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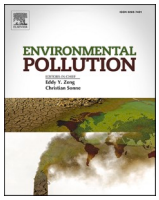

Review

# Application of nail analysis in human biomonitoring of toxic pollutants: A review☆

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ABSTRACT

Nail tissue, as a keratinized biomatrix, serves as a valuable indicator of chronic human exposure to toxic pollutants. The analysis of nail samples has emerged as a prominent method for human exposure assessment, primarily due to its non-invasive sampling procedure and ease of sample storage and transportation. This review examines recent applications of nail analysis in human biomonitoring of toxic organic compounds and heavy metals, along with the various pretreatment methods that have been developed. Studies of human nail samples have revealed distinctive patterns in toxic pollutant accumulation. Brominated flame retardants exhibit significant occupational exposure differences, with concentrations reaching $2.20 \times 10^6$ ng/g in manufacturing workers compared to 67 ng/g in the general population. Organophosphate esters demonstrate notable regional variations, as evidenced by Triphenyl phosphate concentrations of 19.6 ng/g in China versus 770 ng/g in the United States. Additionally, the detection of organic pollutant metabolites in nails provides direct evidence of internal exposure. The 5–14 months detection window characteristic of nail samples enables retrospective exposure analysis, highlighting the promising potential of nail analysis in human biomonitoring. Recent developments include the implementation of in situ analytical methods for rapid heavy metal detection in nail samples. However, a significant challenge remains in differentiating between internal and external sources of most compounds in nails, although the identification of metabolic biomarkers for certain pollutants can minimize external interference and better reflect actual body burden. Further research is required to elucidate the relationships between nail pollutant levels, environmental exposure, and health effects. While existing studies demonstrate the considerable potential of nail analysis in human biomonitoring of toxic pollutants, additional research is necessary to validate and fully realize its practical applications.

## 1. Introduction

Human biomonitoring of toxic pollutants is crucial for understanding exposure patterns and evaluating potential health risks. Traditional matrices, such as blood and urine, are the gold standard; however, they have limitations, including short detection windows, invasive sampling procedures, and complex storage requirements. These limitations have spurred a growing interest in alternative, non-invasive matrices.

Nails are intricate keratinized structures that develop through the growth and division of keratinocytes in the proximal nail matrix, containing approximately 80% protein, predominantly hard keratins, 10–15% water, and trace amounts of lipids and minerals. Throughout nail formation, both endogenous and exogenous substances are incorporated through various mechanisms, including blood circulation in the nail matrix, diffusion from the nail bed, and external contamination

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**Full names and abbreviations**

*Toxic pollutants*

| | |
|---|---|
| AFRs | Alternative flame retardants |
| AFS | Atomic fluorescence spectrometry |
| BDE | Brominated diphenyl ether |
| BFRs | Brominated flame retardants |
| BuP | Butylparaben |
| CPs | Chlorinated paraffins |
| DBP | Dibutyl phthalate |
| DBDPE | Decabromodiphenylethane |
| DEHP | Di(2-ethylhexyl) phthalate |
| DP | Dechlorane plus |
| EtP | Ethyl paraben |
| GC-MS | Gas chromatography-mass spectrometry |
| GC-MS/MS | Gas chromatography-tandem mass spectrometry |
| HBB | Hexabromobenzene |
| HPLC-MS/MS | High performance liquid chromatography-tandem mass spectrometry |
| ICP-MS | Inductively coupled plasma mass spectrometry |
| ICP-OES | Inductively coupled plasma optical emission spectrometry |
| LC-MS/MS | Liquid chromatography-tandem mass spectrometry |
| LLE | Liquid-liquid extraction |
| MBzP | Monobenzyl phthalate |
| MCCPs | Medium-chain chlorinated paraffins |
| MEHP | Mono-(2-ethylhexyl) phthalate |
| MeP | Methyl paraben |
| MEP | Mono-ethyl phthalate |
| MiBP | Mono-iso-butyl phthalate |
| MMP | Mono-methyl phthalate |
| MnBP | Mono-n-butyl phthalate |
| mPAEs | Metabolites of phthalates |
| OH-PAHs | Hydroxyl metabolites of PAHs |
| OPEs | Organophosphates esters |
| PAEs | Phthalates |
| PAHs | Polycyclic aromatic hydrocarbons |
| PBBZ | Pentabromobenzene |
| PBDEs | Polybrominated diphenyl ethers |
| PCBs | Polychlorinated biphenyls |
| PFCs | Perfluorinated compounds |
| PFDA | Perfluorodecanoate |
| PFDoA | Perfluorododecanoate |
| PFHxS | Perfluorohexanesulfonate |
| PFNA | Perfluorodecanoate |
| PFOA | Perfluorooctanoic acid |
| PFOS | Perfluorooctane sulfonic acid |
| PFRs | Phosphorous flame retardant |
| PFTA | Perfluorotetradecanoate |
| PFUnDA | Perfluoroundecanoic acid |
| PrP | n-Propyl paraben |
| SCCPs | Short-chain chlorinated paraffins |
| SPAs | Synthetic phenolic antioxidants |
| SPE | Solid phase extraction |
| TBB | 2-Ethylhexyl-2,3,4,5-tetrabromobenzoate |
| TBE | 1,2-Bis(2,4,6-tribromophenoxy) ethane |
| TBOEP | Tris (2-butoxyethyl) phosphate |
| TBP | Tributyl phosphate |
| TBPH | Bis (2-ethylhexyl) tetrabromophthalate |
| TCC | Triclocarban |
| TCEP | Tris (2-chloroethyl) phosphate |
| TCIPP | Tris(1-chloroisopropyl) phosphate |
| TCS | Triclosan |
| TPhP | Triphenyl phosphate |
| TPrP | Tripropyl phosphate |
| V6 | 2,2-Bis(chloromethyl)-propane-1,3-diyltetrakis(2-chloroethyl) diphosphate |
| 4-HB | 4-Hydroxybenzoic acid |

*Heavy metals*

| | |
|---|---|
| As | Arsenic |
| Cd | Cadmium |
| Cr | Chromium |
| Cu | Copper |
| Hg | Mercury |
| Mg | Magnesium |
| Pb | Lead |
| Sn | Tin |
| Sr | Strontium |
| Zn | Zinc |
| Se | Selenium |

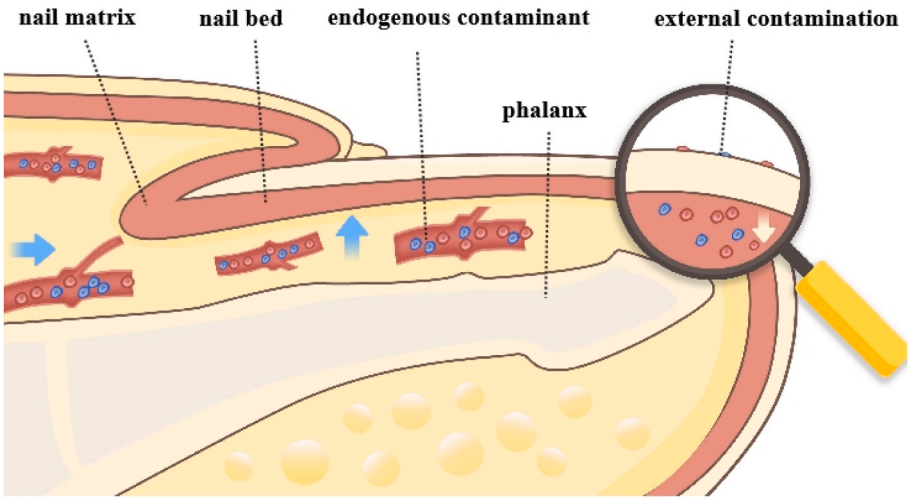


**Fig. 1.** Diagram of nail structure.

(Jaramillo Ortiz et al., 2022) (Fig. 1). Importantly, the presence of endogenous metabolites in nails is particularly noteworthy as it provides concrete evidence of internal exposure and biotransformation. For example, monoesters such as Mono-(2-ethylhexyl) phthalate (MEHP) are generated through Phase I liver metabolism and can be detected in nails months post-exposure, reflecting the body's metabolic processing of parent compounds (Tian et al., 2023). The hydroxylated metabolites of polycyclic aromatic hydrocarbons (OH-PAHs) are produced via cytochrome P450-mediated oxidation and are integrated into the nail matrix during its formation (Zeng et al., 2022).

As biological matrices, nails offer distinct advantages for biomonitoring, such as a prolonged exposure window, uncomplicated storage conditions, stability during transit, and the capacity for retrospective analysis. Nail samples can be obtained through non-invasive procedures, including clippings from the free edge or scrapings from the nail surface, making them ideal for large-scale biomonitoring studies and longitudinal exposure assessments. Given the growth rates of fingernails (average 3.5 mm/month) and toenails (average 1.5 mm/month), nail clippings can be employed to retrospectively evaluate xenobiotic exposure for up to 5 months and 14 months, respectively, before the sample is collected (Krumbiegel et al., 2016). Metabolites typically signify a more recent exposure window than parent compounds due to their quicker elimination kinetics. This temporal dimension enhances the value of nails in assessing chronic exposures, and metabolite measurements assist in verifying the internal dose, providing additional insights into exposure timing and metabolic processing.

