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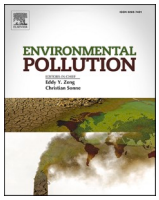

Decontamination promotes the release of incorporated organic contaminants in hair: Novel insights into non-invasive biomonitoring☆

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ABSTRACT

Human hair is increasingly employed as a non-invasive biomonitoring matrix for exposure to organic contaminants (OCs). Decontamination procedures are generally needed to remove external contamination from hair prior to analysis of OCs. Despite various existing decontamination protocols, their impacts on internally incorporated (endogenous) OCs in hair remain poorly understood. This study aims to quantitatively assess the impact of decontamination procedures on endogenous OCs in hair, and investigate optimal decontamination processes and factors influencing the removal of endogenous OCs. In this study, guinea pig was exposed to 6 OCs (triphenyl phosphate (TPHP), tris(1,3-dichloro-2-propyl) phosphate (TDCPP), and tri-n-butyl phosphate (TNBP), bisphenol A (BPA), perfluorooctanoic acid (PFOA), and phenanthrene (PHE)), and 6 decontamination procedures with different solvents (methanol, n-hexane, acetone, ultrapure water, Triton X-100, and sodium dodecyl sulfate) were used to rinse exposed guinea pig hair. All OCs and three metabolites (diphenyl phosphate (DPHP), dibutyl phosphate (DBP), and bis(1,3-dichloro-2-propyl) phosphate (BDCPP)) were detected in the majority of washing solutions. The decontamination procedures apparently resulted in the release of endogenous OCs from hair. The percentages of residual OCs in hair exhibited a linear or exponential decrease with more washing cycles. Furthermore, the residuals of OCs in hair washed with organic and aqueous solvents showed negative correlations with molecular weight, polarizability, and their initial concentrations. Although these findings need to be validated with a broader range of OCs, the results obtained in this study provide compelling evidence that current hair decontamination procedures have significant impacts on the analysis of endogenous OCs in hair. Therefore, it is important to interpret quantitative data on hair OC concentrations with caution and to thoroughly consider each decontamination procedure during analysis.

1. Introduction

Continuous exposure to organic contaminants (OCs) has raised concerns regarding their potential adverse effects on human health. Monitoring OC exposure levels is crucial for evaluating their risk potential. Matrices for human biomonitoring of OCs include blood/serum, breast milk, urine, hair, and nails (Alves et al., 2017; Hoffman et al., 2014; Liu and Mabury, 2018; Liu and Mabury, 2019). Among these, hair

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is a promising non-invasive matrix due to its ease of collection, convenient transport and storage, suitability for follow-up in sensitive populations (e.g., pregnant women, newborns, and children), and applicability in large-scale biomonitoring studies (Cooper et al., 2012; Iglesias-Gonzalez et al., 2020; Peng et al., 2021; Ruan et al., 2019; Zheng et al., 2021). So far, human hair has been widely used to assess exposure to various OCs, including polycyclic aromatic hydrocarbons (PAHs) (Palazzi et al., 2019), per- and polyfluoroalkyl substances (PFASs) (Li et al., 2013; Ruan et al., 2019), polybrominated diphenyl ethers (PBDEs) (Tang et al., 2021), organophosphate esters (OPEs) (Qiao et al., 2019), phthalate esters (PAEs) (He et al., 2018), and several endocrine disrupting chemicals (EDCs) (Rodriguez-Gomez et al., 2017).

Interpreting hair analysis results is challenging due to the complexity of exposure routes. In general, OCs in hair come from 1) internal sources (endogenous), where OCs are incorporated into hair via bloodstream at dermal papilla; and 2) external sources (exogenous), such as sweat or fatty secretions, atmospheric deposition, and contact with dust. Endogenous OCs reflect actual internal exposure, whereas exogenous OCs can obscure the results (Baciu et al., 2015; Kempson and Lombi, 2011). Therefore, developing effective methods to remove exogenous OCs while preserving endogenous OCs in hair is crucial for accurate hair analysis.

Previous studies have demonstrated the varying efficacies of different decontamination solvents, including methylene chloride, acetone, methanol, n-hexane, ultrapure water, and surfactant solutions, in removing exogenous contaminants from hair surface (Duca et al., 2014; Gao et al., 2015; Klys et al., 2007; Lin et al., 2022; Toriba et al., 2003; Zheng et al., 2013). Several studies have shown that appropriate decontamination procedures can completely eliminate exogenous OCs with only removing trace amounts of endogenous OCs (Lin et al., 2019; Toriba et al., 2003). However, other studies have suggested that washing procedures can efficiently remove both exogenous and endogenous OCs from hair matrix (Nakahara et al., 1998; Paulsen et al., 2001). Therefore, investigating the impacts of decontamination procedures on endogenous OCs will facilitate more objective interpretations of hair biomonitoring data and consequent risks of OCs to human health.

To assess the removal of endogenous OCs in human hair, the initial task is to differentiate internally-incorporated OCs from those externally deposited. This is generally addressed using statistical models and animal experiments. For instance, partial least squares discriminant analysis (PLS-DA) was applied to reveal distinct distribution patterns of OCs in washing solutions and hair, indicating different exposure sources (Lin et al., 2020; Lin et al., 2019; Lu et al., 2014). Nevertheless, extraction solvent and washing process can influence OC distribution patterns. Therefore, OCs in washing solutions and hair cannot be simply attributed to exogenous and endogenous sources. Several studies have demonstrated that OCs can significantly accumulate in hair of rats, mice, and guinea pigs after dietary intake, and thus hair can reliably indicate internal OC exposure (Gao et al., 2015; Grova et al., 2017; Sun et al., 2010; Zhu et al., 2020). The incorporation of OCs from sweat into hair of these animals can be disregarded due to the absence of sweat glands in their bodies, except in foot pads. To the best of our knowledge, the effects of washing procedures on endogenous OCs in hair have not yet been investigated using animal experiments.

It is feasible to use guinea pig hair to investigate the influence of decontamination procedures on endogenous OCs in hair because both guinea pigs and humans are mammals. Furthermore, guinea pig hair shares numerous similarities with human hair. Like human hair, guinea pig hair follicles undergo cyclic activity and contain trichohyaline granules (Steinert, 1978; Ito and Hashimoto, 1982). Guinea pig hair also exhibits black, white, and brown coloration, and comprises the cuticle, cortex, and medulla, similar to human hair (Buffoli et al., 2014; Dawson, 1930).

