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Screening of organic pollutants in pet hair samples and the significance of environmental factors

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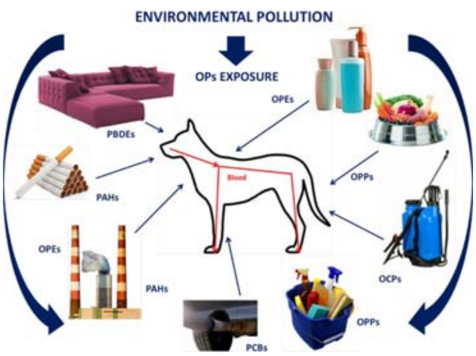
HIGHLIGHTS

- Method for about 70 organic pollutants in pet hair designed and validated
- Recoveries ranged from 75 to 120% with relative standard deviations <20.
- Limits of quantification ranged from 0.11 to 1.9 ng/g in pets' hair.
- ΣOPEs > ΣPAHs > ΣPBDEs > ΣOPPs > ΣOCPs > ΣPCBs in pets' hair
- Significant differences ($p < 0.050$) were found for PAHs for the variables size and sex.

GRAPHICAL ABSTRACT



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ABSTRACT

Organic pollutants (OPs) represent a wide range of chemicals that are potentially harmful for human and wildlife health. Many of these pollutants have been identified as endocrine disruptors that can alter hormonal balance producing adverse biological effects such as neurotoxicity, reproductive disorders, carcinogenicity and hepatotoxicity. For years, hair has been selected as a non-invasive source to assess levels of animal contamination. In the present study, a multiclass screening method for determining about 60 organic pollutants in pet hair was designed and validated for qualitative and quantitative purposes. Concentrations from different classes of organochlorine, and organophosphate pesticides (OCPs, and OPPs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (NDL-PCBs and DL-PCBs), polybrominated diphenyl ethers (PBDEs) and organophosphate esters (OPEs) were identified in the selected pet hair samples from Ourense (NW, Spain). We detected most of these pollutants in the selected hair pets. The mean concentrations found ranged from 89 to 6556 ng/g for OPEs, from 8.6 to 1031 ng/g for PAHs, from 8.6 to 256 ng/g for PBDEs, from 29 to 184 ng/g for OPPs, from 0.29 to 139 for OCPs, from 0.30 to 59 ng/g for NDL-PCBs and from 1.2 to 14 ng/g for DL-PCBs. To our knowledge, this is the first study to document the presence of OPs in pets from North-West Spain and it could provide baseline information for future monitoring of OPs in the area.

1. Introduction

In the last years, the scientific advance has allowed the increase of the quality and life expectancy of the world population due to new chemical compounds. The environmental impact of these chemicals (pesticides, medicines, flame-retardants, plasticizers or paintings) has

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been exceptionally high (Marklund et al., 2003; Fernández-González et al., 2015; Pose-Juan et al., 2016). Problems that concern to the quality of air, water and soil, as well as, ecosystem alterations have relation with the residence in the environment of these chemical substances. Therefore, the presence of organic pollutants (OPs) in humans has become a subject of intense research for health risk assessment (Covaci et al., 2008; Fernández-Cruz et al., 2017a, 2017b), and the reason why over the years, instruments to regulate and control environmental pollutants to protect human health and environment have been created by the international community.

OPs are toxic organic compounds, which are either manufactured for a specific purpose (e.g. pesticides or flame-retardants) or produced as by-products (e.g. incinerated waste). Several studies have shown that OPs can lead to chronic diseases such as reproductive problems, pregnancy complications, cancer, obesity and brain development disorder. (Ali et al., 2013; Andresen and Bester, 2006; European Court of Justice, 2008; Kluwe et al., 1985; Lewtas, 2007; Sévère et al., 2015; Wassenberg and Di Giulio, 2004; Zhao et al., 2005). A large number of researches about OPs were carried out for decades by environmental monitoring programs that provide information about contamination of a specific place. However, such studies in environmental samples provide no data on the degree of exposure and effects on living organisms (Beeby, 2001). It is for this reason that biomonitoring OPs could represent the first important step to determine and assess their toxic risk and their potential adverse effects on human and animal health.

In many studies, pets (dog/cat) have been selected as good sentinels for human exposure to OPs, since they share the same habitat as their owners (Dirtu et al., 2013; Dye et al., 2007; Guo et al., 2016; Kunisue et al., 2005; Maciejewski et al., 2008; Mizukawa et al., 2015, 2017; Ruiz-Suárez et al., 2016; Storelli et al., 2009). Correlations have found between pets and humans in several studies focused on OPs whose primary route of exposure is by inhalation (Backer et al., 2001; Calderón-Garcidueñas et al., 2001; Henríquez-Hernández et al., 2017; Ka et al., 2014; Knapp et al., 2013; Lau et al., 2017; Norrgran Engdahl et al., 2017; Ruiz-Suárez et al., 2016). Moreover, Sonne et al. (2015) have showed lung excretion pathways for several organohalogenated contaminants. Ruiz-Suárez et al. (2016) concluded that dogs could not be used as good sentinels since they do not share dietary pattern with humans and they have not comparable metabolic capabilities.