Some studies have suggested that human exposure to toxic pollutants could be evaluated by measuring the concentrations of compounds in nails, whereas others have expressed reservations about this possibility due to difficulties in distinguishing between internal and external sources of chemicals in nails. Few studies have examined pollutant metabolites and distribution characteristics in nails. Although there have been many reports on the development of methods for nail analysis, the mechanism of compound incorporation into nails, the temporal aspect of exposure assessment, and the relationship between external exposure and nail sample concentration, there are still significant knowledge gaps and controversies. Additionally, previous reviews have rarely considered the correlation and distribution characteristics of pollutants between various matrices, such as serum, urine and nails, which could help to understand the relationship of compounds in nails and other tissues (Gutiérrez-González et al., 2019; Huang et al., 2021; Pena et al., 2021; Waseem and Arshad, 2016). To better exploit the unique role of nails in the field of human biomonitoring, there is an urgent need to summarize current research.

This review aims to critically evaluate the current applications and limitations of nail analysis in human biomonitoring of toxic pollutants, with particular focus on analytical methods, exposure assessment, and future research needs. The current literature pertaining to the detection of toxic pollutants in human nails between 2014 and 2024 were included in this review. Attention is first paid to the existing techniques of nails analysis, with a particular emphasis on the importance of method sensitivity for detecting trace chemicals. Secondly, applications of nail analysis in human biomonitoring of organic pollutants and heavy metals are critically reviewed, the reliability and limitations of nail analysis as an indicator of human exposure levels are discussed and possible improvements are suggested. Finally, the current status and advantages of retrospective exposure studies using nails are discussed. This review provides insights into the potential for nails to be used as an indicator in future human biomonitoring and epidemiological studies.

## 2. Method of literature search

To assess the utilization of nails in human biomonitoring research, we conducted a systematic literature search using keywords categorized into three distinct groups. The first group consisted solely of the term "nail." The second group, following the National Health and Nutrition Examination Survey (NHANES) and the European Human Biomonitoring Initiative (HBM4EU) guidelines, included terms related to toxic pollutants: "Toxic pollutant," "Toxic contaminant," "Brominated flame retardants," "BFRs," "Fluorinated compounds," "PFCs," "Phthalates," "Phenols," "Polycyclic aromatic hydrocarbons," "PAHs," "Polychlorinated biphenyls," "PCBs," "Pesticides," "Cotinine," "Parabens," and "Heavy metals." The third group comprised "HBM," "human biomonitoring," and "biomarkers of exposure." We searched Web of Science, PubMed, and ScienceDirect databases using combinations of keywords from group one paired with either group two or three. Studies were included if they investigated nail biomonitoring for at least one designated contaminant or metabolite and provided sufficient access to study data. We excluded studies published before 2014 and those not presenting original data.

## 3. Results and discussion

Our review encompassed 261 human biomonitoring studies published between 2014 and 2024 (as of November 2024). Of these studies, 38% focused on organic compounds, showing a progressive increase in nail-based organic matter research over the decade. The remaining 62% investigated heavy metals, demonstrating the field's substantial focus on metal contamination.

Fig. 2 shows researches on toxic pollutants in nails in recent years, indicating their increasing popularity as biomaterials for human biomonitoring. However, studies so far have only focused on a few chemical categories, i.e., endocrine disrupting chemicals (Alves et al., 2016a; Alves et al., 2016b; Alves et al., 2016c; Bui et al., 2015 Cladder-Micus et al., 2018; Li et al., 2019), perfluorocarbons (Kim et al., 2019; Lindh et al., 2012; Liu et al., 2011; Wang et al., 2018a), chlorinated paraffins (Han et al., 2021), flame retardants (Alves et al., 2017b; Chen et al., 2019; Liu et al., 2016; Zhao et al., 2022), polycyclic aromatic hydrocarbons (PAHs) (Ma et al., 2021; Zeng et al., 2022) and heavy metals (Ahmad et al., 2018; Lv et al., 2023; Oliveira et al., 2021; Shokoohi et al., 2022). Among them, research on organic pollutants in nails increased from 2020, while research on heavy metals in nails increased from 2014 but decreased from 2018 (Fig. 2).

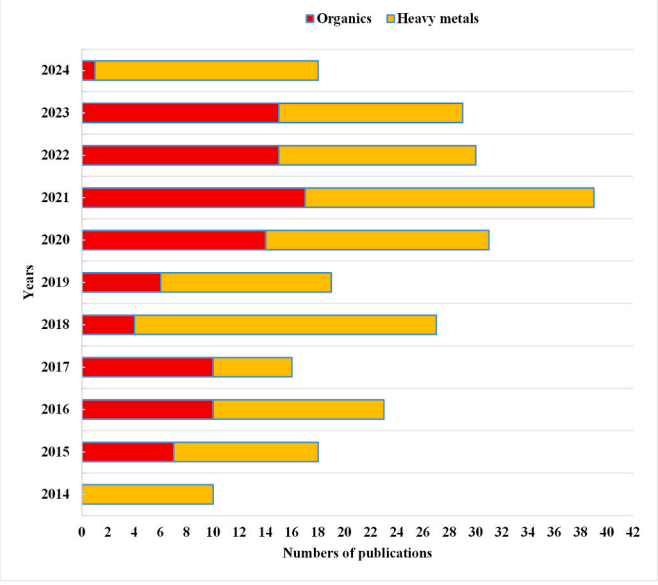


**Fig. 2.** Number of publications concerning toxic pollutants in nails in human biomonitoring applications from 2014 to 2024.

### 3.1. Analytical methodology

A sample preparation procedure that effectively mitigates matrix effects, reduces interference from impurities, and enhances compound detection is crucial for the accurate determination of toxic pollutants in nails, especially for the detection of trace compounds in limited sample sizes. The preparation procedures for nail samples include washing, cutting, digestion, extraction, cleanup, and instrumental analysis (Fig. 3). Table 1 summarizes the reported preparation procedures for nail samples in the analysis of toxic pollutants.

#### 3.1.1. Sample washing process

As depicted in Table 1, nearly half of the studies omitted a washing step prior to nail analysis. Li et al. (2019) and Chen et al. (2019) evaluated the washing efficiency of water and/or 1% Triton-100 solution against the results from an unwashed control and observed no significant differences, leading them to conclude that a washing step may be dispensable for nail analysis. However, in an assessment of various solvents—acetone, ethyl acetate, dichloromethane, n-hexane, and water—acetone was identified as the most suitable solvent. It not only eliminated external contaminants but also preserved the nail matrix from damage and promoted the release of internal analytes of interest (Li et al., 2012; Ma et al., 2021). Endogenous compounds embedded in nails are of the most concern in human nail biomonitoring. Although the importance of including a washing process is still controversial, it is imperative to minimize exogenous interference to ensure the accurate quantification of endogenous substances. Further research is essential to develop a universal sample washing procedure that enables the reliable analysis of multiple toxic pollutants in nail samples. However, if the analysis is confined to endogenous metabolites of toxic pollutants, it may be plausible to bypass the elaborate washing steps.

#### 3.1.2. Sample extraction

The nail sample quantities analyzed generally range from 20 mg to 500 mg (Table 1). Three primary extraction techniques are used for nail sample preparation. The initial method involves cutting the nail into small pieces, followed by ultrasound-assisted extraction, and then centrifugation or filtration to remove particulate matter. This method has been applied in the analysis of synthetic phenolic antioxidants, parabens, phthalate esters, polybrominated diphenyl ethers (PBDEs), alternative flame retardants (AFRs), and organophosphates esters (OPEs) in nails (Chen et al., 2019; Li et al., 2020; Li et al., 2019; Li et al., 2022). The second method includes alkaline or acidic digestion of nail samples, followed by liquid-liquid extraction and further cleanup using solid phase extraction (SPE) cartridges, which has been utilized in the analysis of organic pollutants in nails (Li et al., 2012; Liu et al., 2015; Lv et al., 2023; Ma et al., 2021). A key advantage of complete sample digestion is the formation of a homogeneous solution, which can enhance the extraction efficiency of endogenous organic pollutants from nails. However, this may also increase matrix effects, requiring a cleanup process. The choice of digestion method should be based on the characteristics of the compounds of interest. For example, alkaline digestion, which has been successfully used for analyzing PFCs (using NaOH at room temperature) and PAHs along with their metabolites, is not appropriate for extracting metals from nail samples due to the potential for interfering impurities. Yet, acid-sensitive compounds such as PAHs and their metabolites must be digested with an alkali (Ma et al., 2021). The third method, used for the analysis of toxic metals in nail samples, involves microwave or heat-induced digestion with nitric acid and hydrogen peroxide. This is a typical sample preparation process (Lv et al., 2023; Shokoohi et al., 2022; Ye et al., 2018). Protein removal from nails is an essential prerequisite for metal analysis. Typically, acid digestion is repeated until the solution is transparent (Saeed et al., 2024). It is important to note that the nail scissors used for sampling and the metal grinding steel columns used in the pretreatment process may contribute to background contamination, unless they're solvent-cleaned in between sampling or processing.

