Environmental Contamination by Obsolete Pesticide Stockpiles in Turkey: Case Study for Derince Province

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Introduction

Obsolete pesticides are chemicals that could not be used or are no longer needed for their intended use [1]. Hence, the obsolete pesticides (OPs) problem is not due to use of these chemicals but it is due to associated risks stemming from their improper storage and inadequate management. Chlorinated pesticides such as HCHs and DDTs were banned in Turkey in 1980s. As a signatory to Stockholm Convention (www.pops.int), Turkey is obliged to fulfill all requirements of the Convention including taking necessary measures such as management of the stockpiles. In the 1st National Implementation Plan (NIP-1) [2] of Turkey for Stockholm Convention POPs, it was stated that there were only stocks of HCHs and DDTs. According to NIP-1, DDT stocks were located in Ankara and Gaziantep provinces while HCHs stocks were in Derince county of Izmit province as well as Gaziantep province. A total of 11060 kg of DDTs were disposed by Izaydas Company in Izmit province during 2008-2009 and hence, according to 2nd National Implementation Plan (NIP-2) [3] report of Turkey for Stockholm Convention POPs, as of 2015, around 3000 t of HCHs is the only obsolete organochlorine pesticide stockpile remaining in Turkey. The aforementioned HCH stockpile is located in Sirintepe ground of Derince, which is a county in Kocaeli province. It was produced for industrial purposes and currently is stored in Merkim Industrial Products Inc., Warehouse in 50 kg plastic bags and barrels in white powder form. This last pesticide stock left in the country had been planned to be disposed until 2017 as a component of "Elimination of POPs Stocks and Reducing Releases Project" financed by Global Environment Facility (GEF) [4] but to our best knowledge, it is still in the warehouse of Merkim Company.

The initial aim of the study was to assess the spatial variability of HCHs contamination of soil nearby Sirintepe ground. However, analysis of the soil samples showed that DDTs were also at higher concentrations in the area. Personal communication to Ministry of Environment and Urbanization revealed that the warehouse where HCHs stockpile is kept was used as storage for several types of chemicals that were used in several industrial applications of Merkim Company. In the current study, we present spatial distributions of HCHs and DDTs in soil collected from nearby and surrounding areas of Merkim HCHs stockpile warehouse in 2018.

Materials and methods

The study area is the surroundings of OCP stockpile warehouse that is located in Derince, a county in Kocaeli province in Turkey. The site is located in a water front industrial area on the north side of a long bay on the eastern end of the Marmara Sea approximately 500 m from the waterfront. Twenty three soil samples were collected from nearby (within 20 m) and surrounding areas (0.4-3 km) of the stockpile warehouse in 2018. Equal portions of 3 replicates (over a ~1 m^2 area) collected from the upper 5 cm of the soil surface were combined and homogenized for each sampling site. Then, samples were sieved through a 2.0 mm mesh sieve to remove large particles/stones and organic debris. Approximately 5 and 10 g of soil samples were used for chemical analysis and moisture content determination, respectively.

Soil samples (5-10 g) were stored overnight by adding approximately 40 ml of 1:1 acetone:hexane mixture. Then, they were extracted using an ultrasonic bath for 30 min. The extracts were exchanged into hexane and their volumes were decreased to 2 mL by means of a rotary evaporator and a high purity N_2 stream. All samples were cleaned up using a column containing 0.5 g Florisil. Before the introduction of the sample, the column was rinsed with 10 ml hexane. OCPs were eluted with 8 ml hexane and 12 ml ethyl acetate. The solvent of final extracts was exchanged into hexane and the volume was reduced to 1 mL using a stream of N_2.

Before analysis, 20 ng of an internal standard (PBDE-77, 3,30,4,40-tetrabromodiphenyl ether) was added to samples. Samples were analyzed for OCPs with an Agilent 6890N gas chromatograph (GC) equipped with a mass selective detector (Agilent 5973 inert MSD). First, samples were scanned using electron impact ionization (EI). Three DDT metabolites were identified in addition to DDDs and DDEs using spectral library searches: 4,4'-dichlorobenzophenone (4,4'-DBP), 1-chloro-2-[2-chloro-1-(4-chlorophenyl)ethenyl]-benzene (o-p'-DDMU), and 1,1-bis(4-chlorophenyl)-2-chloroethene (p-p'-DDMU). These identified compounds were analyzed in EI mode and their concentrations were determined semi-quantitatively using average response factors of DDTs, DDDs and DDEs. Remaining compounds were analyzed in negative chemical ionization (NCI) mode.. The capillary column used for analysis was HP5-MS (30 m, 0.25 mm, 0.25 µm). Helium was the carrier gas and high-purity methane was the reagent gas for NCI. All OCPs were analyzed in selected ion monitoring mode (SIM). Compounds were identified based on their retention times and target and qualifier ions and were quantified using the internal standard calibration procedure.

