

DECHLORANE PLUS LEVELS AND ISOMER PROFILES IN SURFACE SOILS FROM ELECTRONIC WASTE DISMANTLING AREA IN SOUTH CHINA

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Introduction

Dechlorane Plus (DP) (CAS No.13560-89-9) is an additive chlorinated flame retardant which was first introduced into the market in the 1960s to substitute Dechlorane or Mirex. DP is created by the reaction of two units of hexachlorocyclopentadiene and one unit of 1,5-cyclooctadiene. The major applications of DP products are in industrial polymers used for coating wires and cables, connectors used in computers and plastic roofing materials(1). Although the annual production of DP was not reported, it was categorized as a High Production Volume Chemical (HPVC) by the United States Environmental Protection Agency's high production volume challenge program with estimated production of more than one million pounds annually(2). Commercial DP comprises two stereoisomers, i.e., *syn*-DP and *anti*-DP.

At present, the production and consumption of DP in China remain unclear, and the measurements in environmental medium are very limited. Since many DP-containing materials and products are widely used in electronic appliance, it is likely that DP is released into the environment during the recycling processes of electronic wastes (EWs).

In this study, surface soil samples were collected and analyzed from an e-waste dismantling area, Guiyu of Guangdong Province located in the south of China. The objective of this study is to investigate DP concentration levels and isomer profiles in the surface soil samples from a typical e-waste dismantling area in southern China.

Materials and methods

Sample collection

A total of 23 sampling sites were shown in Fig. 1. Briefly, Guiyu was divided into three districts, Nanyang district (NY) is located in the north of the town, Huamei district (HM) and Shanglian district (SL) is located in the southwest and southeast, respectively. Five sites from each district were selected to represent the pollution levels of the corresponding district of this studied area. In addition, two contiguous villages named Yaocuwei (YCW) and Longmen (LM), where most of the families worked on e-waste recycling similar to Guiyu, were also included in this research area. The background sites were selected near a northern hill, on the windward side of Guiyu town and far away from the EWs dismantling sites. Three sites located around this e-waste dismantling region named Chendian (CD), Simapu (SMP), and Gurao (GR) were chosen as contrast sites. Surface soils (less than 20cm) were sampled with a stainless steel shovel and stored in brown glass bottles.

Sample extraction and analysis

After the addition of a surrogate recovery standard (DP SYN&DP ANTI, Cambridge Isotope Laboratories, Inc.), the soil sample (about 10g) was extracted with 1:1 *n*-hexane/DCM (v/v) using accelerated solvent

extraction (DIONEX, ASE-300) and then concentrated to approximately 1ml. Afterwards, the extract was purified on the column (1.0 cm i.d.) which was packed sequentially by 1cm anhydrous sodium sulfate (WAKO), 1g florisil (Riedel-de Haën) and 1cm anhydrous sodium sulfate and then eluted with 20ml *n*-hexane. The elution was concentrated and blown to nearly dryness under a gentle nitrogen stream and finally diluted to 100 μ l with decane for instrument analysis.

DP was determined using an Agilent 6890N gas chromatograph coupled with an Agilent 5975C mass spectrometer (GC/MS) under negative ion chemical ionization mode (NCI). A HP-5MS capillary column(30m \times 0.25 mm i.d. \times 0.25 μ m film thickness, Agilent Technologies, Inc.) was used. Splitless injection of 1 μ l was made into an injector set at 270 $^{\circ}$ C. The initial GC oven temperature was set at 100 $^{\circ}$ C, ramped at 35 $^{\circ}$ C/min to 250 $^{\circ}$ C, then ramped at 10 $^{\circ}$ C/min to 300 $^{\circ}$ C, and held for 8.5min. The ion source, quadrupole and interface temperature were set at 200 $^{\circ}$ C, 150 $^{\circ}$ C and 280 $^{\circ}$ C, respectively. The instrument was operated in selected ion monitoring mode (SIM) with the m/z 653.7 ion used for quantification and m/z 655.7 and 651.5 ions used for validation.