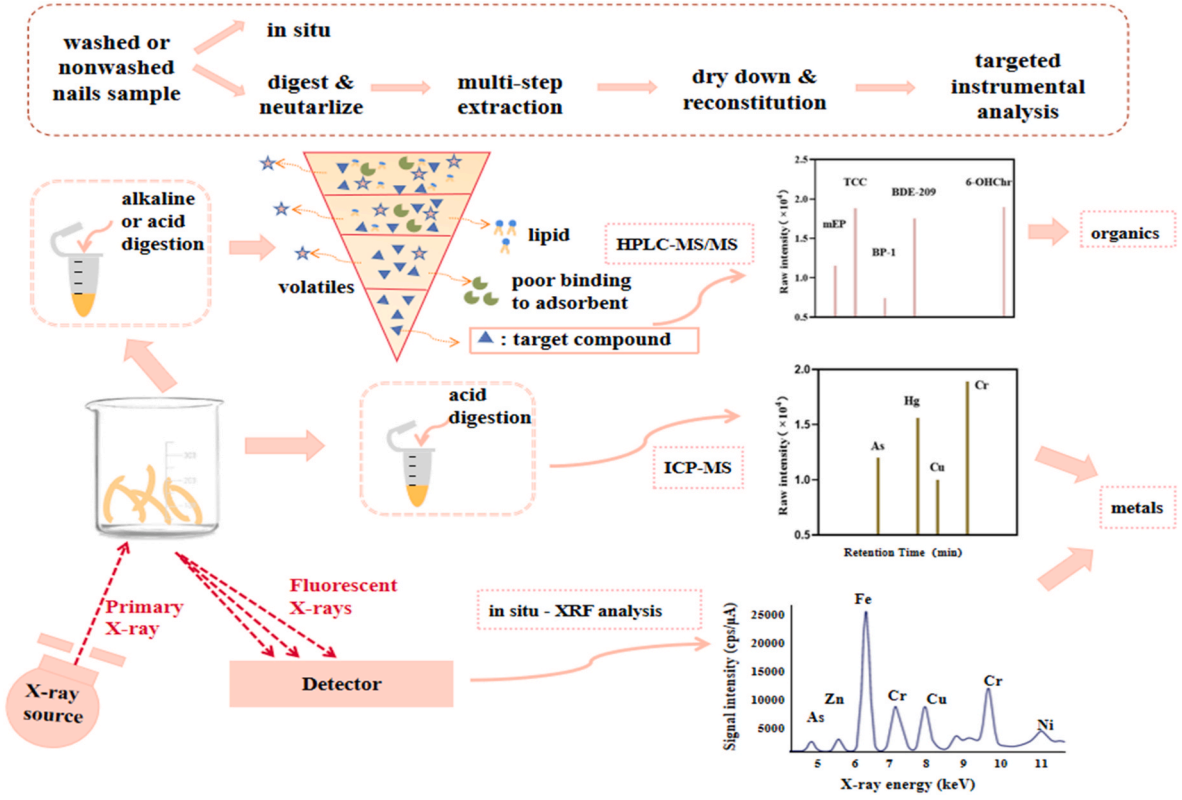


**Fig. 3.** Flow chart of nail sample analysis methods.

**Table 1**
Analytical methodology of nails in human biomonitoring of toxic pollutants. ; MLOQ: method limit of quantification; NA: not available.

| Toxic pollutant | Sample | Washing solvent | Digestion | Extraction | Instrument analysis | MLOD/MLOQ | Ref. |
|---|---|---|---|---|---|---|---|
| PAHs and OH-PAHs | 100 mg whole fingernail clippings | acetone | alkaline digestion: NaOH, 40 °C, 12 h | LLE with silica gel SPE | GC-MS/MS for PAHs; LC-MS/MS for OH-PAHs | 0.03–1.60/ 0.05–4.00 ng/g | Ma et al. (2021) |
| Heavy metals | 500 mg whole fingernail clippings | acetone, ultrapure water | acid digestion: $HNO_3$+$H_2O_2$, microwave | filtration | ICP-MS | 0.006–0.60/ 0.02–2.00 μg/g | Lv et al. (2023) |
| PFCs | 100 mg powdered nail clippings | water, acetone | alkaline digestion: NaOH, room temperature, 8 h, 55 °C, 30 min | LLE with OasisWAX cartridges | LC-MS/MS | 0.023–0.094/ 0.073–0.299 ng/g | Li et al. (2012) |
| | nail clippings | water, acetone | alkaline digestion | LLE with OasisWAX cartridges | UPLC-MS/MS | 0.023–0.094 ng/g, NA | Lindh et al. (2012) |
| | nail clippings | water, acetone | alkaline digestion | LLE with MeOH | LC-MS/MS | 0.04–0.05/ 0.14–0.15 ng/g | Li et al. (2013) |
| | 500 mg powdered nail clippings | water, acetone | alkaline digestion | SPE with WAX cartridges | UPLC-MS/MS | 0.02–0.09/ 0.07–0.3 ng/g | Wang et al. (2018b) |
| | 100 mg nail clippings | water, acetone | alkaline digestion | LLE with MeOH | HPLC-MS/MS | NA, 0.018–0.339 ng/g | Wang et al. (2018a) |
| SPAs | 50 mg tiny fingernail clippings | not washed | – | ultrasound assisted extraction | GC-MS or LC-MS/MS | 0.01–0.3/ 0.04–1.20 ng/g | Li et al. (2019) |
| Parabens | 50 mg tiny fingernail clippings | not washed | – | ultrasound assisted extraction & centrifugation | LC-MS/MS | 0.01–0.22 ng/mL, 0.03–0.76 ng/g | Li et al. (2020) |
| Phthalate esters | 50 mg tiny fingernail clippings | not washed | | ultrasound assisted extraction & filtration | GC-MS/MS | NA | Li et al. (2022) |
| Phthalate ester metabolites | 30 mg powdered fingernail clippings | acetone | | ultrasound assisted extraction & dispersive liquid–liquid microextraction | LC-MS/MS | NA, 2–14 ng/g | Alves et al. (2016c) |
| PFR metabolites | 30 mg whole and powdered fingernails and toenail clippings | acetone | acid digestion: $HNO_3$ | SPE with OasisWAX cartridges | LC-MS/MS | NA, 2.2–46.4 ng/g | Alves et al. (2017a) |
| PBDEs, AFRs, OPEs | 50 mg tiny fingernail clippings | not washed | – | ultrasound assisted extraction | GC-MS/MS for PBDEs and AFRs; LC-MS/MS for OPEs | NA, 0.02–1.51 ng/g | Chen et al. (2019) |
| PBDEs, AFRs, OPEs | all of the ten whole fingernail clippings | not washed | acid digestion: $HNO_3$+$H_2O_2$ | LLE & deactivated Florisil SPE | GC-MS | NA, 0.06–75 ng/g | Liu et al. (2015) |
| Arsenic | 20–50 mg whole fingernail clippings | not washed | acid digestion: $HNO_3$+$H_2O_2$, heating | filtration | ICP-OES | NA | Shokoohi et al. (2022) |

NA:data not available.

#### 3.1.3. Instrumental analysis

Instrumental analysis frequently employs gas chromatography-mass spectrometry (GC-MS) and liquid chromatography-tandem mass spectrometry (LC-MS/MS) for the detection and identification of organic pollutants. GC-MS is used for the analysis of volatile or semi-volatile organic compounds, while LC-MS/MS is used for the analysis of non-volatile organic compounds. For the assessment of heavy metals, inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectrometry (ICP-OES), and atomic fluorescence spectrometry (AFS) are the primary techniques. A number of studies have adopted in situ methodologies to determine metals and elements in nails, such as energy-dispersive X-ray fluorescence (ED XRF) (Mierzynska et al., 2024) and portable X-ray fluorescence (pXRF) (Fleming et al., 2017). These in situ methods eliminate the need for further pretreatment of nail samples, enhancing the efficiency and speed of analysis. However, they require certified reference materials made from hair for the calibration of analytical instruments. Additionally, XRF's sensitivity in metal analysis is lower compared to ICP-MS, with the detectable elements being limited to less than 20 (Mierzynska et al., 2024). The quantitation limits for these methods differ among various toxic pollutants, with ranges from 0.02 to 75 ng/g for organic compounds and from 0.02 to 2.00 μg/g for heavy metals (Table 1).

