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Analysis for sources of atmospheric α- and γ-HCH in gas and particle-associated phase in Dalian, China by multiple regression

Qingbo Li [a, *], Yan Li [b], Xianyu Wang [b], Ruiqi Zhang [c], Jianmin Ma [d], Mengxue Sun [a], Xiaoning Lv [a], Jiaoling Bao [a]

[a] College of Environmental Science and Engineering, Dalian Maritime University, Dalian 116026, China
[b] National Research Centre for Environmental Toxicology, The University of Queensland, 39 Kessels Road, Coopers Plains, QLD, 4108, Australia
[c] Shaanxi University of Science & Technology, Shaanxi 710021, China
[d] Key Laboratory of Western China's Environmental System, Ministry of Education, College of Earth and Environment Sciences, Lanzhou University, Lanzhou 730000, China

HIGHLIGHTS

- Diurnal and seasonal variations of HCHs in Dalian air are first time reported.
- Gaseous and particle-associated HCHs peaked in autumn and spring respectively.
- Multiple regression analysis was used to assess impact of meteorological parameters.
- Concentration of particle-associated HCHs tended to remain stable.

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ABSTRACT

Atmospheric concentrations of α- and γ-hexachlorocyclohexanes were measured once a week in Dalian throughout 2008, using a high-volume air sampler, to estimate diurnal, monthly and seasonal variations. Multiple regression analysis was used to estimate the impact of selected meteorological conditions on atmospheric concentrations of hexachlorocyclohexanes and to identify the potential source regions. Overall, α- and γ-hexachlorocyclohexanes were mainly associated with the gas phase, with an annual mean gas-phase concentration of 36 ± 30 and 10 ± 9.8 pg m^{-3} respectively. On the other hand, mean particle (PM_{10}) associated concentrations throughout the year were 1.9 ± 2.4 and 0.46 ± 0.43 pg m^{-3} respectively. Gas-phase concentration of α- and γ-hexachlorocyclohexanes peaked in the autumn season whereas highest concentrations in the particle phase were measured in spring. Ratio of α-/γ-isomer ranged from 3.7 to 7.4 in the gas phase which was close to the ratio in technical hexachlorocyclohexanes (5–7). In the particle-associated phase this ratio ranged from 1.2 to 3.8, with the exception of daytime samples in spring (up to 16) and summer seasons (up to 14) and this exception could be due to the isomerization from γ- to α- in ambient air, at least partly resulted from the impact of sunlight. Regression analysis showed that, at the sampling site, concentrations of α- and γ-hexachlorocyclohexanes in the gas phase were both elevated with increasing temperature and wind speed, whereas in the particle-associated phase their concentrations tended to remain stable.

1. Introduction

Hexachlorocyclohexanes (HCHs) were used extensively between the 1960s and the 1980s and cumulative consumption of technical HCHs has been estimated as 6 million tons globally (Willett et al., 1998). In China, HCHs were widely used for agricultural purposes and vector control and the amount of technical HCHs used in China and South Asia during the late 1970s was estimated at about 60,000 tons per year (Willett et al., 1998). During and after application, large amounts of HCHs can be released and condensed into environmental reservoirs such as soil, vegetation and cryosphere. Subsequently, the stored HCHs can re-volatilize from these secondary sources into environmental

* Corresponding author.
E-mail address: drliqb@gmail.com (Q. Li).

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compartments and can result in exposure of humans and the whole ecosystem. Temperature is invoked as the major controller for semi-volatile organic compounds (SVOCs) such as HCHs to condense into/(re-)volatilize from environmental reservoirs, effectively accounting for their cycling nature between air and earth's surfaces (Halsall et al., 1999). Several studies have interpreted this phenomenon using the Clausius-Clapeyron equation, in which chemical concentrations in air, expressed as partial pressure, are plotted against ambient temperature (Hoff et al., 1992; Hornbuckle and Eisenreich, 1996; Venier and Hites, 2010). Besides, wind speed and direction are also considered as the major factors, which can be integrated into a multiple regression model including also reciprocal temperature, to interpret the impact of these meteorological parameters on the concentrations of SVOCs in ambient air. For example, Hillery et al. used this equation to relate atmospheric PCB concentrations to meteorological conditions, thereby to study the temporal and spatial trends of gas-phase PCB concentrations near the Great Lakes (Hillery et al., 1997).

Dalian is a seaside city where the distribution of atmospheric pollutants could be influenced by diel cycle of sea-land breeze. However, to our best knowledge, limited reports are available for diurnal and seasonal variations of organochlorine pesticides (OCPs) including HCHs (Li et al., 2011, 2012) and for their source analysis within this city. This study aims to obtain diurnal and seasonal data for atmospheric HCHs in Dalian air and to analysis their sources by a multiple regression model both in the gas and particle-associated phase.

