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Pesticide detection in air samples from contrasted houses and in their inhabitants' hair

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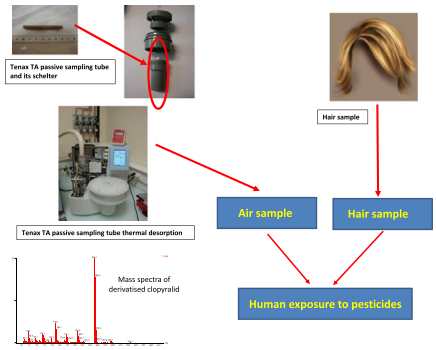
HIGHLIGHTS

- Analysis of pesticides in air of homes by passive sampling
- Several pesticides were detected in human hair
- Pesticides in the two matrices were not necessarily associated
- Exposure profiles varied between houses and between inhabitants of the same house

GRAPHICAL ABSTRACT



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ABSTRACT

In order to identify associations between indoor air contamination and human exposure to pesticides, hair samples from 14 persons (9 adults and 5 children below 12 years) were collected simultaneously with the air of their 5 contrasted houses. Three houses were situated in Alsace (France), one in Lorraine (France) and one in Luxembourg (Luxembourg). Houses were located in urban (n = 3), semi-urban (n = 1) and rural areas (n = 1). Twenty five (25) pesticides were detected at least once in indoor air samples and 20 pesticides were detected at least once in hair samples. The comparison between hair and air samples for the same sampling periods shows that pesticides detected in the two matrices were not necessarily associated. Exposure profiles varied from one home to another but also between inhabitants of the same home, suggesting that exposure can be different between inhabitants of the same home. This study demonstrated the usefulness and the complementarity of hair analysis, for the personalized biomonitoring of people exposure to pesticides, and air analysis, for the identification of airborne exposure and house contamination.

1. Introduction

The processes and levels of air contamination induced by agricultural activities (maize crops, vineyards, etc) are currently well documented (Van Dijk and Guicherit, 1999; Peck and Hornbuckle, 2005; Scheyer et al., 2007; Schummer et al., 2010). Pesticides are however also used in other sectors for different treatments such as parks and

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public roads maintenance, pest control in buildings, private gardens maintenance or pets care. These uses lead to outdoor contamination as well as indoor contamination when pesticides are applied in enclosed rooms, or when transfer from outdoor to indoor trough clothes, shoes or air exchange occurs (Bouvier et al., 2006). Several studies were carried out to evaluate occupational exposure of applicators (Delhomme et al., 2010; Harris et al., 2010; Cattani et al., 2001). Contamination of buildings and subsequent non-occupational exposure were also investigated. Different classes of pesticides such as organophosphates or pyrethroids applied in houses were studied (Lu and Fenske, 1998; Tulve et al., 2007; Williams et al., 2008) and transfer from the area treated to other surfaces was already reported (Stout and Mason, 2003). Such contamination is likely to increase children exposure due to extended contact with the floor as well as hand-to-mouth behaviour (Gurunathan et al., 1998; Harrad et al., 2010; Van Den Eede et al., 2011). Transfer towards indoors through pets after lawn treatment was also identified (Morgan et al., 2008). Furthermore, several studies pointed out the exposure to pesticides used for wood treatment such as pentachlorophenol or lindane (γ-HCH) (Neuber et al., 1999; Wilson et al., 2007).

Human exposure can be evaluated through environmental monitoring such as air analysis. For the collection of air samples, passive sampling constitutes an alternative to traditional methods. This technique is based on the migration of chemicals from the air to the sampling support through molecular diffusion (Gorecki and Namiesnik, 2002). This simple method is easy to set up and cost-efficient, needs no power supply and allows large scale sampling, which is essential for providing a specific description of the spatial and temporal variations of air contamination. There are several kinds of passive air samplers (PAS) with different design and sampling support. PAS have already been used in studies focused on the contamination of air by pesticides in order to evaluate levels of contamination, distribution or transport of contaminants on long distance (Shen et al., 2005; Harner et al., 2006; Bohlin et al., 2008; Schummer et al., 2012a).

Human exposure can also be evaluated through biomonitoring, which consists in the analysis of chemicals and/or their metabolites in biological matrices. For this purpose, urine is classically used and to a lesser extends blood. More recently, a growing interest is currently observed for hair analysis of organic pollutants such as pesticides for assessing human exposure. Contrary to blood or urine which provides information about substances recently absorbed, hair gives the possibility to evaluate the exposure to substances accumulated during weeks or months preceding the sampling time. Consequently, hair analysis is particularly adapted to study chronic exposure (Salquèbre et al., 2012). Furthermore, the sampling is easy to organise, does not required medical personnel and does not pose an infectious risk. Contrary to environmental analysis that requires considering transfer coefficient to assess exposure, biomonitoring provides direct information on the internal dose of pollutants (the dose that actually entered the body). This is the case for blood for example. However, for hair, it must be considered that a potential contribution from external exposure occurred (air, dust) and must be added to the internal dose of pollutants.