### 3.2. Concentration and profile characteristics of toxic pollutants in nails

#### 3.2.1. Brominated organic pollutants

Brominated flame retardants (BFRs), with a focus on polybrominated diphenyl ethers (PBDEs) and their alternatives, constitute the most commonly analyzed brominated organic pollutants in studies of human nails. The research on BFRs in human nails, as detailed in Table 2 and Table S1, is primarily confined to China and the United States, with the majority of studies concentrating on fingernails. The predominant homologs detected in nail PBDE analyses are BDE-28, -47, −99, −100, −153, −154, −183, and −209. The detection frequencies (DFs) for lower-brominated PBDEs in fingernails are notably higher in the United States general population compared to the Chinese general population. Direct comparisons between studies should be approached with caution due to potential discrepancies in analytical methods, detection limits, and sampling protocols. The concentrations of BDE-209 in fingernails exhibit variations, with median levels of 12.7 ng/g in China and 7.7 ng/g in the United States. However, the median concentrations of total PBDEs (∑PBDEs) in fingernail samples from the United States (67 ng/g) and China (67 ng/g) are identical. BDE-47 and BDE-99 are the most frequently detected PBDEs in the United States, whereas BDE-209 predominates in China, reflecting the composition of commercial PBDEs utilized in these nations. Despite its designation as a persistent organic pollutant in the 2017 Stockholm Convention, BDE-209 continues to be produced and used in China (Zhao et al., 2022). The highest BDE-209 concentrations in fingernails were observed among deca-BDE

**Table 2**
Concentration and profile characteristics of toxic pollutants in nails (for details, see Table S1 in the Supporting Information).

| Compounds | Sample type | Population | N | DF (%) | Median concentration (range) (ng/g) | Dominant compounds | Country | Reference |
|---|---|---|---|---|---|---|---|---|
| Brominated organic pollutants | | | | | | | | |
| ∑PBDEs | fingernails | general population | 50 | | 67 (13–2900) | BDE-47, BDE-99 | United States | Liu et al. (2016) |
| | fingernails | general population | 50 | | 67 (9.79–242) | BDE-209 | China | Chen et al. (2019) |
| | fingernails | e-waste dismantling workers | 30 | | 412 (168–1280) | BDE-209 | China | Meng et al. (2020) |
| | fingernails | rural residents | 33 | | 82.1 (3.54–680) | BDE-209 | China | Meng et al. (2020) |
| | fingernails | urban residents | 31 | | 129 (67.2–429) | BDE-209 | China | Meng et al. (2020) |
| | fingernails | deca-BDE manufacturing workers | 38 | | $2.23 \times 10^6$ ($2.99 \times 10^5$–$5.95 \times 10^6$) | BDE-209 | China | Zhao et al. (2022) |
| | toenails | general population | 50 | | 90 (14–3160) | BDE-47, BDE-99 | United States | Liu et al. (2016) |
| TBB | fingernails | general population | 50 | 96 | 40 (11–1210) | | United States | Liu et al. (2016) |
| | fingernails | general population | 50 | 92 | 26.7 (1.67–258) | | China | Chen et al. (2019) |
| | toenails | general population | 50 | 94 | 81 (13–2310) | | United States | Liu et al. (2016) |
| TBPH | fingernails | general population | 50 | 86 | 74 (18–1120) | | United States | Liu et al. (2016) |
| | fingernails | general population | 50 | 100 | (4.21–689) 28.1 | | China | Chen et al. (2019) |
| | toenails | general population | 50 | 80 | (18–1990) 116 | | United States | Liu et al. (2016) |
| PBBZ | fingernails | general population | 50 | 4 | (0.90–1.3) 1.1 | | United States | Liu et al. (2016) |
| | toenails | general population | 50 | 8 | (0.72–2.9) 1.0 | | United States | Liu et al. (2016) |
| PBEB | fingernails | general population | 50 | 12 | (0.25–1.1) 0.42 | | United States | Liu et al. (2016) |
| | toenails | general population | 50 | 24 | (0.20–1.1) 0.32 | | United States | Liu et al. (2016) |
| HBB | fingernails | general population | 50 | 46 | (0.20–3.0) 0.35 | | United States | Liu et al. (2016) |
| | fingernails | general population | 50 | 98 | (0.32–177) 25.5 | | China | Chen et al. (2019) |
| | toenails | general population | 50 | 66 | (0.24–5.3) 0.48 | | United States | Liu et al. (2016) |
| TBE | fingernails | general population | 50 | 14 | (0.75–8.7) 3.1 | | United States | Liu et al. (2016) |
| | toenails | general population | 50 | 12 | (1.5–7.2) 4.9 | | United States | Liu et al. (2016) |
| DBDPE | fingernails | general population | 50 | 54 | (3.43–409) 7.47 | | China | Chen et al. (2019) |
| | fingernails | DBDPE manufacturing workers | 66 | 100 | ($1.06 \times 10^5$–$5.22 \times 10^7$) $5.24 \times 10^6$ | | China | Zhao et al. (2022) |
| Chlorinated organic pollutants | | | | | | | | |
| ∑PCBs | fingernails | e-waste dismantling workers | 30 | | (58.7–341) 108 | PCB 52 | China | Meng et al. (2020) |
| | fingernails | rural residents | 33 | | (2.90–146) 22.1 | PCB 52 | China | Meng et al. (2020) |
| | fingernails | urban residents | 31 | | (4.30–18.2) 8.40 | PCB 52 | China | Meng et al. (2020) |
| syn-DP | fingernails | general population | 50 | 26 | (0.22–1.3) 0.61 | | United States | Liu et al. (2016) |
| | toenails | general population | 50 | 26 | (0.24–2.3) 0.32 | | United States | Liu et al. (2016) |
| anti-DP | fingernails | general population | 50 | 12 | (0.70–3.4) 2.0 | | United States | Liu et al. (2016) |
| | toenails | general population | 50 | 24 | (0.53–5.4) 0.78 | | United States | Liu et al. (2016) |
| DP | fingernails | general population | 50 | 8 | (<0.30–48.7) 1.22 | | China | Chen et al. (2019) |
| SCCPs | fingernails | general population | 62 | 100 | (57.7–355) 154 | $C_{10}Cl_{6\text{-}7}$ | China | Han et al. (2021) |
| MCCPs | fingernails | general population | 62 | 100 | (61.0–476) 233 | $C_{14}Cl_{7\text{-}8}$ | China | Han et al. (2021) |
| TCS | fingernails | general population | 209 | 79 | (nd–5049) 14.0 | | China | Yin et al. (2016) |
| | | general population | 60 | 98 | (<LOD–$8.47 \times 10^3$) 188 | | China | Tian et al. (2023) |
| | toenails | general population | 209 | 69 | (nd–1048) 5.68 | | China | Yin et al. (2016) |
| TCC | fingernails | general population | 209 | 100 | (1.11–9006) 75.4 | | China | Yin et al. (2016) |
| | | general population | 60 | 100 | (1.04–$4.08 \times 10^3$) 4.38 | | China | Tian et al. (2023) |
| | toenails | general population | 209 | 100 | (0.30–9598) 46.3 | | China | Yin et al. (2016) |
| Perfluorinated compounds | | | | | | | | |
| PFOA | fingernails | general population | 63 | 94 | (<0.14–0.56) 0.21 | | China | Li et al. (2013) |
| | fingernails | urban children | 38 | 76 | (nd–117) 15 | | China | Xu et al. (2010) |
| | fingernails | rural children | 55 | 81 | (nd–1600) 27 | | China | Xu et al. (2010) |
| | fingernails | general population | 28 | 30 | (<0.38–16.4) 0.19 | | China | Liu et al. (2011) |
| | fingernails | general population | 39 | 18 | (<0.04–0.46) <0.04 | | China | Wang et al. (2018b) |
| | toenails | general population | 28 | 16 | (<0.38–9.54) 0.19 | | China | Liu et al. (2011) |
| PFOS | fingernails | general population | 63 | 97 | (0.15–5.09) 0.78 | | China | Li et al. (2013) |
| | fingernails | urban children | 38 | 97 | (nd–7830) 351 | | China | Xu et al. (2010) |

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**Table 2** (*continued*)

