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Atmospheric concentrations of PCDD/Fs, dl-PCBs and some pesticides in northern Algeria using passive air sampling

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ABSTRACT

Two monitoring campaigns were conducted in northern Algeria to assess the contamination level of pesticides and persistent organic pollutants (POPs) in ambient air. Six pesticides (α- and γ-hexachlorocyclohexane, fenitrothion, malathion, chlorpyrifos and λ-cyhalothrin) were monitored at two different sampling locations during the first campaign. The passive sampling was performed at a semi urban/industrial site but also in a rural area between July to September 2008. The pesticides levels, analyzed by GC/MS/MS, ranged from 16 pg m^{-3} to 11 ng m^{-3}. The second campaign was carried out from May to November 2009. The polychlorodibenzo-*p*-dioxins, dibenzofurans (PCDD/Fs) and dioxin-like polychlorinated biphenyls (dl-PCBs) concentrations were evaluated at an urban/industrial and at an industrial site. The PCDD/Fs and dl-PCBs, analyzed by HRGC/HRMS, ranged from 249 to 923 fg TEQ m^{-3}. In addition to passive sampling, active sampling using an isokinetic sampler was also performed at an industrial waste incinerator. The PCDD/Fs and dl-PCBs found was 268 pg TEQ m^{-3}. This paper presents the first measurements of PCDD/Fs, dl-PCBs and pesticides in rural, urban and industrial areas of northern Algeria.

1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are ubiquitous environmental contaminants. They have received interest as a result of their toxicity and persistence properties in environmental media. PCDD/Fs emitted from combustion (natural processes or anthropogenic activities) or re-emitted from reservoirs (water, soils, and sediments), are transported to distant locations through atmospheric or aquatic pathways. PCDD/Fs bioaccumulate through the food web, and pose a risk of causing adverse effects to human health. Food consumption is the most predominant route for human exposure to these contaminants. To a certain extent, they are also present in indoor environments (Loos et al., 1997; Wang et al., 2003; Weschler and Nazaroff, 2008).

Particular attention has also been focused on polychlorinated biphenyls compounds (PCB) and, especially, the ones that exhibit a 'dioxin-like toxicity'. The twelve dioxin-like PCBs (dl-PCBs) and the seventeen 2,3,7,8-PCDD/Fs are characterized by their ability to bind to the aryl hydrocarbon hydroxylase (AhR) receptor (Safe, 1986).

The complex nature of PCDD/F and PCB mixtures complicates the risk evaluation for humans. For this purpose, the concept of toxic equivalent factors (TEFs) has been developed and introduced to facilitate risk assessment and regulatory control of exposure to these mixtures (Safe, 1990). The congener 2,3,7,8-tetrachlorodibenzo-*p*-dioxins (2,3,7,8-TCDD) is the most toxic congener and is given a TEF of one. Other congeners are given TEFs that are fractions of one, reflecting a pronounced variability in toxicity. TEFs are reassessed frequently as knowledge progresses (van den Berg et al., 1998, 2006).

The total 2,3,7,8-TCDD toxic equivalent concentration (TEQ) characterizing the dioxin-like toxicity of a sample is obtained using the TEQ formula as reported in the literature (van den Berg et al., 1998).

A series of relevant pesticides are also monitored in this study. Malathion, fenitrothion and chlorpyrifos are organophosphorus pesticides. They are intensively used in the agricultural production system in Algeria. λ-cyhalothrin, a pyrethroid, is also used as an insecticide in urban Algerian areas. Finally, the banned hexachlorocyclohexane (HCH) pesticide (including α and γ-HCH isomers) is also important to monitor based on its intensive usage in the past.

As reported in the literature, the POPs and pesticides sampling can be performed by using either active (using high or low volume sampling) or passive sampling (Gorecki and Namiesnik, 2002; Tuduri et al., 2006). High-volume sampling, as a conventional

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sampling technique, is reported to be a method of choice for air monitoring of POPs (Namiesnik et al., 2005). The sampling-system design is mainly used for daily monitoring of specific parameters. However, sampling cost equipment and maintenance including the need of a pump and power supply are major drawbacks. Meteorological variations and punctual emissions of POPs can also modify their concentrations in air during short time periods (Mari et al., 2008).

The passive air samplers are alternative sampling tools for these compounds. They accumulate chemicals via diffusion and therefore do not require electricity or any other power source to operate (Shoeib and Harner, 2002a). These devices allow semi-quantitative measurement of the atmospheric POPs levels (Harner et al., 2004). Semi-permeable membrane devices (SPMDs), XAD-resin samplers, tristearin-coated fiber glass, polymer-coated glass samplers (POGs) and polyethylene-based samplers have been used as passive samplers. In particular, polyurethane foam (PUF) disks are easy to handle and their price make the technique very attractive (Harner et al., 2004, 2006; Jaward et al., 2004; Pozo et al., 2004; Wilford et al., 2004). However, in order to estimate the uptake rates under field conditions, active sampling can also be performed during one week in parallel with the passive sampling (Tuduri et al., 2006).

Currently, there are no emission inventories in Algeria. On the opposite, PCDD/Fs emission inventories have been carried out in European countries (Quaß et al., 2000, 2004). In Portugal, a survey carried out from 1998 to 1999 revealed PCDD/F concentrations ranging from 24 to 548 fg WHO-TEQ m^{-3} (Coutinho et al., 2001). In Germany, PCDD/F levels in ambient air were determined during 10 years since 1990. A pronounced spatial variability of the concentrations was reported. The range spanned from 29 fg I-TEQ m^{-3} in Bavaria to 900 fg I-TEQ m^{-3} in Saxony (Fiedler et al., 2000). In Italy, concentrations values for PCDD/Fs ranged from 22 to 125 fg I-TEQ m^{-3} in the Po Valley (Italy), while in an industrial district of the Veneto Region, PCDD/Fs concentrations in the air samples were between 144 and 337 fg I-TEQ m^{-3} (Caserini et al., 2004). Ten years of PCDD/Fs monitoring in ambient air in Spain (Catalonia), showed that concentrations ranging from 5 to 1196 fg I-TEQ m^{-3} and from 5 to 45 fg I-TEQ m^{-3} were recorded in industrial and rural locations, respectively (Abad et al., 2007).