Results and discussion

Soil OCP concentrations at surrounding sampling sites (located at 0.4-3 km from the warehouse) ranged between 0.4-9 µg/kg and 4.2-2226 µg/kg (dry weight) for ΣHCHs and ΣDDXs, respectively. Concentrations at nearby sites (located within 20 m of the warehouse) were substantially higher and they ranged between 74-39619 µg/kg and 1592-30419 µg/kg for ΣHCH and ΣDDX, respectively. However, OCP concentrations declined sharply with the horizontal distance from the warehouse indicating different profiles at different transects (Figure 1). Even though average levels of ΣHCH and ΣDDX were similar (12255 and 14342 µg/kg, respectively) at nearby sites, the decline with the distance was much sharper for ΣHCHs.

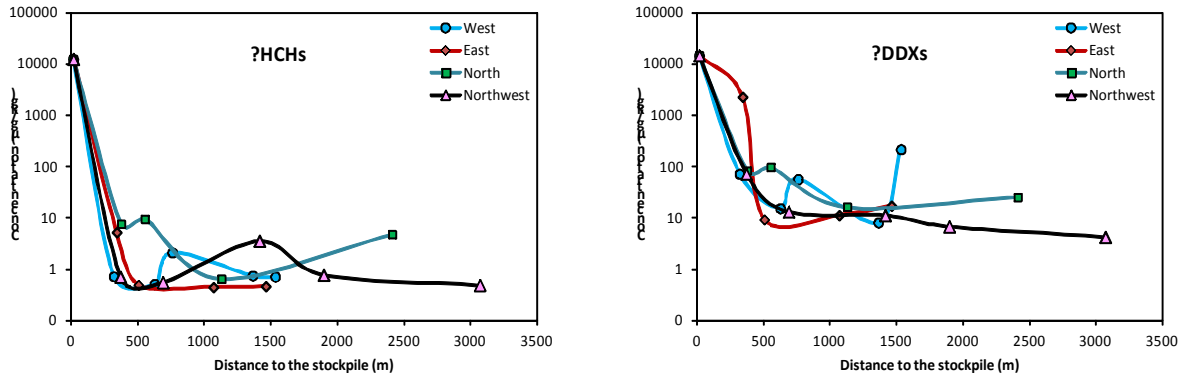

Figure 1. Variation of HCH and DDX concentrations with horizontal distance to the stockpile warehouse.

Generally higher OCP levels were measured at sites located at northwest of the warehouse since the emissions from stockpile are carried with the predominant winds from southeast (Figure 2).