| Compounds | Sample type | Population | N | DF (%) | Median concentration (range) (ng/g) | Dominant compounds | Country | Reference |
|---|---|---|---|---|---|---|---|---|
| | fingernails | rural children | 55 | 96 | (0.2–409) 22 | | China | Xu et al. (2010) |
| | fingernails | general population | 28 | 100 | (1.41–165) 33.5 | | China | Liu et al. (2011) |
| | fingernails | general population | 39 | 87 | (<0.05–1.89) 0.63 | | China | Wang et al. (2018b) |
| | toenails | general population | 28 | 100 | (4.15–153) 26.1 | | China | Liu et al. (2011) |
| Organophosphates esters (OPEs) | | | | | | | | |
| Halogenated OPEs | | | | | | | | |
| TCEP | fingernails | general population | 50 | 20 | (93–1860) 190 | | United States | Liu et al. (2016) |
| | fingernails | general population | 50 | 100 | (13–141) 34.3 | | China | Chen et al. (2019) |
| | toenails | general population | 50 | 8 | (100–150) 150 | | United States | Liu et al. (2016) |
| TCIPP | fingernails | general population | 50 | 36 | (74–2410) 220 | | United States | Liu et al. (2016) |
| | fingernails | general population | 50 | 100 | (16.7–298) 52.4 | | China | Chen et al. (2019) |
| | toenails | general population | 50 | 32 | (90–5150) 230 | | United States | Liu et al. (2016) |
| TDCIPP | fingernails | general population | 50 | 66 | (90–1410) 300 | | United States | Liu et al. (2016) |
| | fingernails | general population | 50 | 100 | (<0.11–54.4) 3.58 | | China | Chen et al. (2019) |
| | toenails | general population | 50 | 50 | (75–2300) 230 | | United States | Liu et al. (2016) |
| Non-halogenated OPEs | | | | | | | | |
| TPhP | fingernails | general population | 50 | 74 | (110–59800) 770 | | United States | Liu et al. (2016) |
| | fingernails | general population | 50 | 100 | (3.50–232) 19.6 | | China | Chen et al. (2019) |
| | toenails | general population | 50 | 74 | (54–232900) 1080 | | United States | Liu et al. (2016) |
| TPRP | fingernails | general population | 50 | 90 | (<0.02–1.83) 0.08 | | China | Chen et al. (2019) |
| TBOEP | fingernails | general population | 50 | 100 | (0.49–87.3) 2.25 | | China | Chen et al. (2019) |
| TBP | fingernails | general population | 50 | 100 | (4.81–101) 12.7 | | China | Chen et al. (2019) |
| Phthalates and metabolites | | | | | | | | |
| ∑PAEs | fingernails | general population | 50 | | ($1.78 \times 10^4$–$1.76 \times 10^5$) 65.4 | DBP, DEHP | China | Li et al. (2022) |
| MMP | fingernails | general population | 60 | 78 | (<LOD–118) 12.0 | | China | Tian et al. (2023) |
| | fingernails | general population | 61 | 51 | (NA) 149.3 | | Norway | Giovanoulis et al. (2016) |
| MEP | fingernails | general population | 60 | 57 | (<LOD–36) 3.89 | | China | Tian et al. (2023) |
| | fingernails | general population | 61 | 100 | (NA) 81.9 | | Norway | Giovanoulis et al. (2016) |
| | fingernails | general population | 20 | 100 | (14.9–977) 146 | | Belgium | Alves et al. (2016a) |
| MnBP | fingernails | general population | 60 | 100 | (1.39–22.1) 5.79 | | China | Tian et al. (2023) |
| | fingernails | general population | 61 | 100 | (NA) 56.0 | | Norway | Giovanoulis et al. (2016) |
| MiBP | fingernails | general population | 60 | 100 | (1.64–29.7) 7.28 | | China | Tian et al. (2023) |
| | fingernails | general population | 61 | 93 | (NA) 17.9 | | Norway | Giovanoulis et al. (2016) |
| ∑MnBP + MiBP | fingernails | general population | 20 | 100 | (38.6–814) 136 | | Belgium | Alves et al. (2016a) |
| MBzP | fingernails | general population | 20 | 60 | (<LOQ –55.3) 5.3 | | Belgium | Alves et al. (2016a) |
| MEHP | fingernails | general population | 60 | 100 | (0.17–32.2) 5.27 | | China | Tian et al. (2023) |
| | fingernails | general population | 61 | 100 | (NA) 103.3 | | Norway | Giovanoulis et al. (2016) |
| | fingernails | general population | 20 | 100 | (54.6–859) 87.4 | | Belgium | Alves et al. (2016a) |
| 5-OH-MEHP | fingernails | general population | 60 | 63 | (<LOD –1.68) 0.23 | | China | Tian et al. (2023) |
| | fingernails | general population | 61 | 68 | (NA) 1.1 | | Norway | Giovanoulis et al. (2016) |
| | fingernails | general population | 20 | 15 | (<LOQ –12.9) < LOQ | | Belgium | Alves et al. (2016a) |
| 5-oxo-MEHP | fingernails | general population | 60 | 100 | (0.06 –0.87) 0.20 | | China | Tian et al. (2023) |
| | fingernails | general population | 61 | 29 | (NA) 0.72 | | Norway | Giovanoulis et al. (2016) |
| | fingernails | general population | 20 | 25 | (<LOQ –2.4) < LOQ | | Belgium | Alves et al. (2016a) |
| Parabens and metabolites | | | | | | | | |
| MeP | fingernails | general population | 50 | 100 | (16.6–21200) 3140 | | China | Li et al. (2020) |
| | fingernails | general population | 100 | 100 | (24.6–13500) 1540 | | China | Li et al. (2023) |
| | fingernails | general population | 60 | 100 | ($22.8$–$1.70 \times 10^3$) 61.3 | | China | Tian et al. (2023) |
| PrP | fingernails | general population | 50 | 100 | (16.2–8290) 1290 | | China | Li et al. (2020) |
| | fingernails | general population | 100 | 100 | (4.07–8480) 961 | | China | Li et al. (2023) |
| | fingernails | general population | 60 | 93 | (<LOQ–21.3) 2.24 | | China | Tian et al. (2023) |
| EtP | fingernails | general population | 50 | 100 | (1.12–6680) 127 | | China | Li et al. (2020) |
| | fingernails | general population | 100 | 100 | (0.71–4440) 154 | | China | Li et al. (2023) |
| | fingernails | general population | 60 | 82 | (<LOQ–10.0) 2.19 | | China | Tian et al. (2023) |
| BuP | fingernails | general population | 50 | 100 | (0.04–3670) 16.3 | | China | Li et al. (2020) |
| | fingernails | general population | 100 | 99 | (<LOQ–1880) 8.97 | | China | Li et al. (2023) |
| | fingernails | general population | 60 | 52 | (<LOQ–2.36) 0.17 | | China | Tian et al. (2023) |
| BzP | fingernails | general population | 50 | 100 | (0.51–6.63) 1.25 | | China | Li et al. (2020) |
| | fingernails | general population | 100 | 93 | (<LOQ–13.8) 0.88 | | China | Li et al. (2023) |

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**Table 2** (*continued*)

| Compounds | Sample type | Population | N | DF (%) | Median concentration (range) (ng/g) | Dominant compounds | Country | Reference |
|---|---|---|---|---|---|---|---|---|
| | fingernails | general population | 60 | 42 | (<LOQ–1.89) 0.21 | | China | Tian et al. (2023) |
| 4-HB | fingernails | general population | 50 | 34 | (<LOQ–16.0) 0 | | China | Li et al. (2020) |
| | fingernails | general population | 100 | 19 | (<LOQ–106) < LOQ | | China | Li et al. (2023) |
| OH–EtP | fingernails | general population | 50 | 22 | (<LOQ–18.7) 0 | | China | Li et al. (2020) |
| | fingernails | general population | 100 | 25 | (<LOQ–7.42) < LOQ | | China | Li et al. (2023) |
| OH–MeP | fingernails | general population | 50 | 74 | (<LOQ–3770) 38.7 | | China | Li et al. (2020) |
| | fingernails | general population | 100 | 100 | (0.79–2190) 21.1 | | China | Li et al. (2023) |
| 3,4-DHB | fingernails | general population | 100 | 11 | (<LOQ–8.75) < LOQ | | China | Li et al. (2023) |
| ∑parabens + metabolites | fingernails | general population | 50 | | (39.9–27400) 5230 | MeP, OH-MeP | China | Li et al. (2020) |
| ∑parabens | fingernails | general population | 100 | | (354–24100) 4840 | MeP | China | Li et al. (2023) |
| ∑metabolites | fingernails | general population | 100 | | (0.79–2190) 24.5 | OH-MeP | China | Li et al. (2023) |
| ∑parabens | fingernails | general population | 60 | | (27.5–1.10 × $10^3$) 66.4 | MeP | China | Tian et al. (2023) |
| Polycyclic aromatic hydrocarbons and metabolites (PAHs and OH-PAHs) | | | | | | | | |
| $\sum_{16}$PAHs | fingernails | e-waste dismantling workers | 36 | | (7.92–551) 127 | | China | Ma et al. (2021) |
| | fingernails | e-waste dismantling managers | 16 | | (7.05–431) 63.2 | | China | Ma et al. (2021) |
| | fingernails | Adult residents | 14 | | (7.93–289) 70.5 | | China | Ma et al. (2021) |
| | fingernails | Child residents | 6 | | (8.88–1275) 509 | | China | Ma et al. (2021) |
| | fingernails | e-waste exposed population | 72 | | (7.05–1275) 101 | | China | Ma et al. (2021) |
| $\sum_{12}$OH-PAHs | fingernails | e-waste dismantling workers | 36 | | (39.5–3282) 375 | | China | Ma et al. (2021) |
| | fingernails | e-waste dismantling managers | 16 | | (27.3–3116) 107 | | China | Ma et al. (2021) |
| | fingernails | adult residents | 14 | | (124–576) 283 | | China | Ma et al. (2021) |
| | fingernails | child residents | 6 | | (181–293) 230 | | China | Ma et al. (2021) |
| | fingernails | e-waste exposed population | 72 | | (27.25–3282) 261 | | China | Ma et al. (2021) |

NA: data not available.

manufacturing workers (median 2.20 × $10^6$ ng/g) and e-waste dismantling workers (median 388 ng/g), both of which exceed levels found in other Chinese populations.

2-Ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB) and bis (2-ethylhexyl) tetrabromophthalate (TBPH) emerged as the most prevalent alternative brominated flame retardants detected in the fingernails of both the United States and Chinese general populations. The levels of TBB and TBPH in the fingernails of the United States general population were notably higher compared to those in the Chinese general population. To date, only one study (Liu et al., 2016) has reported on BFRs in toenail samples, indicating that the concentrations of BFRs in toenails surpass those in matched fingernail samples. Nonetheless, the distribution profiles of BFRs in toenails were found to be similar to those in fingernails.