Target OCs in this study are triphenyl phosphate (TPHP), tris(1,3-dichloro-2-propyl) phosphate (TDCPP), and tri-n-butyl phosphate (TNBP), bisphenol A (BPA), perfluorooctanoic acid (PFOA), and phenanthrene (PHE) and three metabolites (diphenyl phosphate (DPHP), dibutyl phosphate (DBP), and bis(1,3-dichloro-2-propyl) phosphate (BDCPP)). TPHP, TDCPP, and TNBP are flame retardants in various household products (Chokwe et al., 2020). BPA is one of the most used plastic additives (Michalowicz, 2014). PFOA is widely distributed in daily-use products, exhibiting both hydrophilic and hydrophobic functionalities (Jian et al., 2018). Additionally, PHE can be derived from natural and anthropogenic sources, resulting in its ubiquitous presence in the environment (Dat and Chang, 2017). These OCs are frequently identified in human hair samples.

In this study, hair samples from exposed guinea pigs were subjected to 6 different decontamination processes, and target OCs in the resulting washing solutions and hair samples were analyzed. The main objectives were as follows: (i) to accurately quantify impacts of different decontamination procedures on the analysis of endogenous OCs, (ii) to identify optimal washing processes with minimal depletion of endogenous OCs, and (iii) to investigate the factors influencing the removal of endogenous OCs during washing. This study will provide novel insights into the impacts of decontamination on endogenous OCs in hair, and contribute to future development of standardized decontamination methods for accurately assessing human exposure to OCs.

2. Materials and methods

2.1. Chemicals and reagents

Detailed information of 6 target chemicals can be found in Table S1 of the Supplementary Information (SI).

2.2. Animal treatment

This study was approved by the Ethics Committee of the Guangdong Medical Laboratory Animal Center (Approval Number: B202302-7). All procedures were conducted in accordance with the regulations governing the management of medical laboratory animals. Fifteen healthy male guinea pigs, aged 8 weeks (200–300 g), were housed at the Guangdong Medical Laboratory Animal Center. Stainless steel mesh cages were used to minimize external contamination of hair samples from feces or urine. The experiment commenced after a one-week acclimation period for all guinea pigs. Animal facility was maintained at an ambient temperature of 22 ± 2 °C, a relative humidity of 40 ± 5%, and a 12 h/12 h light/dark cycle. Food and tap water were provided ad libitum.

Considering potential environmental background contamination of PHE and BPA, guinea pigs were exposed to the isotopically labeled standards, d_{10}-PHE and d_{16}-BPA. Prior to the commencement of this experiment, 15 guinea pigs were randomly assigned to 5 groups, including 3 experimental groups (A, B, and C), and two control groups (D and E), with 3 guinea pigs in each group. All target compounds were dissolved in a solution containing 10 % DMSO, 40 % PEG300, 5 % Tween-80 and 45 % saline. In group A, guinea pigs were intramuscularly injected with d_{10}-PHE for 20 consecutive days at a dose of 6 mg/kg body weight. Group B received intramuscular injections of d_{16}-BPA for 10 consecutive days at a dose of 3 mg/kg body weight. In group C, guinea pigs were intramuscularly injected with a mixture of PFOA, TPHP, TDCPP, and TNBP for 20 consecutive days at a dose of 10 mg/kg body weight. Before each injection, guinea pigs were weighed to adjust the administered dose and to use weight as an indicator of well-being. Guinea pigs in the control groups (D and E) received the same volume of the solution once per day throughout the entire experiment. Prior to initial chemical administration, back hair of each guinea pig was shaved. After exposure, hair from the same location was shaved to collect samples for quantifying the levels of target analytes incorporated during the exposure period (at least 0.1 g of hair per guinea pig). Moreover, 20 hairs were randomly selected from each guinea pig for length measurement, with an average ranging from 8.24 to 13.7 mm. Twenty-four

hours after the final dosing, all guinea pigs were anesthetized via intraperitoneal injection of ethyl carbamate and subsequently euthanized. All samples were frozen and stored at −80 °C until analysis.

2.3. Decontamination procedures

In this study, we employed 6 washing procedures that have been extensively documented in removing external OCs from hair shaft (Table S4). Each hair sample was homogeneously mixed and divided into 7 groups, including 6 washing groups (methanol (MEOH), acetone (ACE), n-hexane (HEX), ultrapure water (UPW), sodium dodecyl sulfate (SDS), Triton X-100) and 1 no-wash group.

Detailed washing procedures were adapted from the previous literature (Lin et al., 2019). Briefly, 10 mg of guinea pig hair was weighed and placed in a 2 mL centrifuge tube. Then, 1.5 mL of organic solvent (MEOH, ACE, or HEX) was added to submerge the hair. The sample was sonicated in an ultrasonic bath at room temperature for 1 min, and the resulting solution was transferred to another centrifuge tube using a disposable 1 mL glass pipette. This process was consecutively repeated 6 times. The solutions were evaporated to near dryness using nitrogen gas, followed by addition of the labeled isotopic internal standards (IS). Finally, the sample was dissolved in 500 μL of MEOH or isooctane (ISO) solution.

Ultrapure water washing procedure was described in the study of Zheng et al. (2013), which has been demonstrated to effectively remove particles/dust from hair surface without damaging the cuticle. About 10 mg of guinea pig hair and 1.5 mL of ultrapure water were added to a 2 mL centrifuge tube. The washing process was performed at 40 °C in a shaking incubator for 1 h, after which the solution was transferred to another tube. This procedure was repeated 3 times. Each soaking solution underwent liquid–liquid extraction using 4 mL of n-hexane/ethyl acetate (1:1, *V/V*) after being spiked with ISs. The mixture was vigorously vortexed for 10 min and centrifuged at 4000 rpm for 15 min. Then, the organic layer was transferred to a clean tube. This extraction step was repeated 3 times for each sample. The supernatant was combined, evaporated to near dryness, and reconstituted with 200 μL of MEOH or ISO solution.

