HUMAN HEALTH RISK ASSESSMENT FOR ENVIRONMENTAL EXPOSURE TO ORGANOCHLORINE COMPOUNDS IN THE CATALAN STRETCH OF THE EBRO RIVER, SPAIN

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Introduction

Humans are exposed to organochlorine compounds (OCs) mainly through occupational activity, environment, and dietary intake. Anthropogenic activities may generate OCs pollution in air, soil, and water. The Ebro River basin constitutes an important agricultural area in the South of Tarragona Province (Catalonia, Spain). Among other anthropogenic activities also found in that area, certain industries and sewage treatment facilities are of notable concern taking into account the potential adverse impacts on water quality and local soils. In fact, these activities generate a strong impact that can have negative repercussions on soils and river water. The existence of potentially toxic chemicals, such as OCs, metals, and radionuclides in water, sediments, and soils has been reported in the Flix reservoir. Important concentrations of OCs had been detected in the lower part of the Ebro River. Historically, the Flix reservoir has been receiving residues dumped by a chlor-alkali plant[1-3]. The aim of the study was to assess the human health risks derived from the environmental exposure to OCs through soils and drinking water for the population living in the Catalan stretch of the Ebro River and its Delta.

Material and methods

Sampling

During spring of 2006, surface soil samples were collected in 10 different villages/towns located in the riparian zone of the Ebro River in Catalonia. Samples consisted of a composite of 3 subsamples collected at: a) the village centre, b) a recreational area, and c) the riverside. Since high OC concentrations were preliminarily detected in Flix village, in autumn 2006, 5 additional individual surface soils were again sampled. The sampling methodology was previously reported[4, 5]. Moreover, in spring and autumn of 2006, 10 municipal tap water samples from public fountains were collected in clean amber glass bottles, according to the methods of the American Public Health Association[6]. The locations of sampling were divided into two zones: North and South, near and down the Flix chlor-alkali plant, respectively.

Analytical procedure

α-, β-, γ- and δ-hexachlorocyclohexanes (HCHs), hexachlorobenzene (HCB), pentachlorobenzene (PeCB), environmental markers PCB-congeners No. 28, 52, 101, 118, 138, 153 and 180, o,p' and p,p'-DDE, DDD, and DDT were extracted from soils and analyzed by GC-ECD (Agilent Technologies, HP-6890N, Palo Alto, CA, USA)[7]. For drinking water, suspended particles were retained with glass microfibre filters. Those present in the dissolved phase were concentrated by solid phase extraction (C18 disk). The composition of these compounds was analyzed by GC-ECD. A capillary DB5 column was used for all analyses[3].

Data analysis

For calculations, when a specific OC showed a value under the limit of detection (LOD), the concentration was assumed to be one-half of that LOD (ND = 1/2 LOD). A Self-Organizing Map (SOM) procedure, developed by Kohonen[8], was applied to accomplish two objectives: 1) to establish pattern similarities between OCs and sampling

points, and 2) to identify potential hotspots of pollution. SOM is a powerful tool to classify large amounts of data, being considered as a successor of classic statistical tools.