### 3.2.2. Chlorinated organic pollutants

Polychlorinated biphenyls (PCBs), Dechlorane Plus (DP), chlorinated paraffins (CPs), Triclosan (TCS), and Triclocarban (TCC) are chlorinated organic pollutants that have been analyzed in nail samples, as detailed in Table 1. With the exception of TCS and TCC, these chlorinated organic pollutants have been infrequently reported in nail samples.The majority of nail analyses for chlorinated organic pollutants have concentrated on fingernail samples from Chinese populations. DP had a DF below 30%, whereas other chlorinated organic pollutants had a DF above 65% in fingernail and toenail samples. Among the chlorinated organic pollutants detected in fingernail samples, medium-chain chlorinated paraffins (MCCPs) exhibited the highest median concentration at 233 ng/g, which was notably higher than that of the short-chain chlorinated paraffins (SCCPs) at 154 ng/g. The most prevalent MCCPs and SCCPs in fingernail samples were $C_{14}Cl_{7\text{-}8}$ and $C_{10}Cl_{6\text{-}7}$, respectively, a pattern that corresponds with results from matched hair samples (Han et al., 2021).

TCS and TCC, both antimicrobial agents, have been reported twice in nail samples of the Chinese general population. Yin et al. (2016) reported a higher concentration of TCC (median 75.4 ng/g) compared to TCS (median 14.0 ng/g) in fingernail samples, while Tian et al. (2023) observed an opposite trend with medians of 4.38 ng/g for TCC and 188 ng/g for TCS, respectively. These discrepancies may be attributed to regional variations in the usage of antimicrobial agents. Concentrations of TCC and TCS in toenail samples were found to be lower than those in fingernail samples according to Yin et al. (2016), a finding that contrasts with the results observed for BFRs. Because PCBs are legacy contaminants which were banned decades ago and are typically not the focus of current risk assessment, except for some of the unintentional by-products. Therefore, their analysis frequency in nail samples is lower than that of BFRs. Meng et al. (2020) detected 1–2 orders of magnitude higher concentrations of ∑PCBs (median 108 ng/g) in fingernail samples of e-waste dismantling workers than rural (median 22.1 ng/g) and urban residents (median 8.40 ng/g). However, these levels were lower than the concentrations of PBDEs in the same samples. Moreover, PCB-52 was identified as the most abundant PCB in fingernail samples, aligning with findings from dust and hair samples collected in the same regions (Meng et al., 2020).

### 3.2.3. Perfluorinated compounds (PFCs)

As shown in Table 2 and Table S1, four publications have documented the presence of PFCs in fingernail or toenail samples, all of which were sourced from Chinese populations encompassing the general population, urban children, and rural children. Fingernails have emerged as the matrix of choice for PFC analysis in nails. Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) are the most frequently identified PFCs in nail samples, with PFOS being detected more often than PFOA across studies. Nonetheless, the DFs of PFOS and PFOA are comparable in serum samples (Li et al., 2013; Liu et al., 2011; Wang et al., 2018b). Moreover, PFOS concentrations exceed those of PFOA in all human sample types except for nails from urban areas (Li et al., 2013; Liu et al., 2011; Wang et al., 2018b). Conversely, in fingernail samples from rural children, PFOS concentrations were found to be lower than PFOA (Xu et al., 2010), indicating potential geographical variations in human exposure to PFC. When analyses included a broader range of PFCs, such as perfluorodecanoate (PFDA),

perfluorononanoate (PFNA), perfluorododecanoate (PFDoA), perfluorotetradecanoate (PFTA), perfluoroundecanoic acid (PFUnDA) and perfluorohexanesulfonate (PFHxS), PFOS was consistently the most prevalent PFC in both fingernail and toenail samples (Liu et al., 2011). The profiles of PFCs in fingernail and toenail samples are similar, but they differ from those in other human matrices, suggesting distinct accumulation or distribution patterns based on the functional group (Liu et al., 2011).

#### 3.2.4. Organophosphate esters (OPEs)

Some OPEs are used as plasticizers, while others are used as flame retardants to replace discontinued PBDEs. As shown in Table 2 and Table S1, two studies have reported on the levels and profiles of OPE flame retardants in fingernail or toenail samples from United States and Chinese populations (Chen et al., 2019; Liu et al., 2016). The concentration of total OPEs (∑OPEs) in the fingernails of the United States general population were higher than that of the Chinese general population. The predominant OPE congener in the fingernails of the United States general population was triphenyl phosphate (TPhP), while in the Chinese general population it was tris(1-chloroisopropyl) phosphate (TCIPP). These results indicate significant geographical variations in human exposure to OPE flame retardants. Consistent profiles of OPE congeners were observed in toenail and dust samples when compared with matched fingernail samples (Liu et al., 2016). In addition, a novel alternative flame retardant, 2,2-bis(chloromethyl)-propane-1,3-diyltetrakis(2-chloroethyl) diphosphate (V6), was detected in fingernail samples but only with a DF of 12% (Alves et al., 2017b). To evaluate the internal exposure to OPE flame retardants, Alves et al. (2017a) developed a method for quantifying OPE metabolites in fingernail and toenail samples. Four metabolites, i.e., dibutyl phosphate, diphenyl phosphate, bis(1,3-dichloro-2-propyl) phosphate and bis(2-butoxy ethyl) phosphate, were identified in several nail samples. However, a larger sample size is required to ascertain the presence of OPE metabolites in human nail samples.

#### 3.2.5. Phthalates and their metabolites (PAEs and mPAEs)

PAEs are widely used as plasticizers and organic additives in an array of plastic products and everyday consumer products. Only one study has reported on PAEs in human nail samples (Table 1). Li et al. (2022) determined nine PAEs in fingernails, with di(2-ethylhexyl) phthalate (DEHP) and dibutyl phthalate (DBP) being the most prevalent high and low molecular weight PAEs, respectively. Once PAEs enter the human body, they are rapidly metabolized. Three studies have reported PAE metabolites (mPAEs) in the fingernails of general populations from China and Norway (Table 1). Among the low molecular weight mPAEs, i.e., mono-methyl phthalate (MMP), mono-ethyl phthalate (MEP), mono-n-butyl phthalate (MnBP) and mono-iso-butyl phthalate (MiBP), MMP was the most abundant in fingernail samples, even though its DF was lower than those of other mPAEs. Regarding high molecular weight mPAEs, Mono-(2-ethylhexyl) phthalate (MEHP) is a primary metabolite capable of further oxidation to secondary metabolites (5-OH-MEHP and 5-oxo-MEHP). The concentration of MEHP was found to be 1–3 orders of magnitude higher than 5-OH-MEHP and 5-oxo-MEHP in fingernail samples. However, the composition profile of mPAEs in fingernail samples was different from that in urine samples (Giovanoulis et al., 2016; Tian et al., 2023), suggesting distinct distribution patterns of mPAEs between human nails and urine.

#### 3.2.6. Parabens and their metabolites

Parabens, preservatives commonly found in personal care products, have been the subject of analysis in three studies focusing on fingernail samples from the Chinese general population (Table 1). The total concentration of parabens (∑parabens) in fingernail samples from Nanjing was two orders of magnitude higher than those from Guangzhou, suggesting significant geographical differences in human exposure to parabens. Methyl paraben (MeP) was the most abundant paraben detected in fingernail samples, and OH-MeP was the predominant metabolite. The pattern of paraben composition in fingernail samples paralleled that found in urine samples (Li et al., 2023; Tian et al., 2023). In contrast, the composition of paraben metabolites in fingernail samples diverged from urine samples (Li et al., 2023), potentially attributed to the higher hydrophilicity of metabolites, facilitating their excretion via urine over accumulation in nails. To compare the levels of parabens in fingernail samples and personal care products, Li et al. (2020) measured parabens in face cream samples and found that MeP and PrP had the highest concentration, in contrast to fingernail samples. This may suggest that nails selectively accumulate parabens.

#### 3.2.7. Polycyclic aromatic hydrocarbons and their metabolites (PAHs and OH-PAHs)

PAHs originate from both natural sources (e.g., forest fires and volcanic eruptions) and anthropogenic activities, with incomplete combustion of organic matter being a major formation pathway in both cases. They are ubiquitous environmental pollutants. However, to date, only one study has quantified PAHs and OH-PAHs in human fingernail samples (Table 1). Ma et al. (2021) conducted a study on the characteristics of PAHs and OH-PAHs in fingernail samples from workers and residents at a typical electronic waste (e-waste) dismantling site in China. The composition profiles of PAHs and OH-PAHs in fingernail samples from occupational and non-occupational participants were similar, with Phe, Pyr and Fluo being the predominant congeners of PAHs, and 2-OH-Nap being the most abundant OH-PAH. These same predominant compounds were identified in matched hair and urine samples, except for the prevalence of 1-OH-Nap in fingernails which differed from that in matched hair and urine (Lin et al., 2020).

