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Invited paper

Local organochlorine pesticide concentrations in soil put into a global perspective

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ABSTRACT

In this work, agricultural and background soil concentrations of *p,p′*-DDT, *p,p′*-DDE, HCB, α-, β- and γ-HCH from 1993 to 2012 were collected from 73 peer-reviewed publications, and analysed statistically. For the period 2003–2012 and for all chemicals, the mean concentration in agricultural soil is significantly higher than the concentration in background soil. In addition to the statistical analysis, concentrations of *p,p′*-DDT and α-HCH in soils were calculated with a global environmental fate and transport model. A decrease in the mean soil concentration from the first decade to the second was observed with the model, but this decrease is not visible in the measured concentrations, which could result from ongoing use of *p,p′*-DDT and α-HCH Furthermore, modelled background soil concentrations are generally lower than measurements. This implies that background soil may have received *p,p′*-DDT and α-HCH through additional routes not described by the model such as spray drift.

1. Introduction

When the Stockholm Convention on Persistent Organic Pollutants (POPs) came into force in 2004, the use of nine organochlorine pesticides was banned in agriculture in most countries worldwide (UNEP, 2015). An exemption was set for the use of DDT in disease vector control. Three additional organochlorine pesticides, γ-HCH (and also its by-products, α- and β-HCH), chlordecone and pentachlorobenzene were added to the Convention in 2009 and another one, endosulfan, in 2011. Exemptions for endosulfan use on specific crop–pest complexes are listed in the Convention, but except for endosulfan, today there are no legal fresh applications of these pesticides in agriculture.

The effectiveness of the Convention is monitored under the Global Monitoring Plan through ambient air monitoring and human biomonitoring. Air monitoring programs such as the European Monitoring and Evaluation Program (EMEP) (Halse et al., 2011; Tørseth et al., 2012), the Arctic Monitoring and Assessment Program (AMAP) (Hung et al., 2010) and the Integrated Atmospheric Deposition Network (IADN) (Venier and Hites, 2010) provide long-term atmospheric measurements of POPs. Long-term measurements of organochlorine pesticides in human milk (Fürst, 2006; Norén and Meironyté, 2000), bird eggs (Braune, 2007) and aquatic organisms (Lebeuf et al., 2014; Nøstbakken et al., 2015) also exist and help monitor the effectiveness of the Convention on a more regional scale.

Temporal trends of POPs are evaluated in biotic and abiotic environmental media worldwide. Decreasing temporal trends of ΣDDT levels from 1960 until 2008 in human biomonitoring data are visible in the work by Ritter et al. (2011), in which data from Greenland, Northern Europe, Canada and Alaska were evaluated. In wildlife, decreasing concentrations of DDT, HCH and HCB from 1987 to 2007 were observed in beluga whales in Canada (Lebeuf et al., 2014), and of DDT in Swedish farmed salmon over the period 2001–2011 (Nøstbakken et al., 2015). Declining concentrations in the atmosphere are more difficult to confirm. In the Northern Hemisphere, Hung et al. (2010) and Kong et al. (2014) could show a decrease in the air concentration of most POPs (e.g. γ-HCH) from 1993 until 2006; for POPs such as HCB, however, the air concentration over the same period was stable in Southern Norway and in the Arctic, however declining trends were observed at the EMEP station in Kosetice (Šebková et al., 2014). Finally, sediment cores show peak concentrations of ΣDDT in Switzerland (Bogdal et al., 2008), in Chile (Barra et al., 2001) and in South Korea (Barra et al., 2001; Kim et al., 2008) prior to the 1980s. However, in the cores by Barra et al. (2001) and Kim et al. (2008) levels of ΣDDT in

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the sediment core increase again in the last two decades.

Given that the reservoirs of these legacy POPs residing in soil may lead to significant secondary emissions from soil, the extent of the contamination in soil worldwide is important. Many local studies have been conducted over the last few decades in which the soil pesticide contamination was quantified e.g. Aichner et al. (2013); Manirakiza et al. (2003); Zhang et al. (2006), however, long-term soil monitoring is rare. In the study by Meijer et al. (2001) pesticide concentrations in two control plots were measured at intervals of several years from 1944 until 1986 for one plot, and from 1972 until 1990 for another plot. In that study, a local decrease since the 1970s for most organochlorine pesticides was found. On a larger scale, however, no work has yet been reported that shows a global decrease in organochlorine pesticides in soil.

In this work, we aim at collating all publicly available soil measurements of DDT (and its degradation product DDE), the three main isomers of HCH, and HCB from the last two decades and comparing them globally. In this way, the extent of the current global contamination can be assessed for each chemical considered by comparing all the available measurements of the individual chemicals by decade and land type (agricultural and background). To our knowledge, such a global comparison has not yet been performed.

