Environmental Pollution 222 (2017) 609–616

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Assessment of seasonal variations in persistent organic pollutants across the region of Tuscany using passive air samplers☆

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ARTICLE INFO

Article history:
Received 22 February 2016
Received in revised form
30 August 2016
Accepted 31 August 2016
Available online 11 January 2017

Keywords:
POPs
PAS-PUF
Seasonal variability
Urban and rural sites
Tuscany

ABSTRACT

Concentrations of persistent organic pollutants (POPs) were measured for an entire year in the region of Tuscany, Italy. Passive air samplers consisting of polyurethane foam (PUF) disks were deployed over four sampling periods of 3–5 months from April 2008 to July 2009 in urban (n = 6) and rural (n = 4) sites. The aim of the study was to characterize the spatial and seasonal variations in selected POPs. The POP concentrations (pg m^{-3}) in the air were dominated by dichlorodiphenyltrichloroethane and metabolites (DDTs) and polychlorinated biphenyls ($\sum_7$PCBs). DDTs, and $\sum_7$PCBs showed a clear decreasing urban > rural gradient. The concentrations of DDTs and PCBs were up to 10 and 6 times higher, respectively, in urban sites than in rural sites. $\sum_7$PCBs showed a significant correlation with the urbanized areas located <5 km around the sampling sites. For hexachlorocyclohexanes (HCHs), α-HCH concentrations were similar at both sampling sites and were found to be quite uniform during the four sampling periods. Seasonal fluctuations were observed for DDTs, and $\sum_7$PCBs, with the highest concentrations observed during period 4 (summer–spring); this is most likely due to a temperature-driven re-emission from local sources. These findings were also supported by an air back trajectory analysis in the study area. This study contributes new information about POP levels in the Italian atmosphere and demonstrates the feasibility of using PUF disks to simultaneously assess seasonal concentrations at different sampling sites.

1. Introduction

Persistent organic pollutants (POPs) are a heterogeneous group of chemicals of particular concern because of their persistence, bioaccumulation, biomagnification, and toxicity (Roots et al., 2010). The Stockholm Convention (SC) on POPs was adopted in 2001 and was enforced in 2004 (Stockholm Convention, 2015). Initially, only 12 chemicals were recognized as POPs; more recently at the seventh conference of the parties, additional chemicals were included in the SC (Stockholm Convention, 2015). Currently, Italy and Malta are the only European countries that have not ratified the SC on POPs (Stockholm Convention, 2015). However, because Italy is part of the European Union (EU) and the EU is a signatory of the SC on POPs, the production and commercialization of POPs are banned in Italy.

Because of the wide usage of POPs as pesticides, they are directly emitted into the atmosphere as a spray. A large amount is released into the air over a wide range as a product of combustion and many other industrial processes (De Laurentis et al., 2009) and by an agricultural spray drift, post application volatilization, and wind erosion of soil. These emissions are influenced by numerous physical and chemical factors (Bogdal et al., 2013).

The atmosphere is a primordial medium for POP transport and responds relatively quickly to changes in POPs emission; consequently, it has been recognized as a key medium in the Global Monitoring plan of the SC on POPs, which intends to support the evaluation of the effectiveness of the SC (Stockholm Convention, 2015). Furthermore, the UNEP Guidance promotes the use of

☆ This paper has been recommended for acceptance by Prof. von Hippel Frank A.

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http://dx.doi.org/10.1016/j.envpol.2016.08.092
0269-7491/

passive air samplers because of its cost-effective approach. Ambient air monitoring of POPs is therefore particularly relevant for investigating the environmental levels and trends of these chemicals.

In the last 20 years, the emission of polychlorinated biphenyls (PCBs) in Italy has slightly increased from 242 kg in 1990 to 246 kg in 2006; presently, the main sources are combustion in energy production, heating, and industrial production (mainly steel production) (De Laurentis et al., 2009). As secondary inputs, there are numerous diffusive sources such as old capacitors, transformers, plasticizers, paints, and joint sealants in which PCBs were widely used during the 1950s–1970s (Bogdal et al., 2014). However, in Italy, there is a lack of data regarding organochlorine pesticides (OCPs) and PCB levels in the atmosphere because the air monitoring programs mainly rely on the conventional active air sampling techniques. For a better understanding of the regional distribution of atmospheric pollutants, further information (such as higher geographical distribution of the sampling sites, seasonal variations, and meteorological conditions) is necessary.

In the last decade, the development of passive air sampling consisting of polyurethane foam (PAS-PUF) disks has significantly increased and contributed to new data to assess chemicals in the atmosphere, particularly for long-term continuous monitoring programs (Pozo et al., 2009; Bogdal et al., 2013; Klánová and Harner, 2013). PAS-PUF disks can be used to access other main sources and/or diffusive secondary emissions on a local, regional, and continental scale (Pozo et al., 2009; Bogdal et al., 2013). In addition, the slow degradation rate of organic pollutants, i.e., OCPs and PCBs, make them excellent compounds for the study of atmospheric pollutant levels, spatial distribution, temporal variation, and transportation (Roots et al., 2010).