#### 3.2.8. Heavy metals (toxic elements)

Extensive research has been conducted on the use of nails as biological samples for heavy metal analysis between 2014 and 2024. In comparison to organic compounds in nail samples, numerous reviews have focused on the application of nails in biomonitoring for heavy metals (Esteban et al., 2009; Ab Razak et al., 2015; Salcedo-Bellido et al., 2021). Here, we provide a concise overview of the occurrence and characteristics of heavy metal in nail samples. Mercury is the most commonly studied toxic metal (Esteban et al., 2009; Salcedo-Bellido et al., 2021). The distribution of heavy metals in nails is closely associated with gender and age. Batool et al. (2015) identified gender-based disparities in the profiles of heavy metals in nails in Pakistan. The study revealed that nail samples of males exhibited higher levels of Zn, Cu and Cr compared to females, consistent with the findings of numerous other studies (Khalique et al., 2005; Pereira et al., 2004; Sukumar and Subramanian, 2007). The concentrations of heavy metals in human nails have also been demonstrated to fluctuate with age. Ali et al. (2019) observed that the concentration of Cd was lower in men aged 20–30 and women under 20, while levels of arsenic (As), copper (Cu), magnesium (Mg), strontium (Sr), tin (Sn) and zinc (Zn) were significantly higher in individuals aged 31–40. Some studies have reported increased concentrations of Cd, Cr, Cu, As, Zn and other elements in middle-aged individuals compared to younger aged groups (Gault et al., 2008; Hussein Were et al., 2008; Wang et al., 2009). Liu et al. (2017) found that levels of As in nail samples from men, older adults, and individuals with skin lesions were generally higher than in other healthy individuals, and these levels were not influenced by the body mass index (BMI) and smoking habits (Liu et al., 2017). A strong correlation was found between total daily As intakes (TDIAs) and As levels in nails, suggesting that nail samples can be used as bioindicators of As exposure. Moreover, a positive correlation was observed between the severity of As poisoning and TDIAs. These results are consistent with those of Batool et al. (2015), Sera et al. (2002), Ali et al. (2019). However, Chawla et al. found a high correlation between levels of Se in serum and hair, but a weak correlation between levels of Se in serum and nail, indicating, that fingernails may not be the preferred biomatrix for assessing Se content

in the human body when compared to blood and hair (Chawla et al., 2020).

Differences have also been observed in the levels of heavy metals between fingernails and toenails from the same individual Shaabani et al. (2022) conducted a study on the levels of heavy metals in nail samples from pregnant women in Iran, revealing that fingernails contained higher concentrations of heavy metals (Cr, Cu and Pb) than toenails. Przybylowicz et al. (2012) similarly observed that, with the exception of Pb, the average concentrations of metals (Cr, Co, Cu, As, Hg) were higher in fingernails than those in toenails. However, other studies have reported higher concentrations of heavy metals in toenails compared to fingernails (Abdulrahman et al., 2012; Dessie et al., 2020). This discrepancy may stem from the fact that toenails grow more slowly than fingernails, thus providing a longer period of metal accumulation (Abdulrahman et al., 2012). To explain these discrepancies, a comprehensive investigation into the variations in the binding mechanisms of heavy metals between fingernails and toenails is warranted.

### 3.3. Reliability of nail analysis from the perspective of correlation analysis

Table 3 summarizes the current available data regarding correlations between pollutant levels in fingernail samples and other human matrices. Serum and urine are considered to be matrices that reflect the human burden of internal exposure to pollutants. Studies that have investigated the correlation between fingernail and serum samples have revealed significant positive correlations in the levels of BDE-28, -47, −99, −100, −209, decabromodiphenylethane (DBDPE), PFOA, PFOS, PFNA, and PFUnDA, exhibiting weak to moderate correlation strengths (r = 0.261–0.786) (Li et al., 2013; Liu et al., 2016; Liu et al., 2011; Wang et al., 2018a; Zhao et al., 2022). Similarly, significant positive correlations have been identified between fingernail and urine samples in the concentrations of TCS, TCC, MnBP + MiBP, MBzP, MEP, MeP, EtP, PrP and OH-MeP, with moderate to strong (r = 0.420–0.829) correlation strengths (Alves et al., 2016b; Li et al., 2020; Li et al., 2023; Tian et al., 2023; Yin et al., 2016).

Notably, numerous factors may affect the correlation between matrices, such as variations in studied populations, sample sizes and sampling strategies. For example, a correlation between matrices for concentrations of low-brominated PBDEs has only been observed in the general population of the United States (Liu et al., 2016), while correlations for BDE-209 and DBDPE have been noted only among deca-BDE and DBDPE manufacturing workers, respectively (Zhao et al., 2022). Liu et al. (2016) proposed that a non-significant correlation between BDE-209 in matched fingernail and serum samples from the general population could be attributed to the short half-life of BDE-209. However, Zhao et al. (2022) found a significant correlation in individuals frequently exposed to high levels of BDE-209 (e.g., deca-BDE manufacturing workers). Alves et al. (2016a) and Tian et al. (2023) reported no correlation in the concentrations of mPAEs between a single spot urine sample and fingernail samples. However, significant correlations were found when comparing the average concentrations of mPAEs in morning urine collected over a 15-day period with fingernails samples taken at the beginning and end of the that period (Alves et al.,

**Table 3**
Correlation analysis of different compounds between nails and other biological samples.

| Fingernail compounds | population | N | Serum r (p) | Hair r (p) | Urine r (p) | Toenail r (p) | Reference |
|---|---|---|---|---|---|---|---|
| BDE-28 | general population | 50 | 0.445 (0.005) | | | | Liu et al. (2016) |
| BDE-47 | general population | 50 | 0.591 (0.000) | | | | Liu et al. (2016) |
| | general population | 50 | | | | | Chen et al. (2019) |
| BDE-99 | general population | 50 | 0.521 (0.000) | | | | Liu et al. (2016) |
| BDE-100 | general population | 50 | 0.526 (0.000) | | | | Liu et al. (2016) |
| BDE-209 | deca-BDE manufacturing workers | 38 | 0.753 (0.000) | | | | Zhao et al. (2022) |
| ∑penta-BDE | general population | 50 | 0.495 (0.000) | | | | Liu et al. (2016) |
| ∑PBDE | general population | 50 | 0.447 (0.001) | | | | Liu et al. (2016) |
| DBDPE | DBDPE manufacturing workers | 66 | 0.261 (0.035) | | | | Zhao et al. (2022) |
| TBPH | general population | 50 | | | | | Chen et al. (2019) |
| SCCPs | general population | 62 | | −0.356 ($p < 0.05$) | | | Han et al. (2021) |
| MCCPs | general population | 62 | | −0.281 ($p < 0.05$) | | | Han et al. (2021) |
| TCS | general population | 209 | | | 0.715 ($p < 0.001$) | 0.623($p < 0.001$) | Yin et al. (2016) |
| | general population | 60 | | 0.47 ($p < 0.01$) | 0.76 ($p < 0.01$) | | Tian et al. (2023) |
| TCC | general population | 209 | | | 0.829 ($p < 0.001$) | 0.837 ($p < 0.001$) | Yin et al. (2016) |
| | general population | 60 | | 0.59 ($p < 0.01$) | 0.42 ($p < 0.05$) | | Tian et al. (2023) |
| PFOA | general population | 63 | 0.299 (<0.05) | | | | Li et al. (2013) |
| PFOS | general population | 63 | 0.786 (<0.001) | | | | Li et al. (2013) |
| | general population | 28 | 0.510 (<0.01) | | | 0.650 (<0.01) | Liu et al. (2011) |
| | general population | 39 | 0.579 (<0.001) | | | | Wang et al. (2018b) |
| PFNA | general population | 28 | 0.410 (<0.05) | | | 0.430 (<0.05) | Liu et al. (2011) |
| PFUnDA | general population | 39 | 0.624 (<0.001) | | | | Wang et al. (2018b) |
| PFDA | general population | 28 | | | | 0.450 (<0.05) | Liu et al. (2011) |
| PFDoA | general population | 28 | | | | 0.480 (<0.01) | Liu et al. (2011) |
| PFTA | general population | 28 | | | | 0.440 (<0.05) | Liu et al. (2011) |
| MnBP + MiBP | | 9 | | | 0.77 (<0.05) | | Alves et al. (2016b) |
| MBzP | | | | | 0.75 (<0.05) | | Alves et al. (2016b) |
| MEP | | | | | 0.73 (<0.05) | | Alves et al. (2016b) |
| MeP | general population | 100/32 | | | 0.61 (<0.01) | | Li et al. (2023); Li et al. (2020) |
| EtP | general population | 100 | | | 0.62 (<0.01) | | Li et al. (2023) |
| PrP | general population | 100 | | | 0.54 (<0.01) | | Li et al. (2023) |
| OH-MeP | general population | 100 | | | 0.57 (<0.01) | | Li et al. (2023) |
| BuP | general population | 32 | | | | | Li et al. (2020) |

2016b). In fact, the levels of pollutants and metabolites in urine can fluctuate significantly. The average levels from repeated spot urine samples are indicative of continuous exposure and can help reduce intra-individual variability, leading to a more accurate result of total individual exposure over an extended sampling period. Therefore, repeated spot urine samples may be more analogous to fingernail samples, which also represent the average individual exposure over a relatively long period. Hence, a stronger correlation might be expected between the average levels derived from repeated spot urine samples and fingernail samples. Overall, these findings suggest that nails could serve as a supplementary biomatrix for assessing average human exposure to certain pollutants over time, as well as being useful biomarkers for specific research objectives.

