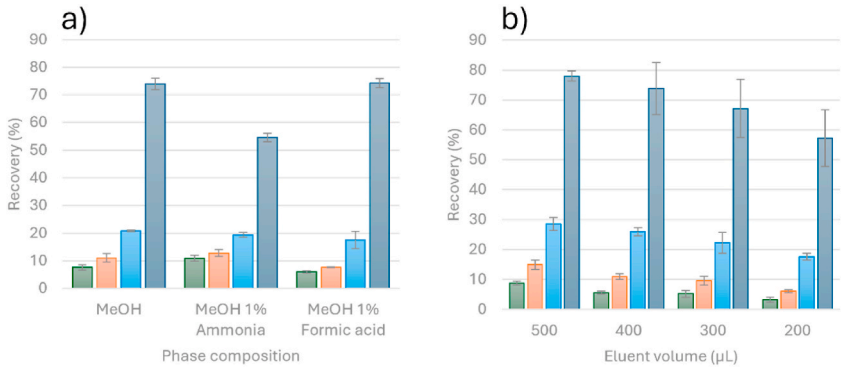

Fig. 5. Results for the optimization of (a) the composition and (b) volume of the eluent phase (solvent pure methanol). Experiments were conducted on MilliQ water spiked at a fixed concentration of 50 µg L^{-1} for each analyte and performing the entire adsorption step at the previous optimized conditions.

3.4. Analytical features of the method

The analytical figures of merit of the method were evaluated. Table 1 summarizes the values obtained in the validation. Matrix-matched calibration curves were prepared for all the analytes in three different real matrices, i.e., pooled saliva and urine samples and environmental water. To control the whole procedure, from the extraction to the direct injection, internal standards (i.e., d_3-methadone, d_6-morphine, d_3-codeine) have been used. For tramadol, d_3-methadone proved to be a good internal standard and for this reason it was used to normalize its analytical signal. Sample solutions were spiked prior extraction with the analytes at six different concentration levels and a fixed concentration of IS of 20 µg L^{-1} and were submitted to the entire analytical procedure. Calibration curves were built by plotting the peak area of each analyte divided by the area of the internal standard versus the concentration (Fig. S4). The determination coefficients R^2 were found to be higher than 0.99, showing a good linear correlation in the dynamic range from the limit of quantification (LOQ) to 100 µg L^{-1}. In Fig. S4, linear models obtained with saliva, urine and water matrices are shown along with the ones obtained in ultrapure water.

Limit of detection (LOD) was calculated as the analyte concentration capable of providing a signal 3 times higher than the background noise (S = 3 N). Likewise, LOQ was calculated as the concentration generating a signal 10 times higher than the background noise (S = 10 N), responsible for precision and accuracy values below 20 %. LODs were below 2.7 µg L^{-1} for saliva matrix and 1.9 µg L^{-1} in environmental water, with LOQs below 9.1 and 6.5 µg L^{-1}, respectively.

Precision and accuracy were estimated at the three different levels of fortification, performing five replicates at each level. The precision was expressed in terms of relative standard deviation (RSD %). As can be seen in Table 1, all RSD values were lower than 15 %, which is in agreement with the FDA criteria (FDA, 2018). The accuracy was evaluated via the relative recovery, calculated as follows:

Table 1
Figures of merit of the 4 opioids analysed in spiked samples of saliva, environmental water and urine. Precision and accuracy are reported at all tested concentration levels (i.e., 10 µg L^{-1}, 50 µg L^{-1} and 100 µg L^{-1}).

Analyte	LOD (µg L^{-1})	LOQ (µg L^{-1})	R^2	Matrix effect (%)	Linear range (µg L^{-1})	RSD intra-day, n = 5 (%)			Accuracy (% relative recovery, n = 5)		
						10 µg L^{-1} [a]	50 µg L^{-1}	100 µg L^{-1}	10 µg L^{-1} [a]	50 µg L^{-1}	100 µg L^{-1}
Saliva											
Methadone	0.0064	0.021	0.997	93	LOQ-100	4.6	2.5	4.2	89.9	97.1	101.4
Morphine	2.7	9.1	0.991	97		13.6	12.4	10.2	108.3	93.8	95.1
Codeine	1.8	5.9	0.996	94		12.3	2.8	11.3	99.7	105.9	104.7
Tramadol	0.92	3.1	0.989	116		14.7	14.9	4.7	108.6	90.9	105.7
Environmental water											
Methadone	0.012	0.04	0.999	97	LOQ-100	3.5	1.7	2.9	100.7	102.7	99.6
Morphine	1.7	5.6	0.998	102		11.0	8.2	10.6	104.2	96.5	94.2
Codeine	1.9	6.5	0.999	93		11.8	8.7	4.0	95.4	103.2	101.1
Tramadol	0.03	0.1	0.994	74		9.4	8.3	9.0	85.2	95.1	114.3
Urine											
Methadone	0.7	2.4	0.999	98	LOQ-100	3.53	1.20	4.64	103.4	96.1	101.5
Tramadol	4.3	14.5	0.998	33		11.9	12.5	14.9	118.2	108.2	104.7

[a] For urine matrix, the lower concentration value to assess the precision and accuracy of the method was 20 µg L^{-1}.

$$Relative\ recovery\ (\%) = \frac{C_{measured}}{C_{spiked}} x100$$

in this case, $C_{measured}$ was calculated by interpolating the average of the chromatographic areas, obtained at each spike level, in the matrix-matched calibration line. C_{spiked} is the known level of fortification of the specific spiking level. The accuracies obtained were in the range 85.2–118.2 %.

