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Self-organizing maps for indications of airborne polychlorinated biphenyl (PCBs) and organochlorine pesticide (OCPs) dependence on spatial and meteorological parameters

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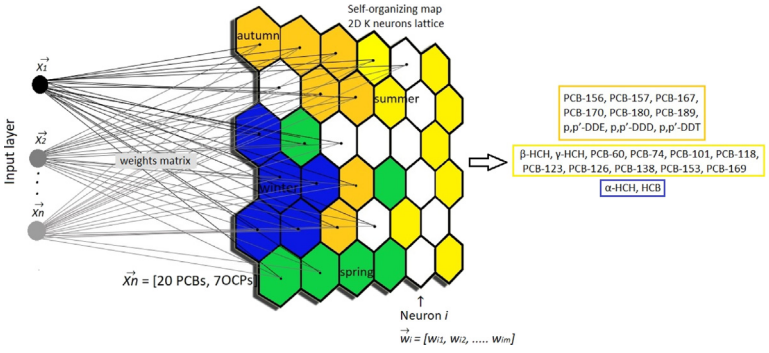
HIGHLIGHTS

- We analyzed 20 PCBs and 7 OCPs in urban air during four seasons.
- Kohonen self-organizing maps were used to interpret the results.
- Significant differences among seasonality of airborne OCPs and PCBs were recognized.
- Spring did not have influence on the concentration trends of OCPs and PCBs.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper investigates the relation of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in air samples with meteorological parameters (temperature, atmospheric pressure and relative humidity) using the Kohonen self-organizing map (SOM). Both gas- and particle-adsorbed phase of 20 PCB congeners and 7 OCPs including the three new ones (α-HCH, β-HCH, and γ-HCH) listed in the Stockholm Convention were collected during a one-year period at urban locations in Zagreb (Croatia). Moving beyond existing studies, the SOM analysis showed that the meteorological characteristics of transient seasons such as spring had no influence on the dissimilarities in the behavior of PCBs and OCPs. Towards the identification of pollutant spatial patterns, the SOM did not isolate a clear phenomenon probably due to the absence of local pollution sources contributing to the elevated concentrations of these compounds. Overall, our results have shown that the SOM method, by recognizing significant differences among PCB and OCP seasonality, could be recommended in the analysis of pollutant distribution depending on temperature and atmospheric pressure.

1. Introduction

Persistent organic pollutants (POPs) are a group of toxic organic substances that persist in the environment, bioaccumulate and biomagnify in the food chain, and are prone to long range atmospheric transport. They have been continuously released into the environment over the

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past several decades. Due to their persistence and capacity for long-range transport, POPs are now distributed in different compartments of the environment worldwide (LRTAP, 1998). Their high lipid solubility results in their bioaccumulation in fatty tissues of animals and humans in which they can induce various adverse effects such as reproductive defects, neurobehavioral abnormalities, endocrine disruption effects, immunological toxicity and cancer (Lerche et al., 2002).

The Stockholm Convention (2001) on POPs was intended to reduce or eliminate the use, discharge and emission of these compounds to improve the health of the environment and reduce risk to humans and wildlife. The Convention now has 158 Parties (Croatia signed the Convention in 2001 and it entered into force in 2007) that continuously revise and adopt decisions and trigger actions towards an enhanced implementation of the Convention, elimination of pollutants and inventory guidance (UNEP, 2015, 2017). Measures taken during the last decades to restrict and reduce POP emission into the environment have led to reduced primary sources and declining environmental levels of POPs in abiotic and biotic samples (http://chm.pops.int/). The Convention initially targeted twelve POPs, which cause adverse effects in humans and the ecosystem. They included the categories of pesticides, industrial chemicals, and byproducts some of which were polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) and hexachlorobenzene. Since 2009, 16 new POPs have been recognized together with isomers of hexachlorocyclohexane (α-, β-, γ-HCH).

The persistence and stability of PCBs, OCPs, and HCH in the environment correspond to the degree of chlorination and position of the chlorine substituent. Of the 209 different PCB congeners, 13 exhibit a dioxin-like toxicity with a half-life from 10 days to one and a half years. Even decades after the use of these compounds was completely limited or prohibited, they are still present at noticeable rates due to remaining sources, their persistent nature and the long life span of their applications. In the Global Monitoring plan (Stockholm Convention, 2001), air was recognized as an essential medium for the emission and transport of POPs. In the air, POP levels undergo substantial changes depending on numerous physical and chemical parameters (Holoubek et al., 2007; Berrojalbiz et al., 2014). For example, a combined measurement and modeling approach showed that the strength of emission source and further emission rates of POPs are related to variations in temperature (Bogdal et al., 2013a).