The behavior of pollutants within the human body also influences the reliability of nail analysis for assessing pollutant exposure. As shown in Table 3, despite a significant correlation being identified in DBDPE between fingernail and serum samples from DBDPE manufacturing workers, the small correlation coefficient limits the use of nails as a biomarker for DBDPE. It was reported that the absorption rate, bioavailability and accumulation of DBDPE are weaker than those of BDE-209, making it more difficult for DBDPE to transfer into nails from the blood than BDE-209 (Zhao et al., 2022). In addition, pollutants that are rapidly metabolized in the human body are less likely to be transported through the body and reach nails. For example, no correlation was found in the levels of TBB, TBPH and OPEs between serum and fingernail samples, as their rapid metabolism and elimination prevent accumulation in serum (Liu et al., 2016). In terms of the physicochemical properties, compounds with higher polarity have a significantly shorter residence time in the body prior to renal clearance, resulting in lower accumulation in nails and relatively high concentrations in urine. This could account for the higher reported DF of 5-OH-MEHP and 5-oxo-MEHP in urine samples (94–100%) compared to fingernail samples (15–25%) (Alves et al., 2016b), as well as the absence of correlation between levels in urine and fingernail samples.

Hair and nails, both originating from the skin, share a certain degree of similarity. Hair has long been utilized as a non-invasive biomaterial in human biomonitoring studies. As depicted in Table 3, four types of pollutants exhibit significant correlations between fingernail and hair samples (Table 3), with a moderately negative correlation strength for SCCPs ($r = -0.356$) and MCCPs ($r = -0.281$), and a moderately positive correlation strength for TCS ($r = 0.47$) and TCC ($r = 0.59$). These findings may indicate differences in pollutant enrichment patterns between nail and hair samples. Melanin plays a critical role in the accumulation of pollutants within hair (Tang et al., 2023). Moreover, pollutants detected in nails and hair reflect the integrated exposure from both internal and external exposure sources, albeit representing distinct exposure durations. The distinction between internal and external sources of pollutants in hair has always been controversial, which may also apply to nail samples.

Overall, determining whether pollutants in nails reflect the actual body burden is a complex process that requires a series of verifications and depends on the properties of the target compounds. Compounds suitable for nail analysis warrant systematic exploration. Moreover, a strict, standardized and unified sampling protocol, as well as a reliable and consistent analysis method, is required. The comparability of data is key to obtaining reliable conclusions.

### 3.4. Retrospective monitoring of nail samples: current status and challenges

The major advantage of nail analysis is its long detection window, which can potentially provide a historical record of human exposure to various compounds. Segmental hair analysis effectively enables retrospective assessment of individual exposure to compounds over a period of time because of the single binding mechanism at the hair root. However, this approach is not feasible for nails due to the challenges associated with achieving complete nail segmentation. Moreover, there are two pathways through which compounds within the human body are incorporated into nails, i.e., via the germinal nail matrix or nail bed (Madry et al., 2014). The concentration and distribution of compounds in the nail bed may influence those within the nail, given that the nail remains in perpetual contact with the nail bed until the growing edge extends beyond the nail plate. The mechanisms by which compounds from the nail bed into nails are ambiguous. Thus, it is challenging to identify which exposure time period the nail sample represents.

In the realm of drug monitoring, Hang et al. (2013) investigated the chronological appearance of zolpidem in nails following a single dose ingestion by subjects. The results showed that zolpidem in fingernail clippings could be detected for at least 18 weeks, during which two peaks in zolpidem concentration were observed. The initial peak in zolpidem levels was identified within the first week, attributing sweat contamination as the main source. The second peak in zolpidem levels was observed in fingernail clippings between the 10th and 15th weeks. According to the growth rate of fingernails, it was deduced that this second peak reflected the period when zolpidem integrated into the nail from the germinal matrix after the drug consumption. Consequently, fingernail clippings from the second peak were more representative of the actual body burden of human exposure to the compound than those from the first peak. This study demonstrated the feasibility of retrospective nail analysis. Of course, this also relies on the size of the chemical structure and how the chemicals partition into the nail after a dose. Some compounds with different properties could take longer and shorter amounts of time to end up in the nails, presumably.

However, so far, no study has been conducted on the retrospective monitoring of human exposure to toxic pollutants using nail samples, attributable to several factors. Firstly, human exposure to organic pollutants is both passive and continuous, which precludes the execution of single-dose experiments akin to drug monitoring. Such experiments are necessary to ascertain the capacity of nail clippings to accurately mirror exposure periods. Secondly, accumulation of environmental pollutants on the surface of the nail plate may overlap with the accumulation of internal pollutants in the nail plate from the germinal matrix area, making it difficult to evaluate the actual body burden of pollutants. Nonetheless, nails serve as a valuable alternative non-invasive biomatrix for detecting human exposure to pollutants (Table 2 and Table S1), discerning whether the exposure is acute or long-term through multiple samplings (Madry et al., 2014), and assessing the levels of exposure across different populations (Meng et al., 2020).

### 3.5. Implications for human health

As an index for chronic exposure, assessing the impact of toxic pollutants in nails on human health outcomes is significant. Several studies have established a link between levels of toxic elements in nail samples and detrimental health effects. Epidemiological and experimental investigations from Li et al. (2018) revealed a significant correlation between As levels in toenail samples and hearing loss in 145 individuals from Bangladesh, as well as a significant correlation between As levels in nails and the inner ear of mice orally exposed to As. Siddique et al. (2020) measured As levels in human nails as a chronic exposure marker to investigate its connection with asthma risk. The results showed an inverse relationship between As exposure and lung function, and a positive association between As exposure and risks of airway obstruction, reversible airway obstruction and asthma-like symptoms. Moreover, a positive association between Mn levels in nail and prolactin levels in serum, and a nonlinear correlation between Mn levels in nail and luteinizing hormone levels in serum were found in a study of the effect of Mn exposure on hormone imbalance in children (dos Santos et al., 2019), suggesting increased exposure to Mn in children may disrupt the secretion of pubertal hormones and lead to the early onset of puberty. However, two investigations found non-significant correlations between levels of heavy metals in nails and the risk of thyroid cancer

(Zidane et al., 2019) or developing diabetes (Yang et al., 2019). Only one study evaluated the health implications of organic pollutants in nail. Zhao et al. (2022) correlated clinical biochemical indicators concerning thyroid hormones and liver and kidney injury markers with levels of BDE-209 and DBDPE in nails and observed significant and positive correlations between BDE-209 or DBDPE levels in nail samples and some biomarkers related to liver and kidney injury. These studies suggest that nail levels of toxic pollutants could serve as biomarkers for some pollutant-mediated adverse health outcomes in certain situations.

## 4. Conclusion and perspective

In recent years, the detection of a spectrum of organic compounds and heavy metals in nail samples has prompted the development of diverse analytical methodologies. Various in situ analysis techniques have been applied to rapid analysis of heavy metals in nails. Research into the concentrations and profile characteristics of various toxic pollutants within nail samples has provided direct evidence of human exposure to toxic pollutants. However, comparison with pollutant concentrations in serum and urine, the levels in nails may not represent the actual burden on the human body. Hence, numerous shortcomings in nail analysis must be addressed to enhance its reliability and practicality as a biological matrix for human exposure assessment.

Firstly, environmental pollutants and sweat on the nail surface are the main factors that interfere with the accurate evaluation of endogenous pollutants within nails. To overcome these problems, it is essential to develop an effective cleaning procedure to remove external contaminants from the nail surface. Additionally, it is crucial to identify and screen endogenous metabolites of pollutants as potential biomarkers of exposure in nails.

Secondly, the potential for retrospective monitoring is a significant advantage of nail analysis. However, the exposure time point represented by a specific segment of a nail is often ambiguous. To enhance the ability of retrospective nail analysis, it is necessary to clarify the binding mechanisms between endogenous compounds and nails. Ideally, a model should be developed to calculate the exposure time of compounds corresponding to a segment of a nail.

Thirdly, while some correlations between heavy metals in nails and health outcomes have been found, further investigation is needed to explore the potential associations between organic pollutants in nails and adverse health effects. The integration of stringent sample collection strategies with epidemiological research methods can facilitate the identification and screening of exposure biomarkers, subsequently focusing on those nail biomarkers related to specific health outcomes. This approach may enable the establishment of health risk thresholds for toxic pollutants in nails.

## CRediT authorship contribution statement

Zhuowen Li: Conceptualisation (lead), Methodology (supporting), Validation (equal), Writing - Original Draft (lead), Writing - Review & Editing (equal). Yanji Qu: Conceptualisation (supporting), Original Draft (supporting), Writing - Review & Editing (equal). Meiqing Lin: Conceptualisation (supporting), Investigation (lead), Formal Analysis (lead), Data Curation (equal), Writing - Review & Editing (equal). Yingxin Yu: Resources (lead), Supervision (supporting). Shengtao Ma: Conceptualisation (lead), Methodology (supporting), Validation (equal), Writing - Review & Editing (equal), Resources (lead), Supervision (supporting).

## 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.envpol.2025.125784.

## Data availability

Data will be made available on request.

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