2. Materials and methods

2.1. Sample collection

The sampling site is located in Dalian (121°31′E, 38°52′N), in the southern tip of Liaodong peninsular in northeast China, adjacent to the Yellow Sea and Bohai Sea (the supplementary information (SI) Figure S1). The city locates in the temperate zone featured by a typical maritime continental monsoon climate. A sampling platform (altitude 12 m above the ground) is mounted on the Technology Building of Dalian Maritime University and is ~10 km to the city center and ~1 km to the Yellow Sea and lacks of major proximate OCP sources. Detailed sampling method has been published elsewhere (Li et al., 2012). Briefly, a high-volume air sampler operating at a flow rate at about 1.0 m^3 min^{-1} was used to collect gas-phase and particle (PM_{10})-associated-phase samples simultaneously once a week throughout the year of 2008. This sampling platform is also equipped with a mini weather station (Watchdog 900ET) for monitoring and recording meteorological parameters continuously, including wind speed and direction, ambient temperature, relative humidity and solar radiance at the height analogues to that the air sampler was mounted. Data were recorded automatically every 6 s into a data-logger and output as hourly mean values.

2.2. Sample analysis

Sample extraction, cleanup and analysis were published in detail elsewhere (Li et al., 2012). Briefly, samples were extracted by *n*-hexane and cleaned up by a silica gel/neutral alumina column. Sample analysis was performed with a Shimadzu 2010 gas chromatograph (GC) equipped with a micro electron capture detector (*m*-ECD).

2.3. Quality control and quality assurance (QC/QA)

Detailed QC/QA procedure was reported elsewhere (Li et al., 2012). In brief, limits of detection (LOD) for α- and γ-HCH in the gas phase are 0.071 and 0.37 pg m^{-3} respectively and in the particle phase, LOD for α- and γ-HCH were 0.033 and 0.052 pg m^{-3}, respectively.

2.4. Multiple regressions

Measured concentrations (pg m^{-3}) of α- and γ-HCH were converted to partial pressures (atm) using the ideal gas law. Air temperature (*T* in K) and wind speed (WS in mph) were regressed into the logarithms of the atmospheric partial pressures (Hillery et al., 1997):

$$\ln P = b0 + b1(1/T) + b2\ WS + b3\ \sin WD + b4\ \cos WD, \quad (1)$$

where b0 is an intercept and b1 and b2 describes the dependence of the partial pressure on reciprocal *T* and WS respectively; b3 and b4 are coefficients of the sine WD (wind direction in degree) and the cosine WD terms.

Two different methods, enter and stepwise method, which are fitted using IBM SPSS statistics 19, are used to run the multiple regression model separately.

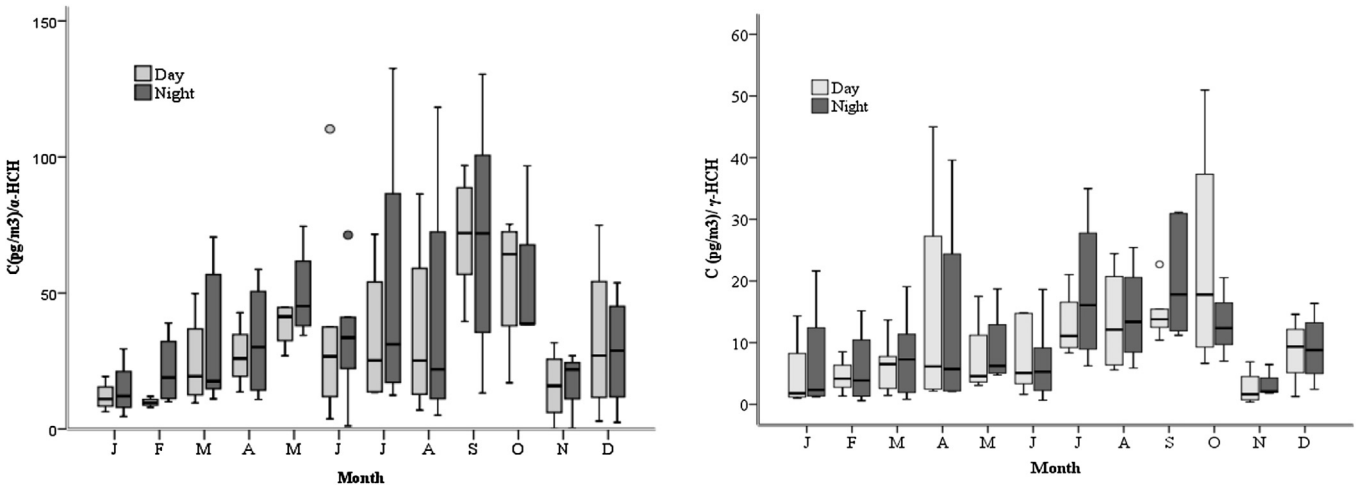

Fig. 1. Monthly variations in α-HCH (left panel) and γ-HCH (right panel) concentrations in gas phase.