The aim of this study is to determine the PCDD/Fs, dl-PCBs, chlorinated pesticides and some current-used pesticides levels in ambient air of northern Algeria. Polyurethane foam disks were deployed in three sampling areas. The monitoring sites represent different levels of industrialization zone across the country (urban/industrial and industrial) including also a rural area. In addition, active sampling, using an isokinetic sampler was carried out at the stack of an industrial waste incinerator (IWI) to determine, in Algeria, the first benchmark of POPs level emitted by an IWI.

This paper adds to the current literature the first report of atmospheric measurements of PCDD/Fs, dl-PCBs and pesticides in rural, urban and industrial areas of northern Algeria.

2. Material and methods

2.1. Passive air sampling and sites

The samplers contain a foam disk (14 cm diameter; 1.35 cm thick; surface area, 365 cm^2; mass, 4.40 g; volume, 207 cm^3; density, 0.0213 g cm^{-3}; PacWill Environmental, Beamsville, ON) positioned in a stainless steel sampling chamber consisting of two domes. This passive air sampler housing protects the foam disks from direct precipitation, sunlight and coarse particle deposition. Air is allowed to flow over the sampling surface through a 2.5 cm gap between the two domes.

The target compounds in ambient air were monitored at three different sampling locations between July 2008 to November 2009. The first sampling site is situated near the Lake of Reghaia, a rural area (36°46′05″N, 3°20′22″E) located approximately 40 km east from Algiers. The sampling was initiated in July and was ended in September 2008 (56 d). Duplicate PUF disk samplers were used for this purpose. The second site is a semi urban/industrial area located at the Institut National de Protection des Végétaux (INPV) in Baraki (36°39′48″N, 3°05′55″E). Two sampling campaigns were conducted from July to September 2008 (56 d) and from May to July 2009 (three PUFs were exposed in duplicates during 28, 28 and 40 d, respectively). The third sampling site is located in Bou-Ismail (36°38′26″N, 2°43′07″E), an industrial area situated 50 km north-west from Algiers. PUF disk samplers were exposed from September to November 2009 (three PUFs were exposed in duplicates during 28, 38 and 56 d, respectively). Detailed position of sampling sites is indicating in Fig. 1.

2.2. Active air sampling and site

The sampling of particles was performed using an isokinetic sampler (Clean Air Engineering, Marseille, France) operating at an average flow of 0.040 $m^3 min^{-1}$. Two cubic meters of air was drawn through a Whatman 110 mm glass micro-fiber filter where atmospheric particles >0.1 μm in diameter were trapped (grade GF/F, Whatman, purchased from Fourni-Labo, Versailles, France). The particle-loaded filters were directly kept in methylene chloride to prevent any degradation and, then stored at 4 °C prior to their analysis. Sampling was carried out at the stack emission of an IWI company (IWI, ECFERAL SPA) located at El Harrach, 10 km at the east periphery from Algiers (Fig. 1).

2.3. Chemicals

Nonane Puriss analytical reagent grade, standard for GC, was purchased from Fluka (Steinheim, Germany). Sodium sulfate anhydrous was Baker analyzed (J.T. Baker, Deventer, the Netherlands). Chromatographic pure grade helium gas (99.99%) was purchased from Air products (Vilvoorde, Belgium). The internal standard solution of the seventeen 2,3,7,8-chloro-substitued $^{13}C_{12}$ congeners labeled PCDD/Fs (EDF-4144), the calibration standard solution (EDF-4143), and the syringe (recovery) standard (EDF-4145) were purchased from Cambridge Isotope Laboratory (Cambridge Isotope Laboratories, Andover, MA, USA). The $^{13}C_{12}$-labeled mono-ortho-PCBs internal standard spiking solution (MBP-MKX) was obtained from Wellington laboratories (Wellington laboratories, Guelph, Ontario, Canada). For PCDD/Fs and non-ortho-PCBs, a mixture of [^{13}C]TeCB-80, [$^{13}C_6$]1,2,3,4-TeCDD, and [^{13}C]1,2,3,4,7,8,9-HpCDF was used as the recovery standard (EDF-4145).

α-Hexachlorocyclohexane (α-HCH), γ-hexachlorocyclohexane (γ-HCH), fenitrothion, malathion, chlorpyrifos and λ-cyhalothrin were purchased from Sigma Aldrich (Seelze, Germany). d_8-naphthalene (ISOTEC, Miamisburg, Ohio, USA), hexane (Sigma Aldrich, Seelze, Germany), acetone (Fisher Scientific, Loughborough, UK), diethyl ether (Sigma Aldrich, Seelze, Germany), mirex (analytical standard grade PS702, Supelco, France).

2.4. Extraction and clean-up

2.4.1. Quality assurance/quality control

The PUF-disks were subjected to a 24 h Soxhlet extraction with hexane/diethyl-ether (95:5; *v*/*v*) to ensure cleanliness. They were then air dried in a clean atmosphere and then wrapped in aluminium foil and placed in polyethylene bags prior to their use in the field. Glass micro-fiber filters were baked at 400 °C for 1 h in the furnace to lower the blank levels for organic carbon species. These filters were then stored and transported in packs of twenty in leak-proof glass jars prior to use. Several steps were taken to assure that