In the case of urine matrix, detection sensitivity of codeine and morphine did not allow to build linear model for these two analytes in the concentration range below 100 μg L^{-1}. Matrix match calibration curves are provided for tramadol and methadone (Fig. S4). LOD and LOQ in this matrix were calculated in the same way, leading to higher values with respect to the saliva and aqueous samples. Urine is a complex matrix due to the occurrence of a vast number of small weight molecules (more than 3000 compounds), which are responsible for suppression of the ESI ionization of analytes (Gosetti et al., 2010), leading to a decline of the analyte's sensibility. To evaluate the extent of interference signal suppression on the studied analytes, a matrix effect study was conducted across all matrices by comparing the slopes of standard models with those of matrix-matched curves. A high matrix effect was observed for tramadol in urine, highlighting the complexity of this sample. In contrast, all other cases showed acceptable values ranging between 74 % and 116 %. The sensitivity ratio, expressed as a percentage, is detailed in Table 1. Selected fortification levels for the evaluation of accuracy and precision are chosen to cover the designated concentration range: 20, 50 and 100 μg L^{-1}.

3.5. Comparison with previously reported methods

Table S3 provides a comparative overview of the performance of the proposed method against various other approaches commonly used for analysing opioids in biological fluids. The analytical figures of merit achieved with our method align closely with those reported in the literature, with LOQs for individual analytes ranging from 0.02 to 14.5 μg L^{-1}.

Our method presents two significant advantages. First, it offers a notably rapid extraction and analysis process, as it bypasses the need for chromatographic separation, substantially reducing total processing time. Second, it incorporates an environmentally conscious approach by utilizing a sorbent material sourced from recycled waste, eliminating the need for newly produced extraction materials. These benefits make the method both time-efficient and sustainable, providing a practical and eco-friendly alternative for opioid detection in biological samples. On the other hand, a more exhaustive sample pretreatment would be needed in the case of urine matrix in order to be able to determine the four analytes with similar sensitivity as in saliva or water.

In recent years, growing awareness of environmental sustainability has underscored the need for precise and reliable metrics to assess the "greenness" of chemical processes. In this context, two prominent methodologies are Sample Preparation Metric of Sustainability (SPMS) (González-Martín et al., 2023) and Analytical Greenness Metric for Sample Preparation (AGREEprep) (Wojnowski et al., 2022). The sustainability of the in-syringe-PS-P microextraction was assessed using both these green metrics. SPMS is highly specifical to the evaluation of sample preparation. The final graphic output is a clock-like diagram, as shown in Fig. S5A, which illustrates the greenness scores for key sample preparation parameters, along with an overall score. For the presented microextraction method, the total SPMS score was 7.26 out of 10. Additionally, the AGREEprep tool was applied in this study. AGREEprep uses a similar color-coding scheme as SPMS but evaluates both sample preparation and the broader analytical process. The diagram resulting from the application of this green metric is displayed in Fig. S5B of the Supplementary Material. For the microextraction at issue, the AGREEprep total score was 0.56 out of 1. The score obtained with such a metric is generally lower compared to SPMS, since it takes into account all the analytical procedure, from the synthetic to the final analysis step. The off-line extraction procedure, the energy-intensive instrumental technique and the lack of integrated and automated steps strongly penalised the final score. Otherwise, both metrics do not account for the origin of the synthetized device, which has been prepare from waste sources, being part of a recycling cycle, potentially endless.

To assess the sustainability of the entire analytical process—from material synthesis to instrumental analysis, including the applied extraction strategy—a greenness evaluation tool that comprehensively considers all methodological steps was applied. For this purpose, advanced metrics such as ComplexGAPI (Płotka-Wasylka and Wojnowski, 2021) and the more recent ComplexMoGAPI (Mansour et al., 2024) provide an assessment system that evaluates all features and characteristics of the analytical method, ultimately yielding a score representative of the process's overall sustainability. Considering the reagents used, the energy demand of the synthesis process, the recycling potential, and the complete environmental and operator safety of the method, the analytical workflow presented here achieved a score of 84 according to the ComplexMoGAPI principles (Fig. S5C). This result confirms the development of a procedure that successfully combines analytical efficiency, plastic waste recycling, and sustainability.

3.6. Synthetic procedure greenness assessment

The emulsion solidification technique, as developed, utilizes green solvents, environmentally friendly processes, and minimizes energy and material waste. To assess the sustainability and recycling benefits of this approach, the procedure was analysed using various evaluation tools and compared with other techniques employing commercial materials.