The washing procedure using Triton X-100 or SDS was adapted from a previously established method (Duca et al., 2014). Briefly, 10 mg of guinea pig hair was placed into a 2 mL centrifuge tube, and either 1.5 mL Triton X-100 solution (1% in water) or SDS solution (5% in water) was added as the washing agent. Hair sample was rinsed with surfactants at 40 °C in a shaking incubator for 5 min, and repeated 3 times. Afterward, guinea pig hair was transferred to a clean tube and briefly rinsed with 2 mL of ultrapure water for 3 times. However, surfactant washing solutions were not analyzed due to potential interference from trace amounts of residual surfactant with mass spectral detection.

2.4. Hair preparation and analysis

After washing, the hair samples were completely dried in a fume hood at room temperature and subsequently pulverized into powder using a MM 400 Grinder (Retsch GmbH, Germany). Additionally, 15 unwashed hair samples were co-analyzed as controls. Hair OC extraction followed a previously published method (Luo et al., 2023) with minor modifications. Initially, the pulverized hair (10 mg) was weighed in a prebaked glass tube and spiked with 20 ng of labeled internal standards. Four mL of acetone/n-hexane/ethyl acetate/acetonitrile (1:1:1:1, *V/V/V/V*) solution was added, followed by vortexing for 10 min, sonication for 20 min at room temperature, and centrifugation at 4000 rpm for 15 min. The organic layer was then transferred to another clean glass tube. This extraction process was repeated 2 more times, and a total of 12 mL of supernatant was collected. The supernatant was evaporated to 1 mL under gentle nitrogen gas and transferred to another centrifuge tube containing 100 mg of C18 (octadecyl bonded silica) and 20 mg of anhydrous sodium sulfate. The mixture was vigorously vortexed for 10 min and centrifuged at 4000 rpm for 15 min. Then the supernatant was transferred to another tube, evaporated to near dryness, and reconstituted with 200 μL of MEOH or ISO solution.

The target chemicals were analyzed using liquid chromatography-tandem mass spectrometry (LC-MS/MS), except for d_{10}-PHE. This chemical was detected using gas chromatography-tandem mass spectrometry (GC-MS/MS). Detailed information about the instrumental analysis is provided in the SI.

2.5. Quality assurance and control

Three procedural blanks and 3 reagent blanks were analyzed in each batch of 12 samples. This analysis was conducted for both washing solution and hair samples to assess potential background contamination from laboratory operations and to evaluate the method's performance. Among 6 target analytes, PFOA, TPHP, TNBP and TDCPP were detected at trace levels in procedural blanks, which were subtracted properly from the measured concentrations in hair samples. All analytes exhibited good linearity, with correlation coefficients exceeding 0.995 within their respective ranges. Recoveries of isotope-labeled internal standards (d_{15}-TPHP, d_{15}-TDCPP, d_{14}-*p*-terphenyl, $^{13}C_{12}$-bisphenol S and $^{13}C_4$-PFOA) ranged from 65% to 107%, while matrix spike recoveries of target analytes ranged from 80% to 115%, with relative standard deviations of less than 20%. The limits of detection (LODs) ranged from 0.01 to 9.75 ng/g. Detailed LODs and recoveries are provided in the SI.

2.6. Statistical analysis

OC concentrations in hair were reported on a dry weight basis (dw). Data analysis was performed using SPSS statistics (version 20.0, SPSS Inc., Illinois, USA). Physicochemical properties of target compounds were retrieved from ChemSpider and PubChem (Table S1). Principal components analysis (PCA) was conducted using Origin 2022 software (Origin Labs, Massachusetts, USA). Differences between the results of experimental and control animals were analyzed using a nonparametric test (Mann-Whitney U). The correlations between the physicochemical properties of analytes and their residuals in hair were assessed using Spearman's rank correlation test (2-tailed). A p-value of <0.05 is considered statistically significant.

3. Results

3.1. Concentrations of OCs in washing solution

All 6 OCs and 3 metabolites (diphenyl phosphate (DPHP), dibutyl phosphate (DBP), and bis(1,3-dichloro-2-propyl) phosphate (BDCPP)) were detected in most washing solutions from hair samples. After washing 6 cycles, the median concentration of these 9 analytes was 944 ng/g in the MEOH washing solution, slightly higher than the HEX washing solution (651 ng/g). In comparison, lower concentrations were observed in the ACE and UPW washing solutions, with median values of 326 and 147 ng/g, respectively.

Fig. 1 presents the mean concentrations of 6 OCs per washing solution for MEOH, HEX, ACE, and UPW decontaminations. Different decontamination protocols extract varying amounts of the same compound from hair. For instance, d_{10}-PHE and d_{16}-BPA exhibited higher levels in the HEX washing solution, with average total concentrations of 0.63 and 8.12 μg/g, respectively. MEOH was more effective in extracting PFOA from the hair shaft, yielding an average total concentration of 18.2 μg/g after washing 6 cycles. UPW showed a low removal efficiency for TPHP and TNBP, with average total concentrations of 3.00 and 0.09 μg/g, respectively.

DPHP, DBP, and BDCPP are the diester metabolites of TPHP, TNBP and TDCPP, respectively. These metabolites were also measured in 4 washing solutions (Fig. S2). BDCPP was not detected in the HEX washing solution, and only small amounts of DBP were observed in the HEX, ACE,

