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Mini review

Hair analysis for biomonitoring of environmental and occupational exposure to organic pollutants: State of the art, critical review and future needs

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ABSTRACT

This paper presents the current state of the art in human hair analysis for the detection of organic pollutants associated with environmental and occupational exposure. The different chemical classes are reviewed with a special focus set on compounds that were only recently investigated. The importance of methods sensitivity and particularly the influence of this parameter on the results presented in previous publications is highlighted. This report also investigates the relevance of hair analysis as an indicator of subjects' level of exposure and underlines limitations that are still associated with this matrix. This study also presents a critical assessment of some specific aspects presented in the literature as well as future needs to strengthen the position of hair as a relevant biomarker of exposure to be used in epidemiological studies.

Contents

Abbreviations: PAH, polycyclic aromatic hydrocarbons; PBC, polychlorinated biphenyls; PBDE, polybrominated diphenyl ethers; PCDD, polychlorinated dibenzo-p-dioxins; PCDF, dibenzofurans; GC–MS, gas chromatography–mass spectrometry; ECD, electron capture detector; HRGC, high resolution gas chromatography; HRMS, high resolution mass spectrometry; DDT, dichlorodiphenyltrichloroethane; DDE, dichlorodiphenyldichloroethylene; DDD, dichlorodiphenyldichloroethane; ERC, easily removable chemicals; HCH, hexachlorohexane; SPME, solid phase microextraction; LOD, limit of detection; LOQ, limit of quantification; HCB, hexachlorobenzene; DMP, dimethylphosphate; DEP, diethylphosphate; DMTP, dimethylthiophosphate; DETP, diethylthiophosphate; DEDTP, diethydithiophosphate; MMA, malathion monocarboxylic acid; 3-PBA, 3-phenoxybenzoic acid.

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1. Introduction

The widespread use of hair as a biological matrix for toxicological analysis is about to make it move from the "alternative matrices" to the "classical matrices" category, on the same account as blood or urine (Esteban and Castaño, 2009). Hair has actually become a natural matrix in numerous domains such as forensic and clinical analysis for the detection of medical drugs or drugs of abuse (Tsatsakis et al., 1997, 2000; Nakahara, 1999; Psillakis et al., 1999; Mieczkowski et al., 2001; Mantzouranis et al., 2004; Boumba et al., 2006; Pragst and Balikova, 2006; Kintz, 2007), assessment of trace element deficiency (Rodrigues et al., 2008; Li et al., 2011) or biomonitoring of the exposure to inorganic compounds (*e.g.* metals) (Yasutake et al., 2004; Gault et al., 2008; Kehagia et al., 2011; Shah et al., 2011). The increasing interest shown in hair analysis is explained by the several advantages associated with this matrix, and primarily its easiness of sampling and storage which does not require restricted measures such as presence of medical staff, adapted settings, or refrigerated conditions. The memory-effect of hair due to accumulation of chemicals in this matrix and possibility of retrospective analysis also amounted for its success in several contexts such as drug-facilitated crime evidence or assessment of the history of drug consumption in addiction treatment. The extended window of detection, compared with biological fluids, has also contributed to consider hair analysis a most relevant biomarker in the assessment of chronic consumption/exposure. The stability of both the matrix itself and the compounds contained therein also accounted for the use of hair in some history-related cases (Kintz et al., 2007; Musshof et al., 2009) and for the increased use of hair in post-mortem analysis in general (Kronstrand and Druid, 2006).

Compared with the forensic and clinical fields, the literature dealing with human hair analysis for the detection of organic pollutants is rather poor. In fact, to the best of our knowledge, about 40 publications only presented experimental results describing the detection of organic pollutants in hair in relation to environmental and/or occupational exposure. These publications concern only few chemical categories namely pesticides (including different chemical classes such as organochlorines, organophosphates, pyrethroids and others), polybrominated diphenyl ethers (PBDEs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and dioxins.