For polystyrene recycling, this study proposes dissolving shredded yogurt container fragments in ethyl acetate. Previous research has explored different solvent compositions for PS recycling, including green and low-environmental-impact options such as D-limonene, *p*-cymene, terpinene, phellandrene, and ethyl acetate (García et al., 2009a, 2009b, Cella et al., 2018). Ethyl acetate was selected due to its high greenness score (6.7) according to GSK's solvent sustainability guide (Alder et al., 2016) and its ability to form a microemulsion with water under salting-out conditions. Other proposed green solvents were unsuitable due to excessive viscosity or

immiscibility with water under standard conditions.

In terms of energy efficiency, the synthesis process requires only brief stirring—less than 1 min per batch—with an energy demand of under 500 J. The deposition step onto the paper disk is performed using a hydraulic vacuum pump, which operates without additional energy consumption. The primary energy-intensive step is thermal curing, requiring approximately 900 kJ; however, this process can be conducted on multiple devices simultaneously, significantly reducing the energy demand per unit.

From a health and safety perspective, all reagents involved in the material synthesis process (ethyl acetate, sodium chloride, and water) have a National Fire Protection Association (NFPA) flammability and health hazard rating of $\leq$1, with the exception of sodium dodecyl sulphate and ethanol, which have respective ratings of 2 and 3 according to the same classification system. These reagents are essential for the successful implementation of the emulsion solidification technique. Ongoing studies within our research group are actively exploring safer alternatives to further enhance the environmental sustainability of the synthetic procedure.

The total waste generated per synthetic procedure is less than 10 mL, while the preparation of the extraction device (paper-supported polystyrene microspheres) results in an Environmental (E) factor of approximately 10.

All the aforementioned aspects contribute to the overall greenness assessment of the synthetic and extraction procedure, as evaluated by the ComplexMoGAPI scoring system (Mansour et al., 2024). This software, developed in 2024, integrates the sustainability assessment of the extraction process with an evaluation of the impact of pre-extraction procedures (in this case, the preparation of the extraction device) on both the operator and the environment. The final rating (84 for the current method), which reflects the entire analytical workflow, confirms the environmental benefits of the proposed method—albeit without accounting for the recycled origin of the device itself.

For comparative purposes, the solid-phase extraction (SPE)-based and dispersive liquid-liquid microextraction (DLLME) methods proposed by Clivillé-Cabré et al. (2025) have been considered as reference techniques for the extraction of opioids from urine. Regarding the extraction procedure, both methods require a significant use of reagents and solvents, leading to a greater generation of procedural waste. Specifically, the SPE-based method necessitates over 28 mL of solvents per extraction. Although the DLLME method is less solvent-intensive, it still requires additional extraction steps, such as vortex shaking and solvent evaporation. Furthermore, the method presented in this study introduces the reuse of end-of-life materials as an extraction support, aligning with a circular approach to production and consumption.

4. Conclusions

A polystyrene modified paper device from a recycled waste source has been developed in this work for the microextraction of opioids. Recycling plays a pivotal role in contemporary research, where efforts are focused on creating innovative applications for end-of-life materials and integrating them into a positive, sustainable cycle of reuse. Thus, a main advantage of this analytical method lies in the use of recycled polystyrene as a sorbent material, allowing for the valorization of common plastic waste. The recycling process yielded a final material with an extensive surface area, optimizing the retention capabilities of the polymer and making it ideal for efficient analyte capture. However, a key limitation is the challenging industrial scalability of the polystyrene microbead synthesis and the manual assembly of the extraction device, which currently restrict its application to the laboratory scale.

The extraction process employs an in-syringe methodology that is not only straightforward to execute but also promotes a rapid and effective workflow. In order to reduce analyte loss and limit sample handling, the design incorporates a linear and consecutive operational sequence that allows all procedural steps to take place within the syringe body itself. This setup not only ensures high reproducibility but also simplifies the user handling. The entire extraction process is completed in less than 5 min, making it a highly time-efficient approach.

The retention performance achieved by combining the cellulosic substrate with polystyrene microspheres ensures a broad-spectrum extraction capability across a diverse range of analytes, varying in chemical moieties and polarities (with logP from 0.8 to 3.9). The extraction procedure and analytical method is cost-effective and user friendly, suitable for employment in an in-situ analysis.

The performance of the device, characterized by high recoveries, precision, and accuracy, demonstrates its reliability and robustness. Furthermore, its environmental sustainability was evaluated using established green metrics, specifically SPMS and AGREEprep, both of which highlighted the method's alignment with green chemistry principles. The results confirm this approach as a viable, environmentally sustainable alternative to more traditional extraction techniques, providing comparable analytical performance with a significantly reduced ecological impact.

CRediT authorship contribution statement

Lorenzo Antonelli: Writing – original draft, Investigation. **Ángela Inmaculada López-Lorente:** Writing – review & editing, Supervision, Conceptualization. **Alessandra Gentili:** Writing – review & editing, Conceptualization. **Rafael Lucena:** Writing – review & editing, Supervision, Funding acquisition. **Soledad Cárdenas:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

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. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scp.2025.102036.

Data availability

Data will be made available on request.

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