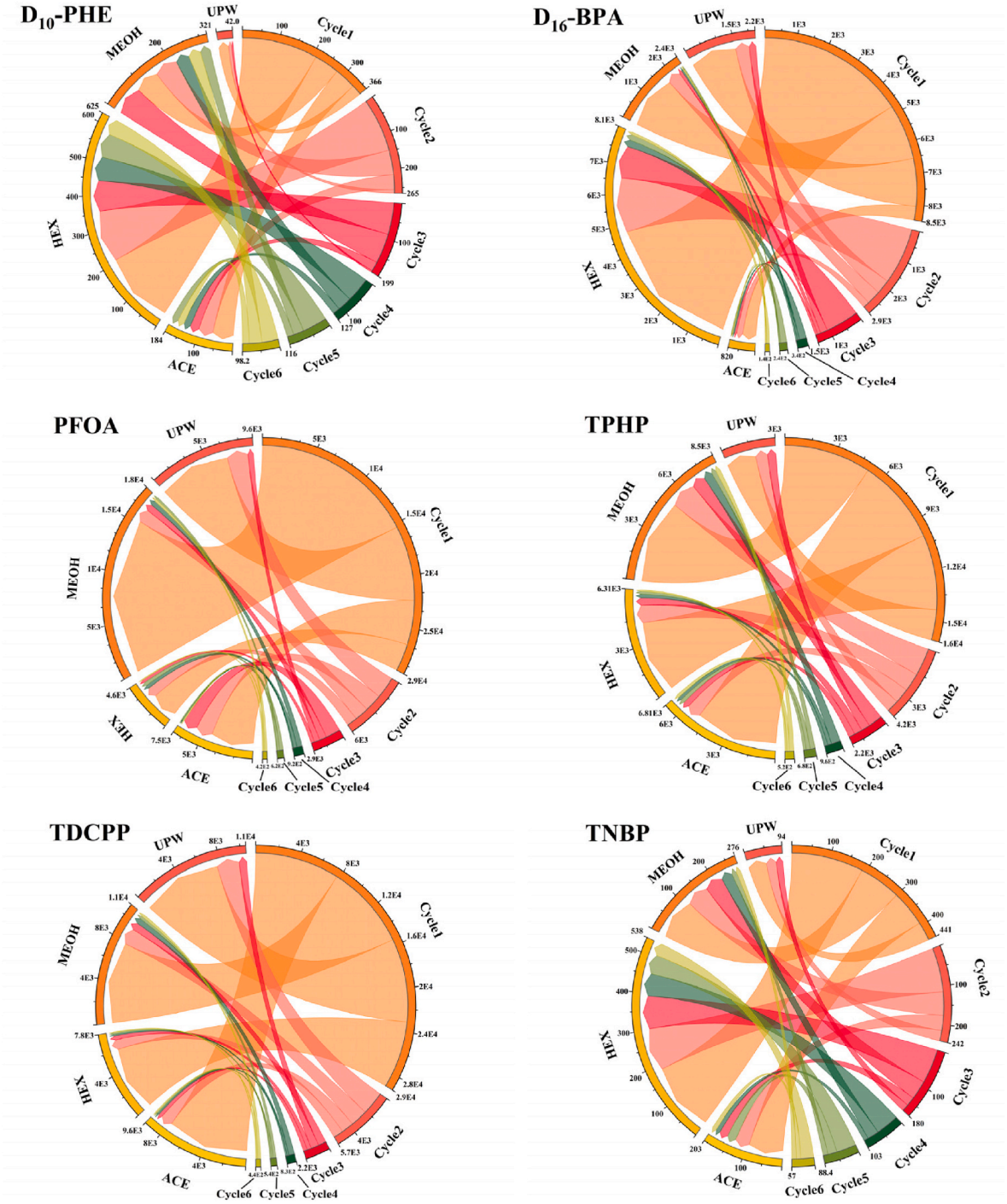

Fig. 1. Average concentrations of six target analytes in each washing cycle and each washing solution for four decontamination procedures (ng/g). The left half-circle represents the washing cycles, while the right half-circle denotes the solvents. The scale represents the average concentration of organic contaminants in each washing cycle or washing solution. ACE: acetone, HEX: n-hexane, MEOH: methanol, UPW: ultrapure water.

and UPW washing solutions. The average total amounts of three metabolites in the MEOH and ACE washing solutions were 1.4–23.8 times higher than the HEX and UPW.

The typical washout kinetics of all analytes from hair were analyzed (Fig. S3). The concentrations of these 9 analytes in washing solutions decreased with more washing cycles. Concentrations of parent compounds in washing solution generally leveled off after 3 to 4 cycles, except for d_{10}-PHE and TNBP. The concentrations of these 2 compounds in washing solutions followed the order of HEX > MEOH > ACE > UPW. The washout kinetics indicate that longer washing time led to fewer OC molecules being extracted from hair. MEOH consistently exhibited higher concentrations of metabolites than the other 3 washing solutions. After 3 to 5 washing cycles, DBP and BDCPP were no longer detectable in ACE and HEX washing solutions, but in most MEOH solutions.

3.2. Concentrations of OCs retained in hair

Concentrations of all target analytes were quantified in unwashed hair samples, except for metabolites, which had high LODs. The 6 OCs were detected in all hair samples from exposed guinea pigs (Fig. S4),

with mean concentrations of 229 to 9.13 μg/g. Only TPHP, TDCPP, and PFOA were observed in hair samples from control group animals, with concentrations 10–37 times lower than the exposure group (only results of experimental group will be discussed below).

Fig. 2 shows the average OC concentrations in hair samples before and after 6 decontamination procedures. Each decontamination procedure resulted in a marked reduction of the analyte concentrations in hair, with an average reduction of 1.8–12.7 times compared to the unwashed samples. Detailed results washed by MEOH, ACE, HEX and UPW have already been presented in washing solution section. Although data on surfactants in washing solution are not available, the hair data suggest that even after 3 brief washing cycles, the reduction of each analyte in hair was comparable to or greater than that achieved with the other 4 strategies, with no significant difference between non-ionic and ionic surfactants.

3.3. Removal efficiency of endogenous OCs from hair

To further assess the effectiveness of decontamination procedures, we examined the residual percentages of 6 OCs in hair over multiple washing cycles (Fig. 3). Residual percentages of d_{10}-PHE linearly decreased with longer washing times for the 4 washing strategies (ACE, HEX, MEOH, and UPW). In contrast, residual percentages of d_{16}-BPA, PFOA, TPHP, and TDCPP exponentially decreased, consistent with the first-order decay exponential model. The residual percentage of TNBP showed a linear decline with more washing cycles of HEX but an exponential decrease with ACE and MEOH.

The initial wash resulted in residual percentages ranging from 23.9% (TDCPP with HEX) to 92.7% (d_{10}-PHE with UPW), with 59.0% on average. After 3 washing cycles, these percentages decreased to 8.74% (TDCPP with HEX) to 90.6% (d_{10}-PHE with UPW), with 36.1% on average. Following 6 washing cycles, less than 60% of the target OCs remained in hair. To estimate the ease of OC extraction from hair, we also calculated the ratio of OC concentrations in washing solution to those in hair before washing at each washing cycle (Fig. S5). Generally, as the washing cycles progress, the ratios of most analytes in washing solution decrease, except for d_{10}-PHE and TNBP rinsed with HEX, which exhibited an opposite trend.