The present publication reviews the current state-of-the art of the literature dealing with the detection of organic pollutants in human hair, with a special focus on chemicals which were only recently investigated. The importance of method sensitivity was also highlighted, insofar as it may significantly influence the results, particularly in the biomonitoring of low-level exposure. The relevance and reliability of hair analysis as an indicator of humans' level of exposure was also investigated. Attention was also paid to the limitations that are still associated with the hair matrix. Finally, studies on organic pollutants in hair were critically reviewed in order to underline possible improvements and future needs to consolidate the use of hair as a biomarker of exposure in epidemiological studies.

2. State of the art

2.1. "Classical" compounds

Dioxins, *i.e.* polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF), which are by-products of industrial and combustion process or direct industrial compounds, were among the first organic pollutants detected in human hair (Schramm et al., 1992). PCDDs and PCDFs are typically analyzed using high resolution gas chromatography coupled with high resolution mass spectrometry (HRGC-HRMS) and limits of detection of the methods presented in the different works are close to 0.1 pg/g; which appears sufficient to allow high rates of positive detection (number of samples with concentration above the limit of detection divided by the total number of samples analyzed) (Table 8). These compounds are the ones for which the lowest levels of concentration in hair are generally reported (around 1 pg/g or below), even though congeners with the highest molecular mass (hepta- and octa-chlorinated congeners) can reach levels of nearly 1 and 27 ng/g for octa-CDF and octa-CDD respectively (Fig. 1). Studies investigating dioxins in hair generally included a limited number of subjects (from 1 to 6) with the exception of the study of Nakao et al. (2005) that compared dioxin levels in hair collected from 68 incineration workers with 64 subjects from the general population. The highest concentrations were observed in samples from Nakao's study (Japan) as well as in a pooled hair sample collected from a contaminated area close to a pentachlorophenol production plant in the region of Tianjin, China (Luksemburg et al., 1997).

PCBs were also among the first organic pollutants analyzed in human hair (Zupancic-Kralj et al., 1992). The different techniques used to detect PCBs in hair included HRGC with electron capture detector (ECD), HRGC-HRMS, GC-ECD and GC–MS, and the reported limits of detection ranged from 0.3 to 320 pg/g (Table 7). The rate of positive detection is generally high but may decrease below 10% for some congeners. The concentration levels described in the different studies covered several orders of magnitude but the median values were generally below 10,000 pg/g. Particularly high concentrations were however reported in hair samples obtained from children living in the urban region of Beijing (Zhang et al., 2007), China, and in hair of residents around e-waste disassembly sites in China (Zhao et al., 2008). Several studies involved populations composed of 10 subjects and more, but comparisons remain difficult as only few PCB congeners were common to the different works.

Pesticides and particularly organochlorine pesticides are by far the organic pollutants which have been the most investigated in human hair. These chemicals also are record-holders of the highest concentrations since all the categories listed in Tables 1–8 (organochlorines, organophosphates, pyrethroids and other pesticides) have already been detected at levels above 1000 pg/mg. Surprisingly, the highest concentration levels were not necessarily detected in hair of subjects with occupational exposure. For instance, the highest concentration of both o,p′-DDT and p,p′-DDT was observed in hair of Romanian adolescents (Covaci et al., 2008) (Fig. 1). The highest concentration of organophosphates (malathion and chlorpyrifos) and pyrethroids (bioallethrin) was observed in hair samples of pregnant women in Philippines (Ostrea et al., 2009). The studies which investigated pesticides in human hair often involved populations composed of hundreds of subjects. Nevertheless, with the exception of some organochlorines, few pesticides were common to several studies. Pesticides were mainly analyzed with GC–MS and GC-ECD and the limits of detection presented in the different publications ranged from below 1 pg/mg up to nearly 500 pg/mg. As a result, the rate of positive detection was significantly different between the studies. The latter aspect is more in depth detailed in the Section 3, with a special focus on organochlorine pesticides.

2.2. Compounds recently investigated

2.2.1. Polybrominated diphenyl ethers (PBDEs)

PBDEs have been used worldwide as flame retardants, added to many products such as textiles, plastics (particularly hard plastics used in electronics) and products containing polyurethane foam (*e.g.* mattresses, carpets) (Alaee et al., 2003). Estimations of the exposure to PBDEs suggested that ingestion and dermal absorption of house dust were the major pathways of exposure to these indoor