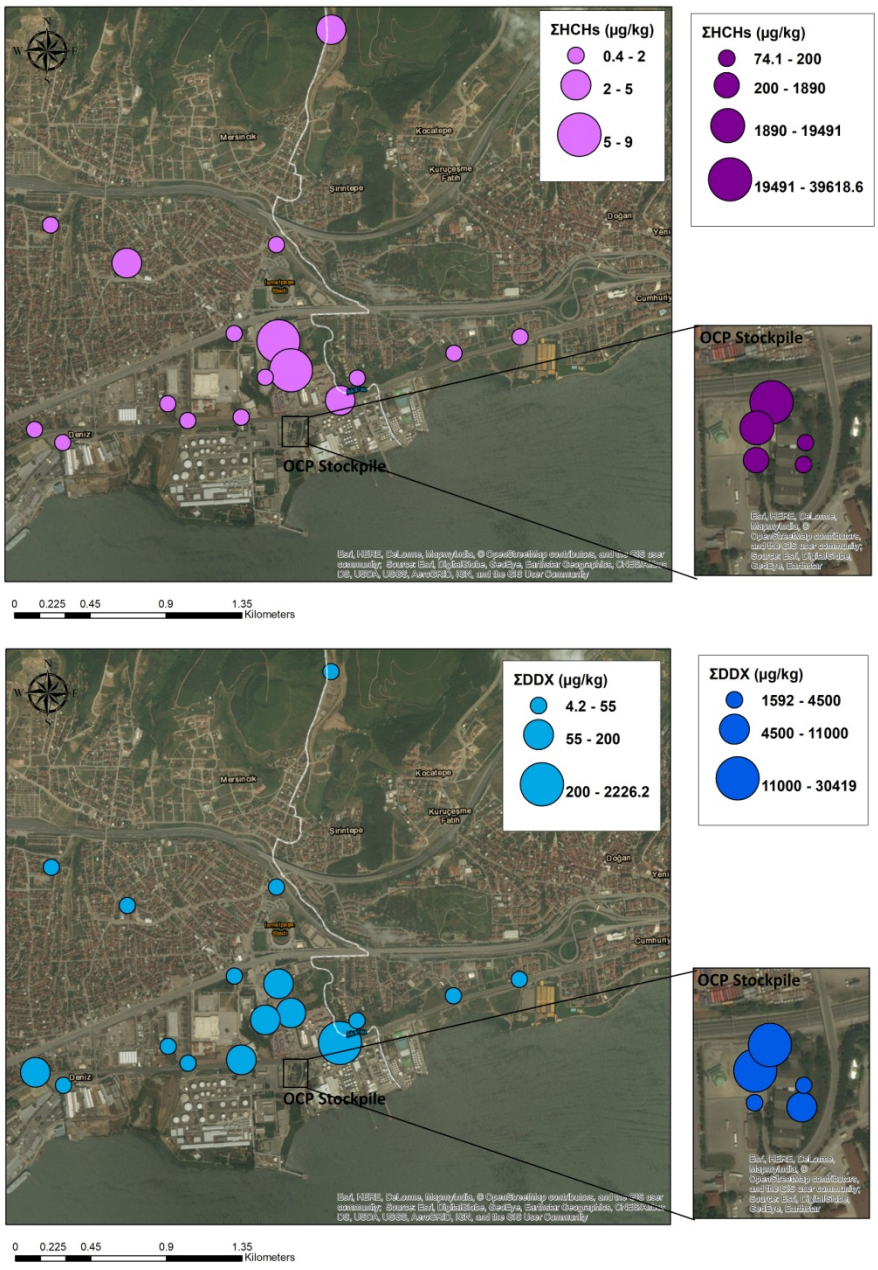

Figure 2. Spatial variation of HCH and DDX concentrations in the study area.

The stockpile has been generally reported to consist primarily of γ-HCH and other HCH congeners but with possibility of some DDT residues. There is some uncertainty regarding to the origin of this material. The 2010 NIP [2] indicates that this material was commercial lindane imported by Agricultural Protection Chemicals

Corporation for agricultural purposes in early 1980s. Other reports suggest that this material was accumulated during the production of DDT and lindane at nearby production facility during 1983-85 when both these POPs pesticides were banned in Turkey[4]. OCP compositions of soil samples collected in the present study were presented in Figure 3. HCH and DDT profiles were generally similar for nearby and surrounding sites. The HCHs were dominated by β-HCH followed by δ-HCH, α-HCH and γ-HCH as minor components. DDTs were dominated by *p*-*p*'-DDT and its metabolites (*p*-*p*'-DDE, *p*-*p*'-DDD) followed by *o*-*p*'-DDT and its metabolites (*o*-*p*'-DDE, *o*-*p*'-DDD). Additionally identified and semi-quantitatively determined metabolites (4,4'-DBP, o-p'-DDMU and p-p'-DDMU) were detected in majority of the samples with comparable levels to other metabolites. The OCP material stored in the warehouse could not be sampled in the present study. However, composition of nearby soil samples could be assumed to be representative of the obsolete OCPs stored in the warehouse. Technical DDTs was a mixture of four forms, mainly including p,p′-DDT (65−85%), o,p′-DDT (15−21%), p,p′-DDE (∼5%) and p,p′-DDD (<5%)[5] while lindane mainly consist of γ-HCH, and main components of technical HCH are γ-HCH and α-HCH.. Based on the soil OCP compositions observed in the present study, it could be suggested that the stockpile material is mainly consisting of byproducts that were accumulated during the production of DDT and lindane at the nearby production facility rather than being of technical HCH and DDT mixtures.

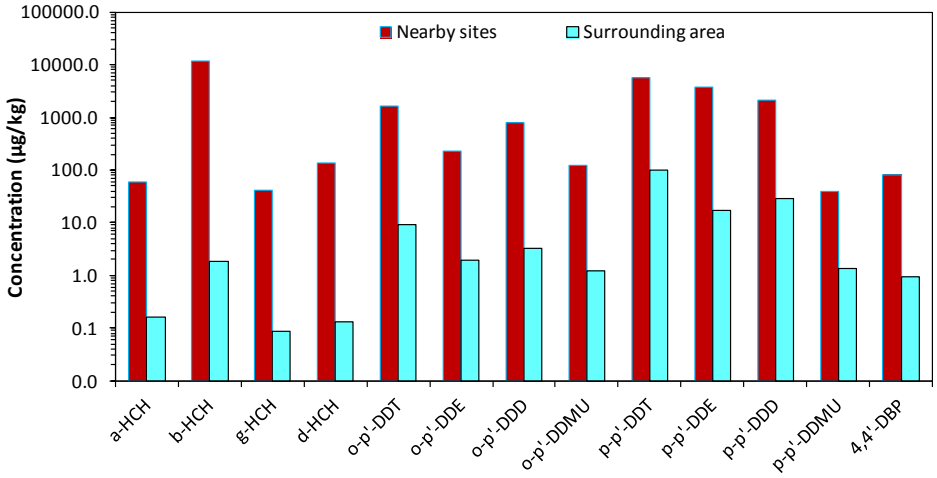

Figure 3. Composition of soil samples

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