

Isomer of Dechlorane Plus in Surficial Water, Soil and Sediment in a Northern Chinese Wetlands

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1. Introduction

Dechlorane Plus (DP), a recently discovered chlorinated flame retardant, which are a series of halogenated compounds synthesized through the Diels-Alder addition of one or two hexachlorocyclopentadiene (HCCPD) molecules to an unsaturated compound. Examples of Dechloranes include: Mirex, Dechlorane 602, Dec 603, Dec 604, and Dechlorane Plus (a mix of anti- and syn-Dechlorane Plus isomers; a-DP and s-DP). It has been manufactured for over 40 years, when production and use of DP was banned and later included in the Stockholm Convention, and has only recently been reported in the environment. The major applications of DP are in industrial polymers used for coating electrical wires and cables, connectors used in computers, and plastic roofing material.

DP has since been detected in North America and China in diverse environmental matrices including air, indoor dust, water, sediment and biota. Recently Wang et al. reported DP and other Dechlorines in water, soil, and air near a DP manufacturer in China, and high DP concentrations were found in the area. Liu and coworkers (18a) presented DP, Decs 602, 603, and 604 in surface soil across China, and the soil-air exchange of DP was first studied. DP was classified as a local contaminant. But most of studies on the DP in China were about the level in single medium, but less data about the bio-medium in a whole wetlands ecosystem.

Zhalong Wetlands was been protected from 1987, which is a close, steady ecosystems. The aim of this paper is to study the concentration and profiles of DP in soil, water, and sediment samples from Zhalong Wetlands in order to investigate the distribution in soil-water, sediment-water. Isomeric ratio profiles in water and sediment are also discussed.

Experimental Procedures

Sampling. In June of 2008, 16 water sample, 10 sediment samples, and 8 soil samples were collected at 15 sites in proximity to the Zhalong Wetlands, Northeast China. The 15 sampling sites are 1 Wenghai paigan, 2 Shuangyanghe, 3 Dongshengshuiku, 4 Yinnengongcheng, 5 Wuyuerhe, 6 Lindian, 7 Jiangdongpaigan, 8 Teleqiao, 9 Dashengyingzi, 10 Wudaiqiao, 11 Tangtugangzi, 12 Zhaokaihouqiao, 13 Zhaotang1/3, 14 Zhaotang2/3, 15 Longhu. The surficial water and ground were both sampled at Zhaokai. Among the 15 sampling sites, 1, 2, 3, 4, 5, 6, 15 were in entry of Zhalong Wetlands, 10, 12, 13, 14 were in core area, 7, 8, 9 in outlet.

Water samples (1 L for each) collected at sampling sites were placed directly into amber glass acetone-rinsed bottles and capped with Teflon-lined or solvent-washed aluminum foil-lined caps. Samples were stabilized with 100 mL dichloromethane (DCM) to prevent bacterial degradation and stored in darkness at 4 °C. Surface sediment and soil samples were collected using a sediment/soil sampler and transferred to a Teflon-lined, capped glass jar and frozen (-20 °C) until extraction. All processes were carried out following the standard operating procedures of the National Laboratory for Environmental Testing (NLET), Environment Canada

Chemical and reagents. All solvents used were of pesticide grade purity (J.T. Baker, USA). Standards for individual anti- and syn-DP (CAS# 13560-89-9) was purchased from Wellington Laboratories (Guelph, Ontario, Canada). Mirex (CAS# 2385-85-5) was purchased from Cambridge Isotope Laboratories Inc. (Andover, MA). Dec 602 (95%, CAS# 31107-44-5), Dec 603 (98%, CAS# 13560-92-4), and Dec 604 (98%, CAS# 34571-16-9) were supplied by Toronto Research Chemicals Inc. Polychlorinated biphenyls 155 (CB-155) and octachloronaphthalene (OCN) purchased from Accustandard Inc. (New Haven, CT) were used as the surrogate and internal standards for all compounds.