Human health risk assessment

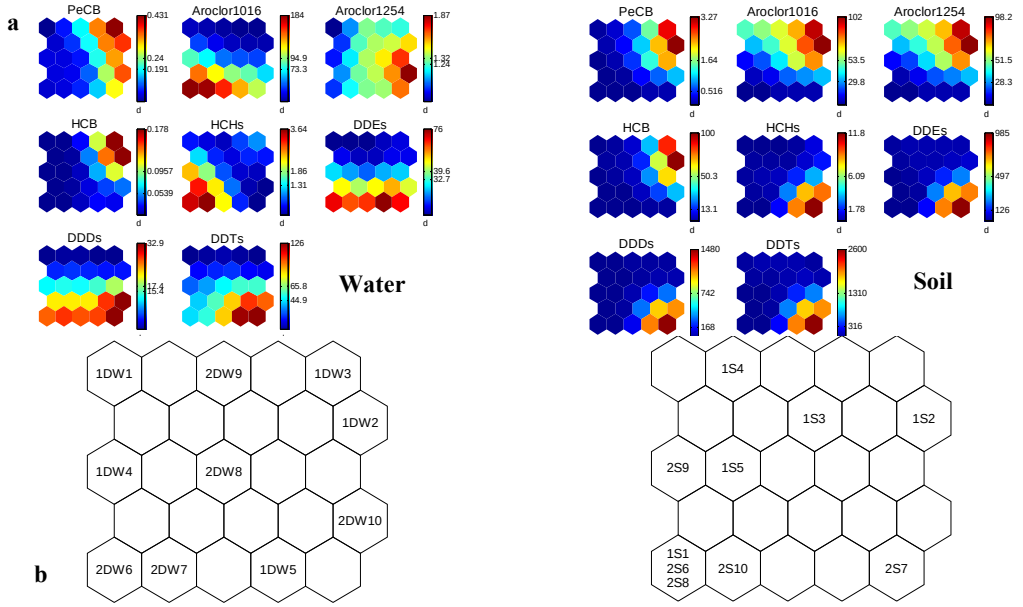
Human health risks potentially associated to the ingestion and dermal absorption of OCs through soil particles and water were assessed. Daily environmental exposure to OCs was evaluated for adults. Mean OC concentrations and standard deviations were used. Monte Carlo simulations were applied separately to calculate probabilistic carcinogenic and non-carcinogenic risks[5]. The criteria used for calculations were taken from the US EPA, as well as from recent studies[5, 9-11].

Results and discussion

OC concentrations

The highest concentrations of OCs in soils corresponded to DDTs, DDDs and DDEs (1.03; 1.56 and 2.74 µg/kg dw, respectively). The differences between sampling areas were not for HCHs (P>0.05). However, the levels of pentachlorobenzene, HCB and ∑PCBs (Aroclor 1016 and Aroclor 1254) were significantly higher in the North area. In turn, DDTs, DDDs and DDEs were significantly higher in the South area (P<0.05). The results in the South area could be expected. It is well known the high persistence and bioaccumulation/bioconcentration properties of DDTs and its two main metabolites, DDEs and DDDs, compounds that were frequently used for the control of plagues in that agricultural area[12]. In Spain, restrictions in DDT use were established in 1977. Notwithstanding, DDT use is still allowed as an intermediate in the production of dicofol in Monzón (in Ebro River basin, North-East of Spain) since 1987[13]. For water, only HCB concentrations were higher in the North area (P<0.05). These findings could be due to the relatively higher concentrations found in the Flix village (North area), where a chlor-alkali plant is located.

Figure 1: Self Organizing Map (SOM) for the levels of OC compounds in soil (S) and drinking water (DW) samples: Component planes (a) and Kohonen's map (b). *Zones*: 1: North and 2: South. *Location*: 1: Riba-Roja; 2: Flix; 3: Ascó; 4: Garcia; 5: Móra d'Ebre; 6: Benifallet; 7: Xerta; 8: Tortosa; 9: Amposta; 10: Deltebre.



Kohonen's SOM and component planes for the levels of the analyzed compounds in 10 sampling points are depicted in Figure 1. The highest and lowest concentrations (marked in red and blue, respectively) of the analyzed elements are depicted in Figure 1a. For soils, Flix village (1S2) showed the highest concentrations of PeCB, ∑PCBs and HCB, while the highest HCH, DDT, DDD and DDE levels were found in the village of (2S7) (Figure 1b). For drinking water, the South area presented the highest DDTs, DDDs and DDEs concentrations (2DW6-10). In general terms, the current OC levels in soils and water are similar to those found in recent surveys performed in Spanish regions, as well as in rural and urban areas[14, 15]. In comparison to the threshold guidelines of OCs in soils and drinking water established by the Spanish legislation[16-17] and the US EPA Preliminary Remediation Goals[18], the levels of the analyzed compounds are inside the safety range for a residential use of soils and municipal tap water.