3.4. Factors affecting the removal efficiency

The relationships between OC residuals in hair after 1, 3 and 6 washing cycles and their lipophilicity, molecular weight (MW) and polarizability were further investigated to assess the influence of physicochemical properties on the analyte removal efficiency from hair. Lipophilicity was quantified using the log of the octanol-water partition coefficient (log K_{ow}). A significant, albeit weak, positive correlation was observed between log K_{ow} and hair residuals washed by HEX ($r = 0.47$, $p < 0.05$, see Fig. 4). The residuals after washing with ACE, MEOH, HEX and UPW consistently showed negative correlations with both MW and polarizability. Interestingly, the residuals of 2 surfactants displayed significant positive relationships with MW and polarizability, suggesting distinct removal mechanism for surfactant solution. Significant negative correlations ($r = -0.88$ to -0.65, $p < 0.05$) were found between ACE or

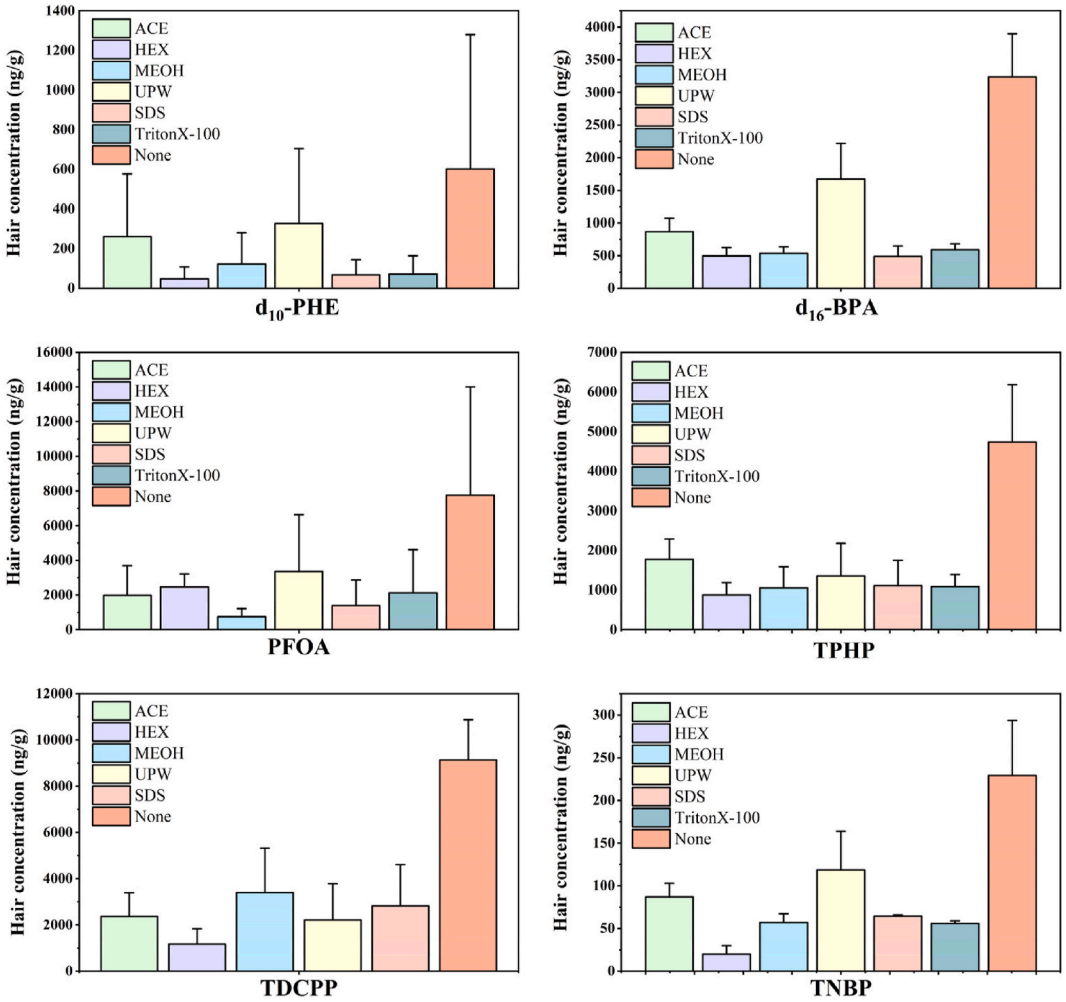

Fig. 2. Mean concentrations of six target analytes in guinea pig hair samples following six decontamination procedures (none indicates unwashed samples).