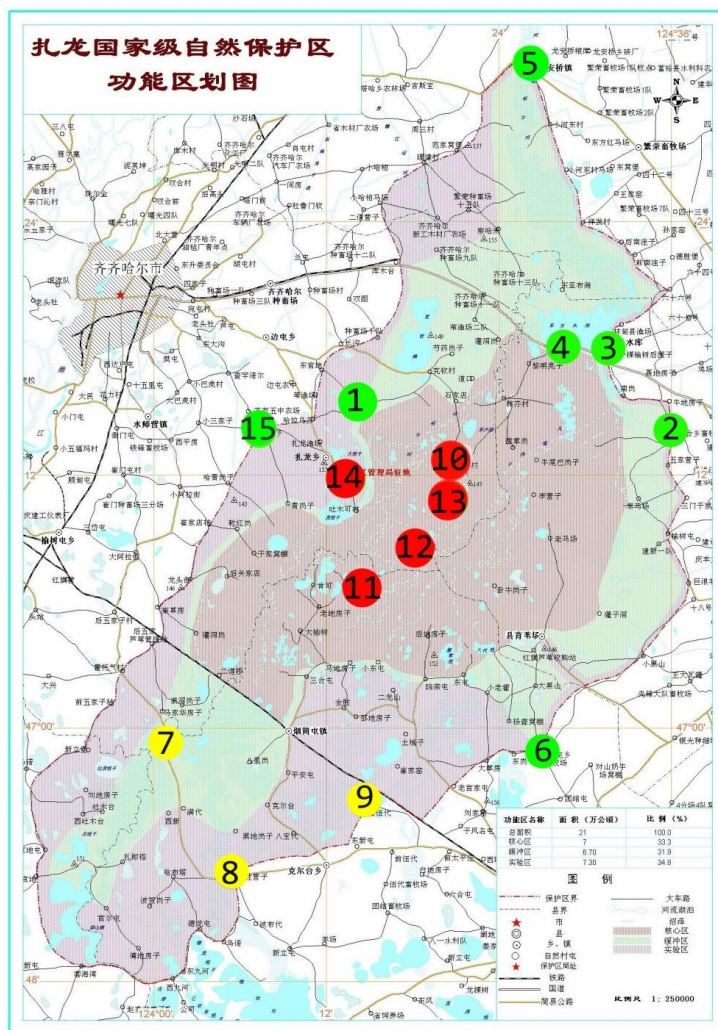


Fig. 1 Sampling sites

Extraction and analyses. Samples were extracted and analyzed according to the methods established at the National Laboratory for Environmental Testing (NLET), Environment Canada. After spiking with CB 155 surrogate, water samples were extracted with 100 mL DCM in a separatory funnel with agitation followed by a 1 h settling time. Extraction was thrice repeated, followed by DCM collection and rotary- evaporation to 1 mL. Ten grams of sediment and 10 g anhydrous sodium sulfate were accurately measured into a pre-cleaned extraction thimble and spiked with a CB155 surrogate standard. After mixing, samples were Soxhlet extracted for 24 h with 100 ml mixed solvent (hexane/acetone, 1:1 v/v). Following extraction, the extract was added to a separatory funnel and washed 3 times using 98% H₂SO₄, which was subsequently discarded. Extracts were then rotary evaporated to 1 mL. The extraction method for oyster was similar with the additional step of gravimetric lipid determination for 10% of the extract after Soxhlet extraction. Further details can be found elsewhere (19). The 1 mL extracts were passed through a 5.5 g silica gel column after a 25 mL hexane pre-rinse and eluted with 40 ml of hexane/DCM mixture (1:1, v/v). The elution was rotary-evaporated to 2 mL, then solvent-exchanged into isoctane and reduced to 1 mL under nitrogen. The internal standard OCN was added to correct volume difference prior to GC-MS analysis.

All samples were quantified using an Agilent 6890 GC coupled to an Agilent 5973N mass spectrometer detector (GC/MSD) equipped with a 60 m × 0.25 mm × 0.25 μm DB-5 MS capillary column (J&W Scientific, Folsom, CA) in selected ion monitoring (SIM) mode. The initial oven temperature was set at 90 °C for 0.5 min, ramped at 25 °C min⁻¹ to 240 °C, then at 2 °C min⁻¹ to 260 °C, 20 °C min⁻¹ to 285 °C and held for 10 min. The MS system was operated in a methane negative chemical ionization (NCI) mode. Selected ion monitoring mode

was applied (m/z 438.7 / 436.7 / 401.7 / 403.7 for Dechlorane; 613.6 / 611.6 / 615.6 for Dec 602; 404 for OCN; 637.6 / 635.6 / 639.6 for Dec 603; 541.6 / 543.6 / 463.7 for Dec 604; 653.5/651.5 / 655.5 for syn- and anti-DP).