Human health risks- non-cancer risks

The non-carcinogenic risks derived from exposure to OCs through soils and water were assessed by calculating the hazard quotient (HQ). The HQ was calculated by comparing the environmental predicted exposure with the available reference dose (RfD) for each OCs[18, 19]. When HQ exceeds the unity, there may be concern for potential human health effects caused by non-carcinogenic substances. The HQs for each chemical are presented in Table 1. In general terms, HQs through dermal exposure were higher than those through ingestion.

Table 1: Hazard Quotients (HQ) and carcinogenic risks (CR) for predicted oral and dermal exposure to OCs from soils and drinking water. Results are expressed as mean ± standard deviation.

		Oral		Dermal	
		HQ	CR	HQ	CR
SOIL	PeCB	$2.4\cdot10^{-7} \pm 1.1\cdot10^{-3}$	-	$1.1\cdot10^{-4} \pm 4.2\cdot10^{-4}$	-
	Aroclor 1016	$9.8\cdot10^{-5} \pm 6.8\cdot10^{-5}$	$6.6\cdot10^{-6} \pm 1.8\cdot10^{-5}$	$4.7\cdot10^{-2} \pm 1.3\cdot10^{-1}$	$6.6\cdot10^{-6} \pm 1.8\cdot10^{-5}$
	Aroclor 1254	$3.4\cdot10^{-4} \pm 7.5\cdot10^{-4}$	$6.3\cdot10^{-6} \pm 1.8\cdot10^{-5}$	$1.6\cdot10^{-1} \pm 4.6\cdot10^{-1}$	$6.3\cdot10^{-6} \pm 1.8\cdot10^{-5}$
	HCB	$6.8\cdot10^{-7} \pm 2.3\cdot10^{-5}$	$7.2\cdot10^{-6} \pm 4.0\cdot10^{-5}$	$5.6\cdot10^{-3} \pm 3.1\cdot10^{-2}$	$7.2\cdot10^{-6} \pm 4.0\cdot10^{-5}$
	∑ HCHs	$4.9\cdot10^{-7} \pm 1.1\cdot10^{-6}$	$6.4\cdot10^{-7} \pm 1.8\cdot10^{-5}$	-	$6.4\cdot10^{-7} \pm 1.8\cdot10^{-6}$
	∑ DDEs	-	$2.6\cdot10^{-6} \pm 9.4\cdot10^{-5}$	-	$2.6\cdot10^{-6} \pm 9.4\cdot10^{-6}$
	∑ DDDs	-	$1.9\cdot10^{-6} \pm 9.2\cdot10^{-5}$	$4.0\cdot10^{-3} \pm 1.9\cdot10^{-2}$	$1.9\cdot10^{-6} \pm 9.2\cdot10^{-6}$
	∑ DDTs	$5.7\cdot10^{-5} \pm 5.6\cdot10^{-4}$	$5.7\cdot10^{-6} \pm 2.8\cdot10^{-5}$	$3.3\cdot10^{-2} \pm 1.7\cdot10^{-1}$	$5.7\cdot10^{-6} \pm 2.8\cdot10^{-5}$
WATER	PeCB	$9.9\cdot10^{-6} \pm 4.2\cdot10^{-5}$	-	$9.2\cdot10^{-6} \pm 2.7\cdot10^{-5}$	-
	Aroclor 1016	$1.3\cdot10^{-4} \pm 3.9\cdot10^{-4}$	$1.5\cdot10^{-8} \pm 2.9\cdot10^{-8}$	$3.8\cdot10^{-4} \pm 9.5\cdot10^{-4}$	$2.6\cdot10^{-7} \pm 4.0\cdot10^{-7}$
	Aroclor 1254	$2.4\cdot10^{-3} \pm 6.0\cdot10^{-3}$	$2.3\cdot10^{-6} \pm 3.7\cdot10^{-6}$	$7.3\cdot10^{-3} \pm 1.7\cdot10^{-2}$	$1.4\cdot10^{-6} \pm 1.9\cdot10^{-6}$
	HCB	$2.7\cdot10^{-6} \pm 1.2\cdot10^{-5}$	$7.8\cdot10^{-8} \pm 2.1\cdot10^{-7}$	$6.5\cdot10^{-6} \pm 2.3\cdot10^{-5}$	$2.0\cdot10^{-7} \pm 4.8\cdot10^{-7}$
	∑ HCHs	$1.8\cdot10^{-5} \pm 6.3\cdot10^{-5}$	$1.3\cdot10^{-6} \pm 2.8\cdot10^{-6}$	$2.4\cdot10^{-6} \pm 7.3\cdot10^{-6}$	$1.1\cdot10^{-7} \pm 2.1\cdot10^{-7}$
	∑ DDEs	-	$4.1\cdot10^{-8} \pm 7.7\cdot10^{-8}$	$1.0\cdot10^{-5} \pm 2.6\cdot10^{-5}$	$1.6\cdot10^{-7} \pm 2.7\cdot10^{-7}$
	∑ DDDs	-	$6.4\cdot10^{-8} \pm 1.1\cdot10^{-7}$	-	$1.1\cdot10^{-7} \pm 1.4\cdot10^{-7}$
	∑ DDTs	$5.4\cdot10^{-6} \pm 2.2\cdot10^{-5}$	$2.1\cdot10^{-8} \pm 4.8\cdot10^{-8}$	$2.4\cdot10^{-5} \pm 7.5\cdot10^{-5}$	$9.7\cdot10^{-8} \pm 2.1\cdot10^{-7}$

