

# HUMAN OCCUPATIONAL AND RESIDENTIAL EXPOSURES TO DECHLORANE PLUS AT A HIGHLY CONTAMINATED SITE IN CHINA

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## Introduction

Dechlorane Plus (DP) are chlorinated flame retardants and used in commercial polymer products such as electrical wires and cables, plastic roofing materials, and connectors used in computers and televisions. DP are high volume production chemicals and are listed on the Canadian Domestic Substances List (DSL). DP are potentially persistent and bioaccumulative compounds (1, 2), and are resistant to photolysis and biodegradation. Recently, the long-range atmospheric transport potential of DP was reported by Möller et al. (3), who detected DP in the air and seawater sampled from the Arctic and Antarctica. These results suggest that DP have typical characteristics of persistent organic pollutants (POPs): persistence, bioaccumulation, and long-range transfer potential.

Recently, we reported very high concentrations of DP were detected in air, soil and sediment samples collected from a new manufacturing facility in China(4). These results spurred our efforts to examine DP concentrations in food and biota, and to assess occupational and residential exposures in this region.

## Materials and methods

A total of nine species of vegetation and eight species of aquatic organism samples were concurrently collected from Huai'an in Jiangsu province of China in May, 2010. Wild and cultured aquatic species were collected from Beijing-Hangzhou Grand Canal and a farm pond.

The leaves of vegetables and moss, grains, muscle of fish, and soft tissues of freshwater prawn and river snail were ground and approximately 5 g of the sample was mixed with dried anhydrous sodium sulfate and Soxhlet-extracted. All samples were analyzed using a GC-MS (PolarisQ, Thermo) equipped with a DB-5 MS capillary column (J&W Scientific, Folsom, CA).

## Results and discussion:

Concentrations of DP isomer in vegetables and moss are given in Table 1. The total DP ( $\sum$ DP) concentrations in the collected vegetables varied from 15.9 to 67.6 ng g<sup>-1</sup> wet wt. The average concentrations of  $\sum$ DP were 67.6, 60.2, 40.8, 35.7, and 15.9 ng g<sup>-1</sup> for green onion, pakchoi cabbage, lettuce, garlic chive, and field mustard, respectively. In the willow moss collected from the canal, syn-DP was only detected with an average of 0.300 ng g<sup>-1</sup> wet wt, at concentrations 53-225 times lower than in the vegetables.  $\sum$ DP in the leaves of vegetables may originate from atmospheric wet/dry deposition and soil-root-leaf transfers. The absorption from water is the only exposure route for the willow moss living in water. The pathways of soil-root-leaf transfer and absorption from water for the vegetables and willow moss were limited for the reason that very low water solubilities of DP isomers (207 and 572 ng L<sup>-1</sup>). Higher concentrations of DP in the vegetables compared to willow moss are attributed to the direct contact from atmospheric wet/dry deposition.

The average concentrations of  $\sum$ DP were 1370, 194, and 6.28 ng g<sup>-1</sup> lipid wt for common wheat, maize, and soybean, respectively. The corresponding concentrations based on wet weight are 30.4, 8.45, and 1.12 ng g<sup>-1</sup> wet weights.  $\sum$ DP concentrations in vegetables and grains depend on the sampling distance from the facility. There exists a significant negative correlation between  $\sum$ DP concentrations in vegetables and grains with distance from the facility ( $r = -0.97$ ,  $p < 0.001$ ). This result implies that the DP in vegetables and grains originated from the atmospheric transport from the facility.

$\sum$ DP concentrations in the wild aquatic species varied from 319 to 1740 ng g<sup>-1</sup> lipid wt. The highest concentration was found in common carp (1740 ng g<sup>-1</sup>), followed by northern snakehead (1510 ng g<sup>-1</sup>), crucian carp (669 ng g<sup>-1</sup>), river snail (583 ng g<sup>-1</sup>), bleaker (574 ng g<sup>-1</sup>), shrimp (406 ng g<sup>-1</sup>), and loach (319 ng g<sup>-1</sup>).  $\sum$ DP concentrations (829  $\pm$  560 ng g<sup>-1</sup> lipid wt) in this study are extraordinarily similar to those (737  $\pm$  863 ng g<sup>-1</sup> lipid wt) in aquatic species from an e-waste recycling site in China(5).