Quality assurance/quality control. Strict quality assurance and quality control measures were put in place to monitor the analytical process. All samples were spiked with a labeled CB155 recovery standard prior to extraction. Surrogate standard recoveries in samples ranged from 83% to 103% (mean $95 \pm 12\%$). When the GC retention time matched those of the standards within 0.05 min, the compound was selected. Procedural and solvent blanks were generated for each batch of 10 samples. No dechloranes were found in the procedural and solvent blanks. The spike samples for DP were included at a rate of one for every 10 samples extracted, and the average spike recoveries were $72 \pm 12\%$ for syn-DP, $76 \pm 16\%$ for anti-DP. Final sample concentrations were not surrogate recovery corrected. For water samples, detection limits (DL) values were 0.01 ng/L for Dec 602, 0.05 ng/L for Dec 603, 1 ng/L for Dec 604, 0.1 ng/L for Mirex, 0.1 ng/L for both syn- and anti-DP. For sediment samples, the DL values were 0.001 ng/g dry weight (dw) for Dec 602, 0.006 ng/g dw for Dec 603, 0.2 ng/g dw for Dec 604, 0.02 ng/g dw for Mirex, 0.01 ng/g dw for both syn- and anti DP. For oyster samples, DL values were 0.001 ng/g wet weight (ww) for Dec 602, 0.005 ng/g ww for Dec 603, 0.1 ng/g ww for Dec 604, 0.01 ng/g ww for Mirex and 0.01 ng/g ww for both syn- and anti DP.

Results and Discussion

Dechloranes in water, sediment and soil Concentrations of Dechloranes in water, sediment, and soil samples are statistics listed in Table 1. DP (syn- and anti-isomers) were detected in all water samples and most of soil and sediment samples. In this study, average Σ DP concentrations in water, sediment, soil were 137.81 pg/g dw, 70.56 pg/g dw, 25.64 pg/L, respectively. Syn-DP respective ranges from below the detection limit (BDL) to 160 pg/L in Lindian for water samples, BDL-18.47 pg/g dw in Jiangdongpaigan for sediment samples, BDL-22.99 pg/g dw in Wuyuerhe for soil samples. Anti-DP ranges from BDL-210 pg/L in Zhaokai for water samples, BDL-24.9 pg/g dw in Yinnengogcheng for sediment samples, BDL to 45.98 pg/g dw for soil samples. Mirex, Dec602, Dec603, Dec604 were below the BDL in all the samples. All the sample site where the concentration of DP was higher were located around the wetlands. The concentration of DP in water and sediment were an order of magnitude lower than those reported in Northern Chinese River (Hong Qi et al, 2010) and far below the concentrations in the soil, sediment nearby the source (Lake Ontario, Huaian) (Qiu 2007) and the reservoir near the e-waste recycling plants (Wu, Zhang et al. 2009).

The highest water concentration of DP was found at #5, and the highest sediment concentration of DP was found at #7, the highest soil concentration of DP was found at #2. All the sample sites where concentration of DP were higher were in the entry or outlet. This can be explained by the purified activities by the upriver area. The soil, water and biology in upriver area absorbed part of the pollutants. This also indicated that the pollution source of core area were most come from the downstream. But DP of the sample site of water entry and outlet possibly related to the inputs of sewage and agricultural runoff.

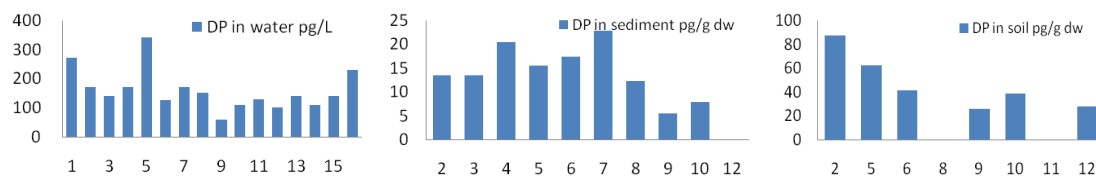


Fig. 2 Concentrations of DP in water, sediment and soil samples in Zhalong Wetlands

Fractional abundances of DP isomers. The stereoisomer ratios of DP can be described by the fractional abundance given by

$$f_{syn} = [syn - DP] / ([syn - DP] + [anti - DP]) \quad (1)$$

The f_{syn} values were calculated using equal for water, sediment and soil samples. The mean values of f_{syn} were

0.56 ± 0.10, 0.62 ± 0.036 and 0.42 ± 0.11 for water, sediment and soil samples respectively. With a Log K_{ow} value of 9.3 for both syn- and anti-DP, DP stereoisomers in the river have a greater affinity for sediment than water. Values of f_{syn} higher than technical mixtures were observed in all samples in Zhalong Wetlands, indicating an enrichment of syn-DP in these matrices.