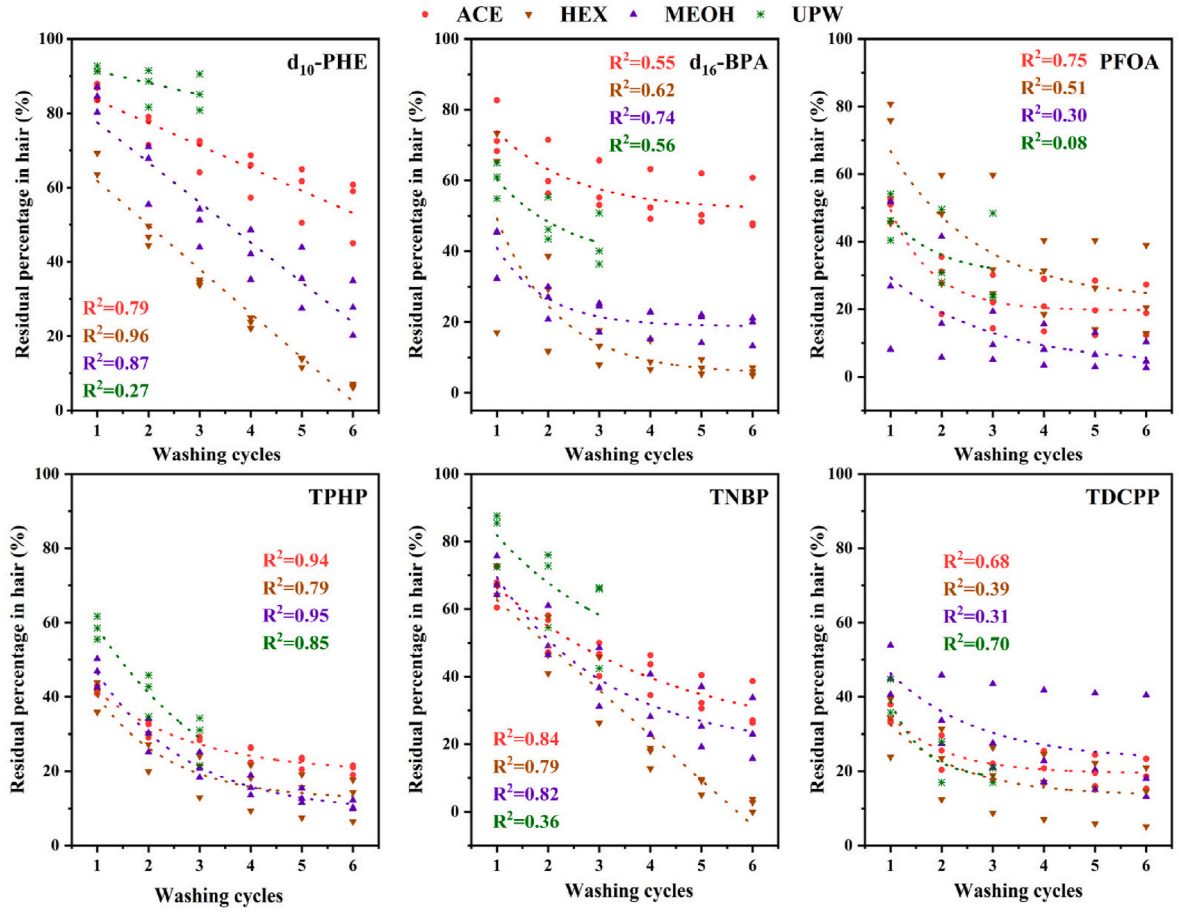

Fig. 3. Changes in the residual percentages of six target analytes in hair with repeated washing cycles. Linear fitting was applied to d_{10}-PHE across all four decontamination methods and to TNBP in HEX decontamination, while exponential fitting was used for the remaining analytes.

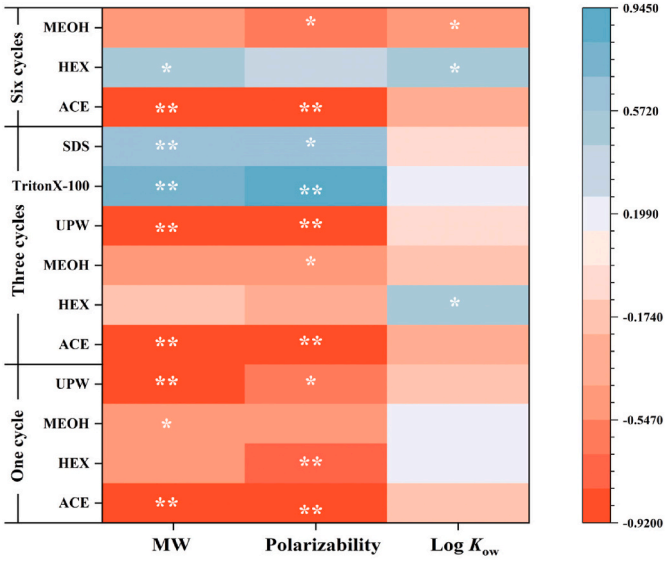

Fig. 4. Spearman correlations between the residual percentages of OCs in hair after one, three and six washing cycles and the lipophilicity, molecular weight, and polarizability of analytes (*: $p < 0.05$; **: $p < 0.01$).

UPW rinse residuals and the polarizabilities of all analytes except PFOA. This can be explained by the unique hydrophobic and oleophobic properties of PFOA. Furthermore, MW of analytes showed significant negative correlations with the residuals in hair rinsed with ACE and UPW ($r = -0.92$ to -0.83, $p < 0.05$).

PCA was performed to explore additional factors influencing wash results, including OC hair concentrations, solvent types, and washing cycles (Fig. 5). The first principal component (PC1) and second principal component (PC2) accounted for 47.7% and 20.9% of the total

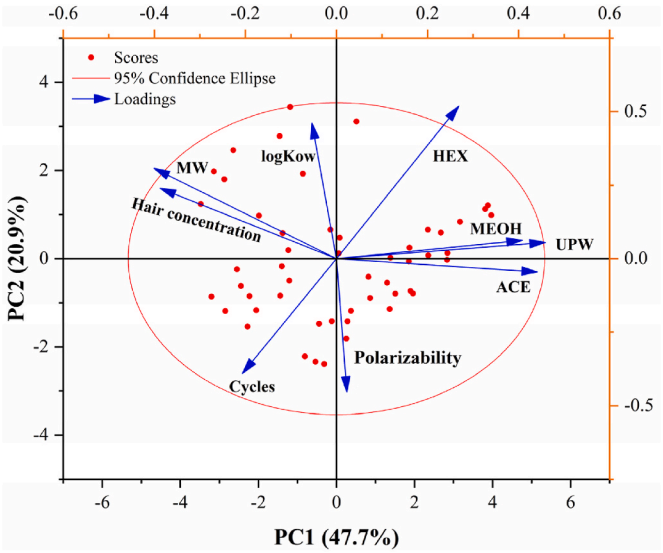

Fig. 5. Principal component analysis (PCA) was conducted based on the residual percentages of six OCs in hair, considering five related parameters: hair concentrations, washing cycles, wash solvent, polarizability, and log K_{ow}.

variability, respectively. The residuals showed strong negative associations with washing cycles, hair OC concentrations and MW for hair washed with ACE, MEOH, or UPW. However, these residuals exhibited weaker relationships with log K_{ow} and polarizability. In contrast, the residuals rinsed with HEX demonstrated an inverse association with hair concentrations, polarizability, and MW of OCs, but positive association with log K_{ow}.