In addition, with the help of the global environmental fate and transport model BETR-Research (MacLeod et al., 2011; Wöhrnschimmel et al., 2012) and the emission inventories of *p,p′*-DDT and α-HCH, we model the long-term time trends of these chemicals globally. We limited the modelling to the pesticides *p,p′*-DDT and α-HCH since it is only for these two pesticides (from the ones included in this study) that both globally and temporally-resolved emission data exist. Modelled concentrations are compared with measurements to understand the distribution of *p,p′*-DDT and α-HCH in several different regions of the world over two decades. Finally, the model-to-measurement comparison will allow us to determine the effectiveness of the Stockholm Convention based on the available soil measurements from 1993 until 2012.

2. Methods

2.1. Measurements

2.1.1. Data collection

Soil concentrations of *p,p′*-DDT, *p,p′*-DDE, HCB, α-, β-, and γ-HCH were collated from 73 peer-reviewed journal publications; these data cover two decades of measurements from 1993 until 2012. The data were sorted by latitude, longitude, date of sampling and land type, namely agricultural and background (including forest and remote sites). Measurements from industrial and rural sites were excluded as it is unclear whether or not pesticides were applied to these land types. The comparison of pesticide concentrations from agricultural and background land is well defined because it distinguishes between land receiving direct pesticide input and land receiving no direct pesticide input. When possible, the arithmetic mean soil concentration was calculated from the raw data per study; in doing so, we set any measurements below the limit of detection/quantification to half the limit of detection/quantification. If a study reported several mean concentrations of measurements taken within the same area, the weighted mean of these mean concentrations was calculated (with the numbers of measurements as weights). A full list of all studies included in this work is available in the Table S1 of the Supplementary Material.

2.1.2. Statistical analysis

All data collected were analysed with the statistical package R (R Development Core Team, 2008). The distribution normality was tested through q–q plot comparison of the measured concentrations with simulated normally distributed data with the same mean and standard deviation as the original data set. In addition, significant differences in soil concentrations among different land types and among different decades were identified with an independent t-test. The significance level was set at $\alpha = 0.05$.

2.2. Modelling

2.2.1. BETR model

Considering the global distribution of the soil measurements, we used the global multimedia environmental fate model BETR-Research. This model has been previously used to describe the fate and transport of a range of pollutants globally (Lamon et al., 2009; Wöhrnschimmel et al., 2012). The model is constructed of 288 grid cells of the size $15^\circ \times 15^\circ$, and includes in each grid cell up to seven different environmental compartments (upper air, lower air, soil, vegetation, freshwater, freshwater sediment and ocean water). Further information on parameterisation and model mechanics is provided by Wöhrnschimmel et al. (2012), and the publicly available version of BETR-Research can be accessed as described by MacLeod et al. (2011).

As a modification to the model, the soil compartment in BETR was divided into two separate compartments for agricultural soil and background soil. The surface area of agricultural soil was parameterised according to the percentage of cultivated land in each grid cell as defined by the Harmonized World Soil Database V1.2 from the FAO soil portal (Fischer et al., 2008). All chemical exchange processes connecting soil to air and water are identical to the original soil compartment in the model.

2.2.2. Substance property data

The physicochemical property data for *p,p′*-DDT were obtained from Schenker et al. (2008) and for α-HCH from Wöhrnschimmel et al. (2012) and are provided in Table S3 of the Supplementary Material.

2.2.3. Chemical emissions

The *p,p′*-DDT emission scenario for the years from 1941 until 2015 was set up according to the emission scenario established by Schenker et al. (2008). However, in the work by Schenker et al. the emissions were set up as yearly zonal emissions as required by their zonally averaged environmental fate model (CliMoChem), which provides no emission resolution in west–east direction as required for BETR. Resolution according to the grid cells of BETR was obtained by including information from the annual continental DDT usage inventory set up by Wegmann (2004). The emission rate in each latitudinal zone from Schenker et al. (2008) was first subdivided into contributions from each continent and then these continental emissions were further broken down according to the percentage of agricultural soil per grid cell.

The emission inventory for α-HCH was set up by Wöhrnschimmel et al. (2012) for use in BETR, based on work by Li et al. (2000) for the period between 1945 until 2015. However, in the version of BETR used by Wöhrnschimmel et al. (2012), no distinction was made between agricultural and background soil. Therefore, similar to *p,p′*-DDT, the emissions were adjusted according to the percentage of agricultural soil in each grid cell. For both *p,p′*-DDT and α-HCH, fractions of 10% and 90% were assumed for emissions to air and soil, respectively (Linders et al., 2000). Finally, as assumed by Wöhrnschimmel et al. (2012), emissions in the northern hemisphere were assumed to occur in March and April; in the southern hemisphere, emissions were assumed to take

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