These concentrations are several orders of magnitude greater than those in aquatic species from urban-industrial rivers in Korea and the Great Lakes. Kang et al.(6) measured DP in fish samples ( $36.1 \pm 35.3 \text{ ng g}^{-1}$  lipid wt) collected from 15 Korean urban sites. The  $\sum$ DP concentrations in aquatic species from the Great Lakes are markedly lower than those from Korean urban areas, e-waste recycling site, and manufacturing facility in this study. Hoh et al.(7) reported that DP concentrations ranged  $0.14\text{--}0.91 \text{ ng g}^{-1}$  lipid wt in archived fishes from Lake Erie. Tomy et al.(8) reported the DP concentrations in plankton, mussels, and fishes from Lake Winnipeg ( $0.035\text{--}0.816 \text{ ng g}^{-1}$  lipid wt) and Lake Ontario ( $0.015\text{--}4.415 \text{ ng g}^{-1}$  lipid wt). Ismail et al.(9) analyzed the DP in lake trout collected from Lake Ontario between 1979 and 2004 and found the concentrations in the range  $2.3\text{--}7.2 \text{ ng g}^{-1}$  lipid wt. Shen et al.(10) reported that DP concentrations varied from  $0.061\text{--}2.4 \text{ ng g}^{-1}$  lipid wt in fishes from the Great Lakes.

Table 1. Concentrations (mean $\pm$ standard error) of DP in vegetables ( $\text{ng g}^{-1}$  wet wt), moss ( $\text{ng g}^{-1}$  wet wt), grain ( $\text{ng g}^{-1}$  lipid wt), and fish ( $\text{ng g}^{-1}$  lipid wt),  $f_{\text{syn}}$ , and number, distance (km) from the facility, and lipid content (mean $\pm$ standard error) of samples collected from surrounding environment near the facility.

sample	<i>n</i>	lipid (%)	<i>syn</i> -DP	<i>anti</i> -DP	$\sum$ DP	$f_{\text{syn}}$	distance
vegetables and moss							
green onion	12		19.2 $\pm$ 3.8	48.3 $\pm$ 1.6	67.6 $\pm$ 5.1	0.28	0.74
pakchoi cabbage	15		19.4 $\pm$ 3.2	40.8 $\pm$ 0.8	60.2 $\pm$ 2.5	0.32	0.73
lettuce	8		11.0 $\pm$ 1.8	29.8 $\pm$ 0.1	40.8 $\pm$ 1.6	0.27	0.71
garlic chive	18		9.20 $\pm$ 1.83	26.5 $\pm$ 0.1	35.7 $\pm$ 1.7	0.26	0.72
field mustard	10		5.35 $\pm$ 0.92	10.6 $\pm$ 0.6	15.9 $\pm$ 1.5	0.34	0.92
willow moss	7		0.300 $\pm$ 0.119	<0.135	0.30 $\pm$ 0.12	0.97	0.69
grains							
common wheat	50	2.22 $\pm$ 0.27	622 $\pm$ 116	745 $\pm$ 81	1370 $\pm$ 183	0.45	0.82
maize	40	4.36 $\pm$ 0.89	36.1 $\pm$ 4.5	158 $\pm$ 33	194 $\pm$ 34.8	0.19	1.4
soybean	40	17.8 $\pm$ 2.1	3.91 $\pm$ 2.14	2.37 $\pm$ 0.71	6.28 $\pm$ 2.70	0.62	2.2
wild aquatic species							
common carp	8	1.32 $\pm$ 0.42	511 $\pm$ 104	1230 $\pm$ 10	1740 $\pm$ 92	0.29	3.9
snakehead	3	0.95 $\pm$ 0.44	868 $\pm$ 151	640 $\pm$ 30	1510 $\pm$ 120	0.58	3.9
crucian carp	9	1.26 $\pm$ 0.84	170 $\pm$ 49	499 $\pm$ 29	669 $\pm$ 72	0.25	3.9
river snail	28	0.60 $\pm$ 0.02	105 $\pm$ 26	477 $\pm$ 14	583 $\pm$ 37	0.18	0.73
bleeker	12	1.03 $\pm$ 0.37	490 $\pm$ 91	83.2 $\pm$ 28.1	574 $\pm$ 64	0.86	3.9
shrimp	15	1.03 $\pm$ 0.27	79.8 $\pm$ 37.3	326 $\pm$ 70	406 $\pm$ 105	0.20	3.9
loach	7	2.06 $\pm$ 1.10	81.8 $\pm$ 21.9	237 $\pm$ 8	319 $\pm$ 18	0.26	3.9
cultured crucian carp							
liver	5	1.80 $\pm$ 0.15	109 $\pm$ 22.9	490 $\pm$ 10	599 $\pm$ 13	0.18	1.1
ovary	5	1.93 $\pm$ 0.32	96.0 $\pm$ 19.1	108 $\pm$ 15	204 $\pm$ 30	0.47	1.1
muscle	5	1.16 $\pm$ 0.24	44.8 $\pm$ 15.9	108 $\pm$ 7	153 $\pm$ 14	0.29	1.1
gill	5	1.56 $\pm$ 0.33	15.1 $\pm$ 2.0	<0.135	15.1 $\pm$ 2.0	0.99	1.1