The aim of this study is to contribute new data on selected POPs and characterize their concentrations in air, including spatial and seasonal distribution, by using PAS-PUF disk samplers for 1 year in urban and rural areas throughout Tuscany, Italy.

2. Material and methods

2.1. Sampling sites

Ten locations were selected throughout the region of Tuscany (Fig. 1). This region is located in central Italy, has an area of approximately 23,000 km^2, and houses a population of approximately 4 million inhabitants. The agricultural land use represents about 30% of the total surface, and it is generally located around the urban areas. The Apennines Mountain range to the northeast and the Tyrrhenian Sea on the west make the region relatively isolated and interesting in order to assess the local and regional concentrations and variations of air pollutants. The 10 sampling locations were divided into urban (n = 6) and rural (n = 4) sites (Fig. 1) [Sampling Material (SM), Table S1]. Information about Tuscany and about each sampling site is presented in a previous study (Estellano et al., 2015). PUF disks were deployed for 60–160 days (d), with one sampler per site, for four different periods of simultaneous monitoring for 2–5 months each. Approximately, Period 1 was from April to July 2008 (spring–summer), Period 2 was from August to November 2008 (autumn), Period 3 was from November 2008 to April 2009 (winter), and Period 4 was from April to July 2009 (spring–summer).

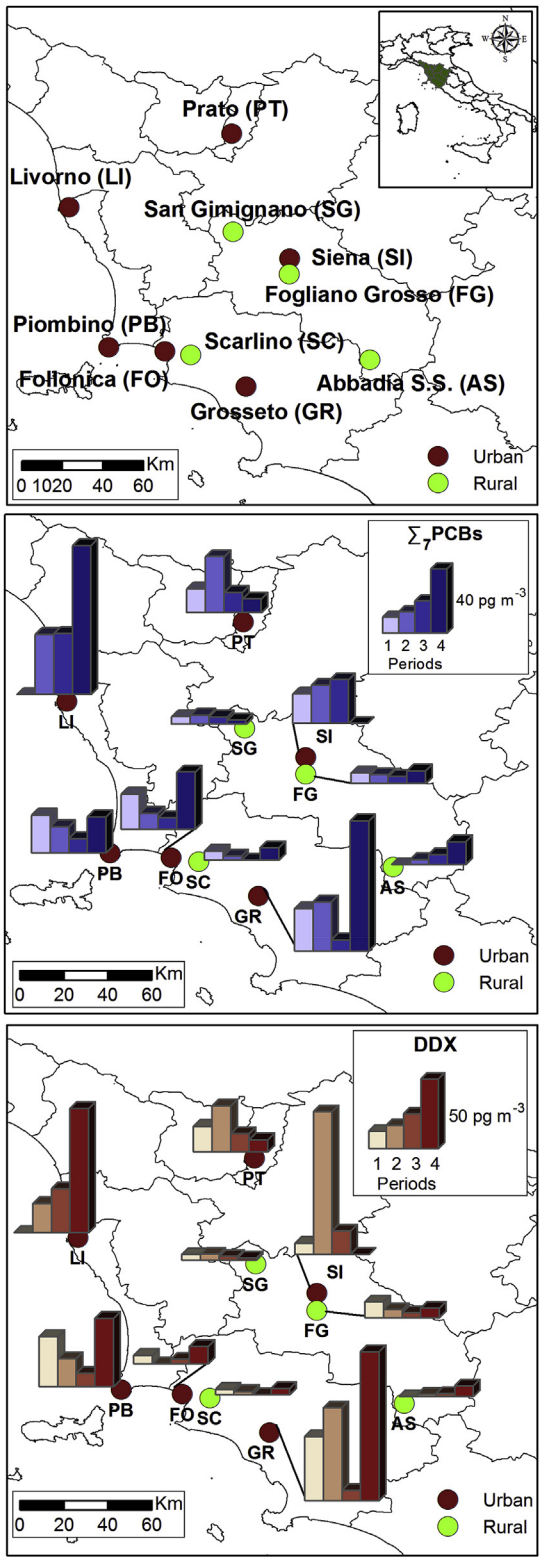

Fig. 1. Location of passive air sampling sites and the spatial and temporal distribution of the concentrations of $\sum_7$PCB and sum of DDTs and their metabolites in the air during four consecutive sampling periods across Tuscany.

2.2. Sampler preparation and deployment

The PUF disks have the following characteristics: diameter, 14 cm; thickness, 1.35 cm; surface area, 365 cm^2; mass, 4.40 g; volume, 207 cm^3; and density, 0.0213 g cm^{-3} (Tisch Environmental, Village of Cleaves, Ohio). They were precleaned by Soxhlet extraction for 48 h using acetone (24 h) and petroleum ether (24 h); for more details, refer to Pozo et al. (2012) and Estellano et al. (2012, 2014). The PUF disks were then stored in 1-L glass jars that were