In this study, we investigated the Kohonen self-organizing map (SOM) as a method for screening of the relation between the concentration patterns of PCBs and OCPs and meteorological parameters. The SOM, introduced by Kohonen (1982, 1991), represents a type of neural network method that provides a projection of multidimensional data into the nodes of a regular, usually two-dimensional grid. The SOM algorithm constructs the neurons in such a way that more similar neurons are associated with nodes that are closer in the grid, whereas less similar neurons are situated gradually further away in the grid (Kohonen, 2013). Regarding traditional methodology, SOM clusters data according to some similarity or distance measure, but it surpasses traditional cluster analysis (Budayan et al., 2009). Although the SOM has been successfully applied to clustering and visualization in the exploration of persistent organic compounds (POPs) in environmental samples including water, soil, plant and food (e.g., Domingo et al., 2012; Mari et al., 2010; Olkowska et al., 2014), to the best of our knowledge, it has only been used to assess the potential relationships between polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) in air samples (Mari et al., 2010), but not PCBs or OCPs.

In this perspective, the aim of this research was to examine how the levels of PCBs and OCPs differentiate at two dissimilar urban sampling locations using the SOM method and pollutant concentrations along with meteorological parameters (temperature, atmospheric pressure, and relative humidity). The SOM, as a clustering tool, allowed the inclusion of one-year data and a more detailed investigation of pollutant seasonality unlike the common approach that usually takes in traditional statistics of single-season measurements.

2. Materials and methods

2.1. Sampling

The samples were taken in Zagreb, the north-western Croatian city and capital with about 1,000,000 inhabitants. It is situated at the foothill of Medvednica Mountain (1035 m high) in the north and on the banks of the River Sava in the south. The sampling location Ksaverska cesta (Z) (45° 50′ 9.4″ N and 15° 58′ 58.6″ E) is at the north edge of Zagreb in an area characterized by a low-rise neighborhood with moderate traffic and no industry. Between June 2007 and June 2008, 47 consecutive weekly air samples were collected. The other sampling location, Siget (NZ) (45° 46′ 24.7″ N and 15° 59′ 4.5″ E), is at the south edge of Zagreb, the so-called New Zagreb, characterized by a high-rise neighborhood with frequent traffic. Between December 2007 and September 2008, 38 consecutive weekly air samples were collected at this sampling location. Data on ambient temperature, atmospheric pressure, and relative air humidity were obtained from the Meteorological and Hydrological Service of Croatia (*personal communication*).

A high volume ambient air sampler (Bibus, Zagreb, Croatia) was used with a speed pump of approximately 100 L min^{-1} (approximately 144 m^3 per day), which means that for every weekly sample approximately 1000 m^3 of air was sampled. The sampled air volumes were converted to standard conditions ($p = 105$ Pa, $T = 273.15$ K) according to the general gas equation. Besides sample collection on quartz fiber filters (diameter 10 cm), we used polyurethane foam plugs (diameter 5.5 cm, 9.5 cm high) to collect both organochlorines in the gas-phase and adsorb on particulate matter. The PUF disk were placed into a glass container immediately below the carrier with filter; and both were set in a sampling "head" connected to the sampling pump. The head were placed in a container, which provides protection against the dry deposition of coarse particles and precipitation, and eliminates sunlight. Prior to use, polyurethane foam plugs were pre-cleaned in a Soxhlet apparatus with 10% diethyl ether in n-hexane. After collection, the samples were wrapped in aluminum foil and stored at 4 °C.

2.2. Methodology

The quartz fiber filter and PUF plugs were extracted together in the Soxhlet apparatus with 650 mL of 5% diethyl ether in n-hexane for 12 h (4 cycles per hour). The extracts were reduced to approximately 5 mL using a rotary evaporator. The concentrated extracts were treated with sulphuric acid and by adsorption chromatography on a multilayer silica column with 4% diethyl-ether in n-hexane as a solvent (detailed in Herceg Romanić and Krauthacker, 2000, 2003). The cleaned extracts were dried under a nitrogen flow, dissolved in n-hexane and applied on commercial tubes pre-packed with carbon (ENVI-Carb SPE tubes, 3 mL, 0.25 g, Supelco. USA). Afterwards, different solvents were used for elution to achieve separation of non-*ortho* congeners (detailed in Klinčić et al., 2014).

High-resolution gas chromatography with electron capture detector (s) was performed on a *CLARUS 500* chromatograph using two capillary columns (Restek, Bellefonte, PA, USA) simultaneously: (1) 60 m × 0.25 mm, Rtx-5 film thickness of 0.25 μm, and (2) 30 m × 0.25 mm, Rtx-1701 film thickness of 0.25 μm. The column temperature was programmed from 100 °C to 110 °C at 4 °C min^{-1} (isothermally 5 min at 110 °C) and then to 240 °C at 15 °C min^{-1} (50 min isothermally at 240 °C). The carrier gas was nitrogen. The injector and detector temperatures were 250 °C and 270 °C, respectively. For the analysis of three non-*ortho* PCBs, we used gas chromatography mass spectrometry (*Varian 3400* chromatograph) with a *Varian Saturn* II detector using RTX-MS column (Restek, Bellefonte, PA, USA): 30 m × 0.25 mm, film thickness of 0.25 μm. The column temperature was programmed from 60 °C to 200 °C at 20 °C min^{-1} (isothermally 1 min at 60 °C) and then to 260 °C at 2 °C min^{-1} (6 min isothermally at 260 °C). The injector was programmed from 100 °C to 300 °C at 20 °C min^{-1} (isothermally