In the last years, hair was widely used as non-invasive bio-indicator for human exposure to metals and drugs, but not often to OPs. Table 1 shows the published manuscripts of the proposed topic. The first works, determined whether hair analysis would be a suitable method to assess pollution exposure to PCBs (dioxin like (DL-PCBs and non-dioxin like (NDL-PCBs))), PCDD/Fs (polychlorinated dibenzo-p-dioxins/dibenzofurans), OCPs and OPPs (Schramm, 1997; Shin et al., 2004; Tutudaki et al., 2003). In this way, Margariti and Tsatsakis (2009) and Maravgakis et al. (2012) used non-specific OPP metabolites as indicators of long-term exposure of OPPs. Correlations between hair samples and internal tissue samples to some OPs were subsequently published (Ali et al., 2013; Chata et al., 2016; D'Havé et al., 2005; Spoon et al., 2014). They concluded that a hair sample could be a suitable indicator of OP exposure in terrestrial mammals. In 2015, Sévère et al. evaluated the chemical exposure to POPs in dogs in order to find cancer association. Nevertheless, some authors (Martín et al., 2015; Schramm, 2008) have showed certain scepticism to the use of these non-invasive samples. They listed four open questions (differences between OP sorbed from atmospheric environment or incorporated by ingestion, long-term behaviour of OPs, relationship between exposure and levels of OP in hair as well as their relationship with those levels found in other body fluids) that until the moment were not answered thoroughly. However, these authors thought that hair analysis is essential as an approach in biomonitoring of human exposure.

Hair samples ($n = 51$) were collected with the aim to assess human exposure due to environmental pollution in Ourense, (NW Spain). To our knowledge, the selected target substances are in need of monitoring due to their human risk and mainly for their effects on vulnerable population groups. For such purpose, analytical methods have been developed, optimized and applied in the selected samples. Solid-liquid extraction was employed and subsequently, the extracts were analysed by gas and liquid chromatography coupled to a tandem mass spectrometry.

Table 1
Previously studies about the determination of OPs in hair samples from animals.

Matrix	Compounds	Main results	Author
Rat hair	PCBs, PCDD/F, OCPs	Hair samples present high levels of POPs after intentional exposure	Schramm (1997)
Rabbit hair	OPP (diazinon)	Determination of diazinon as an indicator of long-term exposure.	Tutudaki et al. (2003)
Rat hair	OCPs	Optimization of an extraction method for determining OCPs in rat hair	Shin et al. (2004)
Hair and internal tissues of bears	PBDEs and OCPs	Maritime bears present higher contamination levels than interior bears. Salmon consumption explains the increases in the concentrations of the targeted OPs	Christensen et al. (2005)
Hair and internal tissues of mammals	PBDEs	Positive relationships between PBDE levels in hair and internal tissues were found.	D'Havé et al. (2005)
Hair and adipose tissue of polar bears	PCBs, OCPs and PBDEs	PCBs were the pollutants with the highest concentrations in polar bears.	Bechshøft et al. (2009)
Rabbit hair	OPP metabolites	Determination of non-specific OPP metabolites as an indicator of long-term exposure.	Margariti and Tsatsakis (2009)
Hair and internal tissues of bears	PCBs, OCPs and PBDEs	Correlations between hair and internal tissues for PCBs were found.	Jaspers et al. (2010)
Rabbit hair	OPP metabolites	Determination of non-specific OPP metabolites as an indicator of long-term exposure of diazinon and chlorpyrifos.	Maravgakis et al. (2012)
Hair and serum of dogs and cats	PCBs, OCPs, NBFRs and PBDEs	Higher OHC levels were described in serum and hair from cats. Correlations were found for DDTs in paired hair and serum cat samples.	Ali et al. (2013)
Hair and internal tissues of rats	PBDEs	Positive correlations between PBDEs levels in hair and invasive matrix were found.	Spoon et al. (2014)
Dog hair	PCDD/Fs, PBDEs, PCBs and OCPs	Identification of pollutants linked with mammary cancer (PCB 105,114,118,156).	Sévère et al. (2015)
Hair and plasma of rats	OCPs, OPEs, pyrethroids, phenylpyrazoles, oxadiazines, carboxamides, carbamates, anilines	Positive association between plasma and hair for several target compounds was found.	Chata et al. (2016)