The maximum HQ through soil and dermal exposure corresponded to Aroclor 1254, with a level of 0.16 ± 0.46 (Table 1). This high variability in HQ would be due to the wide range of the concentrations of PCBs 101, 118, 138, 153 and 180 found in soils, especially in the Northern area ($3.14\cdot10^{-2} \pm 9.68\cdot10^{-2}$ µg/kg dw), as well as the hypothesis that the sum of PCBs would present the same toxicity than that of Aroclor 1254 (mixture of different PCBs). For oral exposure, the maximum HQ corresponded to Aroclor 1254 and 1016 (mixture of different PCBs with PCB 28 and 52) in water, with levels between $2.4\cdot10^{-3} \pm 6.0\cdot10^{-3}$ and $1.3\cdot10^{-4} \pm 3.9\cdot10^{-4}$, respectively. For soils and water, all HQ

values were also below the safety level (1.0). Consequently, human environmental exposure to soils and water was not found to be a pathway of concern for OCs. Similar results were also reported in urban area in China and Pakistan when organochlorine pesticides were applied in areas for agricultural yield and/or sanitation[14, 15].

Human health risks- cancer risks

The cancer risk was calculated by multiplying the slope factor (SF) by the lifetime predicted exposure. The carcinogenic risks through oral intake, dermal absorption of OCs from soils, and water are shown in Table 1. Slope factors through ingestion and dermal absorption of OCs have been established for all the elements[18], with the exception of PeCB. The cancer risks by dermal contact and ingestion were lower or similar to 10^{-6}. Although obviously to get the maximum protection for human health from the potential carcinogenic effects due to OCs exposure in drinking water and soils, the concentration of this element should be zero, lifetime risks of 10^{-6} to 10^{-4} are considered as acceptable for environmental carcinogens. For instance, cancer risk for ∑HCH in drinking water for oral exposure was $1.3 \cdot 10^{-6} \pm 2.8 \cdot 10^{-6}$. For cancer risk calculations, ∑HCH was assumed to be as toxic as α-HCH, the most cancerigen compound (worst-case scenario). For the remaining compounds, values lower than 10^{-6} were found. The environmental cancer risk to OCs exposure in the Catalan Stretch of the Ebro River Basin was also lower than the levels detected in Pakistan or in Nebraska, USA[15,20]. In general terms, OC environmental exposure through tap water and soils in the Ebro River basin should not mean additional significant non-carcinogenic and carcinogenic risks for the population living in the neighbourhood.

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