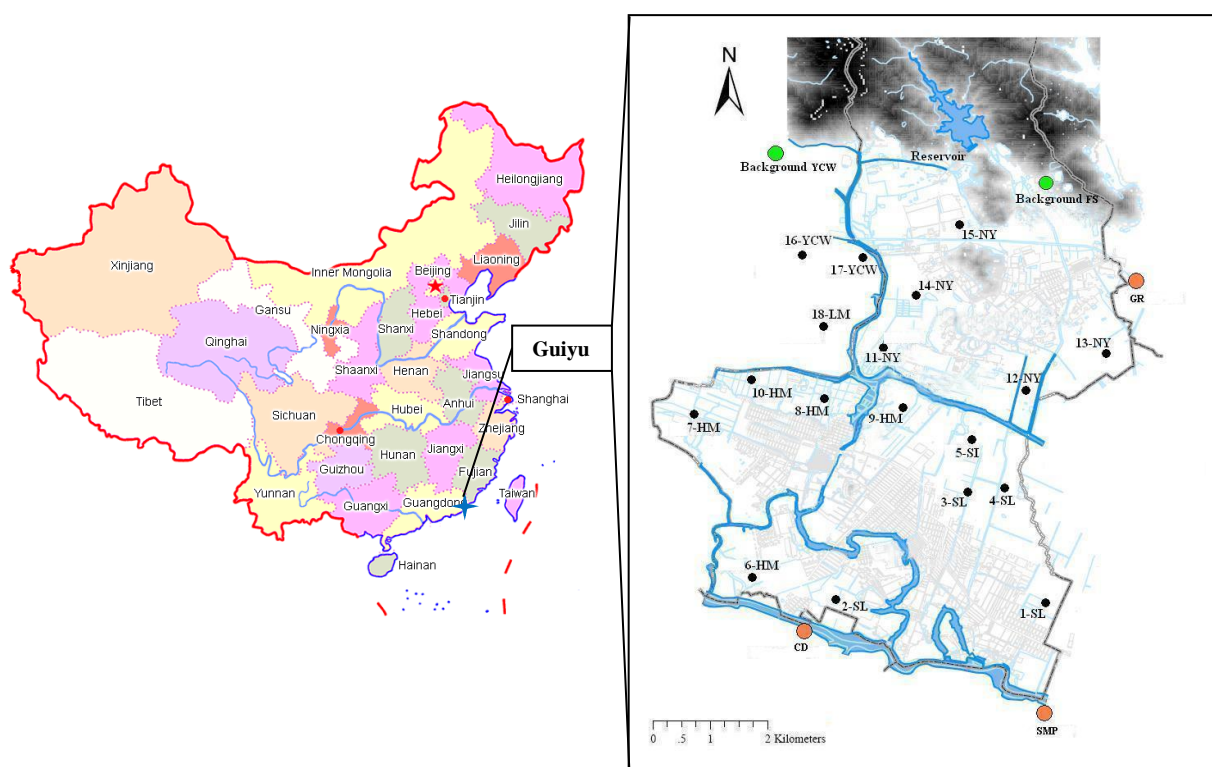


Figure 1. Locations of sampling sites in Guiyu, Guangdong Province, China

Quality assurance and quality control

All calibration standards and spiking solutions were prepared by serial dilution in decane. Daily multi-level calibration curve (1-500 ng/ml) was conducted and the regression coefficient (r^2) values for *syn*-DP and *anti*-DP were both greater than 0.99. Instrument Detection Limits (IDLs) for *syn*-DP and *anti*-DP were 0.84 ng/ml and 0.93 ng/ml, and Method Detection Limits (MDLs) were 0.019ng/g and 0.023ng/g, respectively. All recoveries for *syn*-DP and *anti*-DP were 82 ± 11 % and 93 ± 17 % (mean \pm standard deviation), respectively. One laboratory blank and one duplicate sample were included in each analytical batch of 12 samples.

Results and discussion

Total DP concentration levels

DP was detected in all surface soil samples in this study. The concentrations of *syn*- plus *anti*- isomers (total DP) ranged from 0.308-209 ng/g, which were illustrated in Figure 2. The total DP concentration level in this study was higher than that detected in the sediments from Lake Erie (0.061-8.62 ng/g), but comparable to Lake Ontario (2.23-586 ng/g) (2), to which the Niagara River, a likely DP source flows. The total DP concentration levels in this area exhibited the following trend: NY>SL>HM≈LM>YCW>area around the e-waste dismantling regions (except SMP). The total DP of three districts in Guiyu ranged from 4.13-9.24 ng/g (mean: 6.60 ng/g), 10.2-18.7 ng/g (mean: 13.2 ng/g) and 4.48-209 ng/g (mean: 56.8 ng/g) for HM, SL and NY, respectively. The mean concentration levels of total DP in YCW and LM, where manual disassembly of EWs predominates like NY district in Guiyu, were 3.96 and 6.26 ng/g, respectively. In comparison, total DP concentrations in area around the e-waste dismantling region were clearly lower, except for SMP (18.6 ng/g), where high I-TEQ PCDD/Fs concentration was also detected in our previous study (3). This may be attributed to a potential pollution source present at this specific site. The total DP concentration was highest at NY-11, where the concentration was 209 ng/g and second highest at NY-12 adjacent to NY-11.