4. Discussion

We measured concentrations of 6 OCs and 3 metabolites in washing solutions to investigate the influence of different wash methods on endogenous OCs in hair. All target analytes were observed in washing solutions, indicating that the decontamination process can extract endogenous OCs from hair fiber. However, the extraction capability greatly varied depending on the wash solvent. MEOH and HEX washing solutions showed higher levels of extracted analytes compared to ACE and UPW. HEX is a competitive non-protic solvent, since it does not cause hair swelling, and thus ideally removes only surface contaminants. However, in this study, HEX demonstrated a strong capacity for extracting internally incorporated OCs. The full scan chromatograms of HEX washing solutions revealed more miscellaneous peaks than other solvents (Fig. S1). It can be that the compromised integrity of the hair matrix resulted in an increased release of both impurities and endogenous OC molecules into the solution.

MEOH can swell hair to provide better access to all compartments of hair, and thereby enhance extraction during the washing process (Cuypers et al., 2016). ACE has a greater capacity for dissolving water-soluble compounds than HEX. The high levels of metabolites in MEOH and ACE washing solutions can be attributed to their higher polarity (log *K*ow = 2.18–2.88), which makes them susceptible to extraction during the washing process. Previous studies have documented that polar metabolites were incorporated into hair matrix to a lower extent than their precursors (Nakahara et al., 1992). This observation aligns with our findings, which revealed significantly lower levels of metabolites in the washing solution compared to their parent compounds. These results confirmed that endogenous OCs and their metabolites can be removed from hair matrix by 4 decontamination procedures (MEOH, ACE, HEX and UPW). Generally, the removal of OCs from hair is influenced by the physicochemical properties of the analytes, the characteristics of the washing solvents, and the distribution patterns of OC molecules within hair. To our knowledge, this is the first study to quantitatively investigate the effect of various decontamination strategies on endogenous OCs in hair using animal experiments.

The analytes in the washing solution from the first washing cycle consistently showed higher concentrations than the subsequent cycles, indicating that the majority of OC molecules were extracted during this initial step. This observation aligns with previous research on hair samples contaminated with aqueous solutions, where drug concentrations in the initial washing solution were one to two orders of magnitude higher than the fifth washing solution (Cairns et al., 2004). In the case of zolpidem consumers, the analyte concentration slightly increased after the initial hair wash, but was stable after 10 washing cycles (Erne et al., 2019). However, the authors only performed a qualitative analysis of analyte intensity without quantifying concentrations of target compounds in hair or washing solutions. In comparison, quantitative results were provided in this study. Another study of 3 OCs in human hair, including PBDEs, PAHs and hydroxyl PAHs (OH-PAHs), revealed that all analytes in the washing solution fell below LODs after 4 to 5 washing cycles (Lin et al., 2019). This was inconsistent with our findings. The discrepancy was likely due to the difference in hair samples, as hair samples collected from continuously exposed guinea pigs had higher OC concentrations compared to human subjects, and can result in substantial amounts of analytes in washing solution even after washing 6 cycles.

The levels of 6 OCs in hair are consistent with previous findings, where a remarkable enrichment of OPEs, PFASs, and PAHs was observed in the hair of exposed rats and mice (Gao et al., 2015; Grova et al., 2013; Zhu et al., 2020). The reported concentrations ranged from tens of ng/g to μg/g, and varied with various administered doses. Therefore, it is reliable to apply hair as a bioindicator for animal exposure.

After washing, the concentrations of OCs in hair exhibited a noticeable decrease. High standard deviations in the hair concentrations from parallel groups can be attributed to the limited number of guinea pigs, high levels of pollutant accumulation in hair, individual variability, etc. Several studies have investigated the effects of washing procedures on internally incorporated drugs and metal ions in hair. The concentrations of cocaine and its metabolites in rat hair markedly decreased after rinsing with MEOH or phosphate buffer (Paulsen et al., 2001). Using time-of-flight secondary ion mass spectrometry, Kempson and Skinner (2012) observed a substantial decrease in signal of 4 metal elements in human hair after undergoing 2 decontamination procedures, and concluded that the washing process significantly affected the metal content of hair.

The use of surfactants for hair decontamination is well-documented in the literature. Comparable results were reported in a prior study, where the majority of N-acetyl-methamphetamine (AcMA) in black rat hair was eliminated after 3 brief rinses with SDS (Nakahara et al., 1998). Furthermore, in a study of OCs, a single shampoo wash resulted in a substantial decreases in ∑PCBs and ∑*p,p'*-DDEs in human hair (Altshul et al., 2004). SDS exhibited remarkable decontamination efficiency (maximum: 100%) for 20 pesticides in hair artificially contaminated with cellulose (Duca et al., 2014). Clearly, surfactants demonstrate a robust capacity to remove both internally incorporated and surface OCs from hair. Surfactants therefore need to be prudently used in hair decontamination procedure to prevent the underestimation of OC concentrations.

Our study provides the first quantitative assessment of decontamination efficacy in promoting endogenous OC release from hair (Fig. S5). Despite identical processes, extraction of OCs from hair matrix became increasingly challenging with each successive washing cycle. Therefore, endogenous OC molecules from the bloodstream may bind to the hair matrix with varying affinities. Further testing is warranted. The increased extraction for d_{10}-PHE and TNBP can be attributed to the HEX wash solvent. In our previous study, the hair cuticle remained intact after a shaking rinse with HEX (Zheng et al., 2013). However, in the current investigation, successive ultrasonic treatments may have contributed to the erosion of internal hair matrix. Thus, controlling the number of decontamination cycles is crucial to minimize the impact on endogenous OCs. Duca et al. (2014) proposed that a single wash effectively removed surface-deposited contaminants from hair. In contrast, Kucharska et al. (2015) concluded that no single procedure completely eliminated external contaminants from hair. Based on these findings, we advocate reducing the frequency of hair washing during the decontamination process.