On the other hand, biomonitoring does not allow the identification of the origin of the exposure and results integrate the contribution of the different sources of exposure. Among the different studies already carried out in the field, organochlorines were the most investigated pesticides, and lindane and DDT the most frequently detected (Covaci et al., 2008; Tsatsakis et al., 2008, 2014; Appenzeller and Tsatsakis, 2012). Hair analysis enabled to highlight differences in the level of contamination between different groups of population as for example higher exposure of inhabitants of urban area compared to rural area (Zhang et al., 2007). In the agricultural sector, occupational exposure was already demonstrated by hair analysis (Cirimele et al., 1999), and correspondences between the nature of the pesticides detected in hair of farmers and their agricultural activities were observed in a study carried out in Luxembourg (Schummer et al., 2012b). Hair analysis also allowed the identification of significant exposure of pregnant women to pesticides due to domestic use (Ostrea et al., 2006).

The aim of this pilot study was to identify possible associations between air contamination and human exposure to pesticides of inhabitants from 5 contrasted houses. Passive sampling was chosen for air sampling and human exposure was evaluated through hair samples from 14 persons collected during the same period as air. A method of extraction and analysis was developed for each kind of matrix. 31 and 26 pesticides of different chemical families were investigated in air and hair samples respectively. These pesticides were chosen to be representative of local pesticides application in agriculture, of non-agricultural application and of indoor domestic used.

2. Methods

2.1. Chemicals and reagents

Pesticides standards of Pestanal® quality were purchased from Riedel de Haën (Sigma Aldrich, St. Quentin Fallavier, France). Internal standards were purchased from Dr. Ehrenstorfer (Augsburg, Germany). The pesticides stock solutions (1 g L^{-1}) and a mix standards solution (10 mg L^{-1}) were prepared in acetonitrile. A solution of internal standards was also prepared in acetonitrile (p,p′-DDE d^8, pentachlorophenol $^{13}C_6$, MCPA d^6, permethrin d^6 at 1 mg L^{-1} and trifluralin d^{14}, γ-HCH d^6, endosulfan-b d^4 at 0.1 mg L^{-1}). The purity of the standard pesticides and stable isotope labelled analogues was always above 98%. Pentafluorobenzyl bromide (PFBBr), N-(t-butyldimethylsilyl)-N-methyltrifluoroacetamide (M*t*BSTFA) purity ≥97% and potassium carbonate anhydrous (K_2CO_3) from Fluka were purchased from Sigma Aldrich (St. Quentin Fallavier, France). Acetonitrile and ethyl acetate were supplied by Biosolve (Dieuze, France) and by Prolabo (LPCR-Schiltigheim, France). Ultrapure water was produced using a water purification chain (Milli-Q A10 Advantage) from Millipore (Brussels, Belgium).

2.2. Samples collection

Hair samples from 14 persons (9 adults and 5 children below 12 years) were simultaneously collected with the air of their 5 contrasted houses. Three houses (A, B, C) were situated in Strasbourg and its suburban area (Alsace, France), one in a town (D) near Metz (Lorraine, France) and one in (E) Luxembourg (Luxembourg). Houses were located in urban (n = 3), semi-urban (n = 1) and rural areas (n = 1). One home situated in Strasbourg centre was an old building with apparent wood structure on which protection treatments were classically applied in the past (but with no indication available). The other houses were possibly submitted to pesticides contamination due to private gardens or pesticides treatments surrounding their location. Air samples were collected using passive air samplers (PAS), which consisted in a Tenax® resin tube protected by a specially designed shelter allowing airflow. The shelters were produced in the laboratory on the basis of a model proposed by Wania et al. (2003) for XAD-2 resin. PAS were placed in a room and outdoor of each of the 5 houses during 2 to 13 weeks over a period of 1 year (October 2010–October 2011). Details on sampling periods and number of samples are described in Table 1.

Hair samples were collected by a member of the laboratory staff, as previously described (Schummer et al., 2012b; Salquèbre et al., 2012). Strands of hair were sampled from the back of the head, as close as possible to the scalp. Hair samples were collected as possible on a monthly basis and were stored in aluminium foil at room temperature before extraction and analysis (Becker et al., 2014). Volunteers were informed about the objectives of the study and gave their authorization for the hair sampling. The study was approved by the Committee of the protection of persons East IV (France).