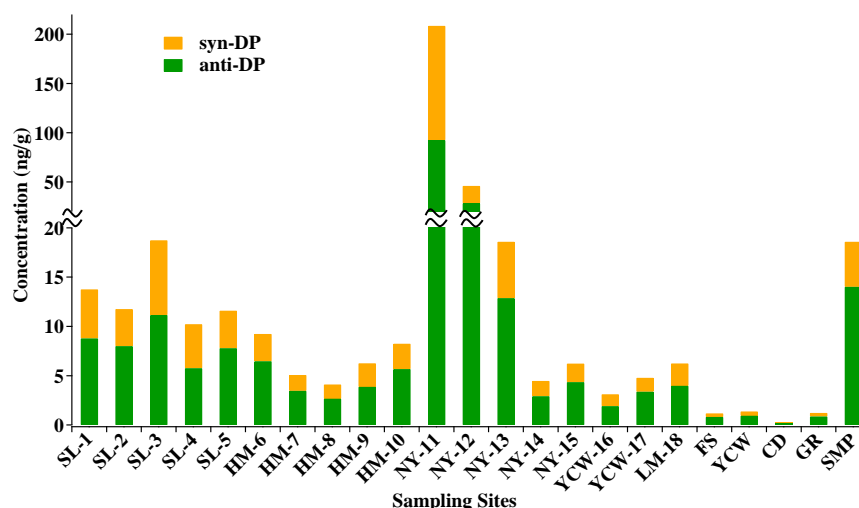


Figure 2. Total *syn*- and *anti*-DP levels in surface soil samples from the 23 sampling sites located in Guiyu

DP isomer profiles

The isomer ratios f_{anti} shown in Figure 2 were calculated as the concentration of *anti*-DP divided by the total of the concentrations of *syn*-DP and *anti*-DP. The average of f_{anti} (mean \pm standard deviation) was 0.652 ± 0.064 , very close to that of the commercial product derived from OxyChem's technical DP mixture ($f_{\text{anti}}=0.65$) (4). Actually, different districts in Guiyu have their typical dismantling processes. Roasting circuit boards is the main dismantling activity in HM; open burning, acid leaching, chipping and melting plastics are the dominant disposal manners in SL; and as for NY, most of the families engage in manually disassembling EWs. Although our previous study indicated that the dismantling manners had obvious influence on the I-TEQ congener profiles of PCDD/Fs (3), similar conclusion could not be derived in DP isomer profiles, and there was no direct relationship between total DP and PCDD/Fs concentrations. PCDD/Fs were released into environment as an unintentional

POPs from thermal processes, but as an additive chlorinated flame retardant, DP may be released into the environment in different ways.

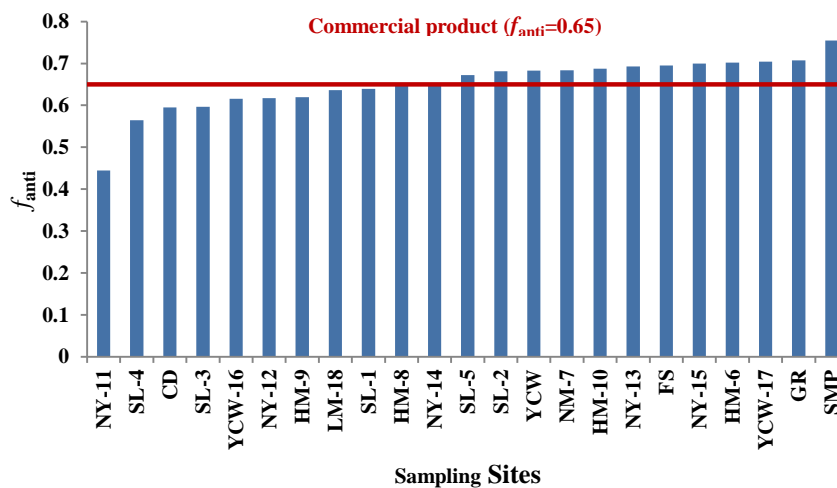


Figure 3. The f_{anti} values for all soil samples from the e-waste dismantling and nearby regions. The red line represents the f_{anti} in commercial product.

Acknowledgements

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