To identify the distribution of DP in fish, the concentrations in the liver, ovary, muscle, and gill tissues of cultured crucian carp were measured and presented in Table 1.  $\sum$ DP concentrations in the tissues of cultured crucian carp exhibited the following order from high to low values: liver ( $599 \text{ ng g}^{-1}$ )>ovary ( $204 \text{ ng g}^{-1}$ )>muscle ( $153 \text{ ng g}^{-1}$ )>gill ( $15.1 \text{ ng g}^{-1}$ ). There was no correlation between DP concentrations and lipid contents of the tissues. High concentrations in the liver may be attributed it being a blood and plasma-enriched tissue. Low concentrations in the gill suggest that accumulation via the gill from river water was limited in fish.

In comparison to the wild crucian carp ( $669 \text{ ng g}^{-1}$ ), the concentration ( $153 \text{ ng g}^{-1}$ ) is approximately 5 times lower in the muscle of cultured species. DP can accumulate in wild species via preying on plankton and invertebrates as well as bioconcentration from water. However, for cultured species, bioconcentration from river

water is the probably only accumulation route. This may be the reason that DP concentrations in the wild species are much higher than cultured species.

To evaluate human exposure to DP isomers via dietary intake, dermal contact, and inhalation from the DP manufacturing facility, estimated exposure doses (EED) for workers, residents, and children were calculated based on the previous study(4). The total EEDs were estimated as  $3.00 \times 10^{-4}$ ,  $2.96 \times 10^{-4}$ , and  $2.96 \times 10^{-4}$  mg kg<sup>-1</sup>d<sup>-1</sup> for workers, residents, and children, respectively (Table 2). The dietary intake dose ( $2.95 \times 10^{-4}$  mg kg<sup>-1</sup> d<sup>-1</sup>) accounts for >98% in daily intake for all people in this study, indicating dietary intake is a more important pathway than dermal contact and air inhalation for people living in this region. Vegetables, grains and fishes account for 69%, 30% and 1% of total dietary intake, respectively. DP in the vegetables and grains mainly originate from atmospheric transport from the facility. The concentrations of DP in the grains rapidly dropped by a factor of 27 within 1.4 km. Therefore, farming should be prohibited at least 5 km from the facility to control the human exposure dose.

The doses of dermal and inhalation exposure can vary among workers, residents, and children due to differences in exposure concentrations, body surface, body weight, etc(11). Both exposure doses appear to be relatively low (<2%) in present study. The exposure dose for children via dermal and inhalation are similar to the adult residents. However, the occupational exposures for workers via dermal and inhalation are 37-fold and 4-fold greater than the residential exposures because of higher soil and air concentrations at workplace than residential areas.

A comparison is made for risk assessment between the reference dose (RfD) and the EED via three exposure routes (Table 2). The hazard ratios (EED/RfD) were markedly lower than 0.001 for people in the facility and the e-waste recycling site via these three routes. These results imply that the occupational and residential exposures to DP fell in a relatively safe range for the people who live in the regions of the facility and e-waste recycling site. However, it should be noted that the potential health risk from long-term occupational exposure till needs further investigation due to a possible toxicity from DP metabolites in the human body.

Table 2. Estimated exposure dose (EED, mg kg<sup>-1</sup> d<sup>-1</sup>) of DP for worker, resident, and children via dietary intake, dermal contact, and inhalation in manufacturing facility and oral, dermal and inhalation reference dose (RfD, mg kg<sup>-1</sup> d<sup>-1</sup>) calculated from the repeated dose toxicity.

exposure route	EED in the facility			RfD
	worker	resident	children	
dietary	$2.95 \times 10^{-4}$	$2.95 \times 10^{-4}$	$2.95 \times 10^{-4}$	7.6
dermal	$3.14 \times 10^{-6}$	$8.50 \times 10^{-8}$	$9.25 \times 10^{-8}$	2
inhalation	$2.08 \times 10^{-6}$	$5.20 \times 10^{-7}$	$7.90 \times 10^{-7}$	$1.02 \times 10^{-2}$

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