After washing 1 cycle, comparable removal efficiencies were observed for MEOH and HEX, with average values of 44.7% and 43.2%, respectively. In contrast, ACE and UPW exhibited relatively lower extraction efficiencies, with average rates of 40.7% and 35.4%, respectively. Our study specifically aimed to evaluate the impact of decontamination procedures on endogenous OCs in hair. We did not analyze exogenous OCs, as their removal efficiency from artificially-contaminated hair has been extensively documented. MEOH, for instance, removed 54–96% of the deposited pesticides from silica-contaminated hair (Duca et al., 2014). In vapor-contaminated hair, ACE exhibited varied removal efficiencies (15%–94%) for 8 OPEs, whereas water removed only 0–10% of the external PBDE congeners (Kucharska et al., 2015). However, the internal loss of OCs within the hair matrix was not evaluated in any of these studies.

The efficacy of solvents in extracting OCs from hair significantly depends on their chemical properties. Both MEOH and water can result in fluffy hair, and thereby facilitate the release of OC molecules through diffusion (Cuypers et al., 2016). MEOH effectively dissolves neutral,

hydrophilic, and lipophilic compounds, while water shows reduced efficiency in removing lipophilic compounds (Poon et al., 2015). ACE, in contrast, is recognized for its hair-friendly properties (Zheng et al., 2013) and robust dissolving capacity for both water-soluble and lipophilic compounds.

Although decontamination is necessary, it must be carefully managed to minimize its potential influence on endogenous OCs. Our findings indicate that acetone and water have minimal impact on endogenous OCs and provide gentle treatment of the hair matrix. Our previous study has demonstrated that water efficiently removes external contaminants such as particles, dust, and cosmetics (Zheng et al., 2013), while another study has showed that acetone effectively removes external lipophilic OCs from hair fiber (Kucharska et al., 2015). Therefore, a combination of acetone and aqueous solvents in the decontamination process is expected to efficiently eliminate exogenous OCs while preserving endogenous OCs. Additionally, it is recommended to minimize prolonged washing times and cycles when using this combination of solvents.

Except for wash solvent, removal efficiency of OCs from hair may have been influenced by the distribution of molecules within hair matrix and the affinity of OCs to biological components in hair. Previous studies have emphasized the significance of hydrophobicity and hydrogen bonds in PAE-protein interactions (Xie et al., 2011). Ionic bonds and van der Waals forces have been proposed as the primary binding mechanisms for perfluorooctane sulfonate (PFOS)-protein and decabromodiphenyl ether (BDE209)-protein, respectively (Chi et al., 2017; Tu et al., 2021; Zhang et al., 2009). During the washing process, certain biogenic mechanisms of incorporation may result in OC molecules weakly binding to the hair matrix, thereby facilitating their removal. Additionally, Kempson et al. (2006) observed distinct distributions of Ca, Fe, Pb, Cu, and Zn in human hair. This implies marked variability in the distribution of OC molecules within the hair matrix. Various OC molecules can display diverse distributions and bonding strengths within the hair, resulting in variations in their removal efficiency during the identical washing procedure.

The correlation results indicate that nonpolar OCs or those with low MWs are likely to remain in the hair matrix, with limited influence from decontamination. To our knowledge, the binding interactions between biological components and OCs within hair matrix have not yet been fully understood. However, this phenomenon could be because lipophilic OC molecules easily penetrate matrix cells and subsequently bind with proteins and other macromolecules, thereby becoming resistant to washing processes. Conversely, cell membranes may act as barriers to hydrophilic or polar OC molecules, resulting in their extracellular distribution within hair and facilitating their extraction by washing solvents. Nevertheless, more OCs should be further investigated to confirm this finding.

The pronounced negative association between washing cycles and residual percentages reinforces the previously posited hypothesis that HEX may compromise the integrity of the hair matrix. The factors influencing the extraction of endogenous OCs with ACE, MEOH, and UPW appear similar, in contrast to those observed with the nonpolar solvent HEX. The PCA findings align with the results from the *Spearman* correlations. The levels of organic pollutants in guinea pig hair in this study were notably elevated compared to typical levels in the general population. Given the inverse correlation between hair levels and washing residuals, it suggests that the observed removal efficiencies in this study are likely higher than those of the general population using similar decontamination processes. Further research is necessary to confirm this inference.

5. Conclusions

Decontamination is essential in hair analysis for removing sebum, dirt, and exogenous chemicals from hair surface. However, it can cause the release of endogenous chemicals from hair. The impact of different decontamination procedures on endogenous OCs was evaluated in this study, but several limitations merit consideration. Firstly, the exposure conditions for guinea pigs do not fully mimic human exposure scenarios. Additionally, the shorter length of guinea pig hair increases its surface area, potentially enhancing the extraction of endogenous OCs, whereas longer hair lengths may exhibit lower removal efficiency. As this study aims to assess documented decontamination procedures, the non-standardized washing times could affect the extraction data for different wash solvents. Finally, this study was limited to 6 common organic contaminants within a narrow physicochemical range, limiting correlations between specific parameters and washing outcomes.

Despite these limitations, this study for the first time quantitatively demonstrated that decontamination procedures can promote the release of OCs and their metabolites internally incorporated in hair matrix. Acetone and water have minimal impact on endogenous OCs, whereas surfactants, with their strong removal capacity, should be cautiously used. To minimize the loss of internal OCs, extensive washing should be avoided. This study also emphasized that nonpolar OCs or those with low molecular weights tend to remain in the hair during the decontamination procedure. Furthermore, we hypothesize that endogenous OC molecules from the bloodstream may bind to the hair matrix with varying affinities. These findings clearly demonstrate that the influence of decontamination procedures on endogenous OC molecules should not be underestimated; therefore, decontamination methods should be carefully considered when using hair as the biomonitoring matrix.

Notes

The authors declare no competing financial interest.

CRediT authorship contribution statement

Rui-Xin Qin: Writing – review & editing, Writing – original draft, Investigation, Data curation. **Xue Cao:** Writing – review & editing, Conceptualization. **Shi-Yi Zhang:** Writing – review & editing, Methodology. **Hong Li:** Investigation. **Bin Tang:** Methodology. **Qi-Long Liao:** Supervision. **Feng-Shan Cai:** Project administration. **Xian-Zhi Peng:** Validation, Supervision, Conceptualization. **Jing Zheng:** Validation, Supervision, Resources, Funding acquisition.

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

No data was used for the research described in the article.

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Appendix A. Supplementary data

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