Table 1. Dechlorane Plus in Soil (pg/g dw), Sediment (pg/g dw) and Water (pg/L)

| Sampling site | Syn-DP | | | Anti-DP | | | ΣDP | | | Mirex | | |
|-----------------|--------|----------|--------|---------|----------|--------|-------|----------|--------|-------|----------|-------|
| | Soil | Sediment | Water | Soil | Sediment | Water | Soil | Sediment | Water | Soil | Sediment | Water |
| Wenghaipaigan | | | BDL | | | 120.00 | | | 120.00 | | | BDL |
| Shuangyanghe | 17.76 | 6.69 | 110.00 | 69.25 | 6.69 | 60.00 | 87.01 | 13.39 | 170.00 | 69.67 | BDL | BDL |
| Dongshengshuiku | | 6.23 | 50.00 | | 7.14 | 120.00 | | 13.37 | 170.00 | | BDL | BDL |
| Yinenngongcheng | | 12.93 | BDL | | 7.48 | 80.00 | | 20.41 | 80.00 | | BDL | BDL |
| Wuyuerhe | 20.69 | 6.95 | BDL | 41.38 | 8.47 | 210.00 | 62.07 | 15.42 | 210.00 | BDL | BDL | BDL |
| Lindian | 15.74 | 5.13 | 160.00 | 25.76 | 17.43 | 110.00 | 41.50 | 17.43 | 270.00 | BDL | BDL | BDL |
| Teleqiao | BDL | BDL | 50.00 | BDL | 7.05 | 75.00 | BDL | 12.18 | 125.00 | 89.10 | BDL | BDL |
| Dashengyingzi | 12.24 | 5.44 | 70.00 | 13.11 | BDL | 70.00 | 25.35 | 5.44 | 140.00 | 22.63 | BDL | BDL |
| Wudaiqiao | 17.09 | BDL | BDL | 21.37 | 7.84 | 110.00 | 38.46 | 7.84 | 110.00 | BDL | BDL | BDL |
| Tangtugangzi | BDL | | BDL | BDL | | BDL | BDL | | 40.00 | BDL | | BDL |
| Zhaokai | 5.22 | BDL | 60.00 | 22.63 | BDL | BDL | 27.85 | BDL | 60.00 | BDL | BDL | BDL |
| Zhaotang 1/3 | | | 60.00 | | | BDL | | | 60.00 | | | BDL |
| Zhaotang 2/3 | | | BDL | | | 110.00 | | | 110.00 | | | BDL |
| Groundwater | | | 90.00 | | | 50.00 | | | 140.00 | | | BDL |
| Longhu | | | 50.00 | | | 80.00 | | | 130.00 | | | BDL |
| Jiangdongpaigan | | 12.07 | BDL | | 10.65 | 310.00 | | 22.71 | 310.00 | | BDL | BDL |

Interestingly, significantly positive correlations were found between total DP concentration levels of soil and water ($R^2=0.241$, $\rho<0.05$). But the relationship between the concentration levels of sediment and water was lower than that relationship of soil ($R^2=0.920$, $\rho<0.05$) (Fig.2). This indicated may because the dynamic adsorption from water to sediment occurred frequently than that from soil to water.

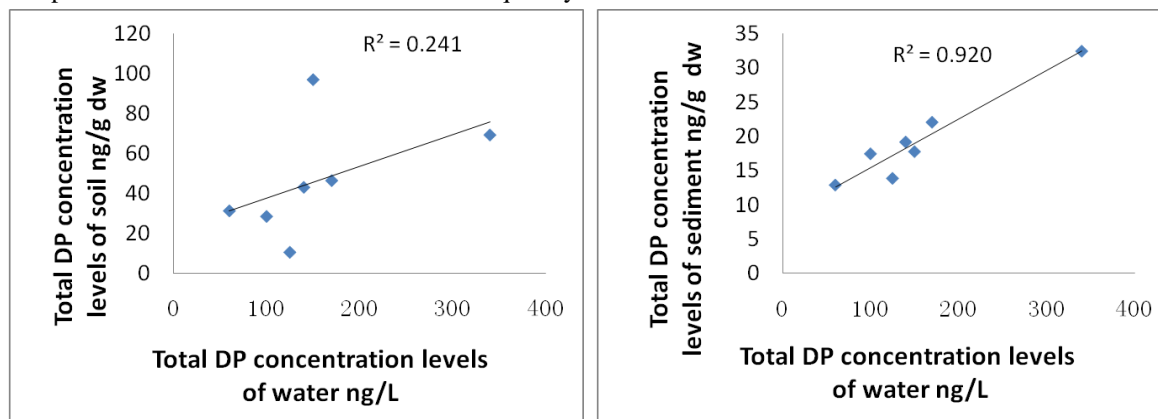


Fig. 2 Relationship between the ΣDP of water soil, and sediment

Literature Cited

1. Liu, L., H. Jia, et al. (2010). "Dechlorane Plus in Surficial Water and Sediment in a Northeastern Chinese River." *Environmental Science & Technology*.
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