

Title:

A comparative study of chlorinated paraffins (CPs) in seawater and sediments between the Bohai Sea, China and Seto Inland Sea, Japan.

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Aim:

- (1) To investigate the occurrence and distribution characteristics of CPs in the Seto Inland Sea.
- (2) To compare the concentrations and compositional distributions of CPs between the Seto Inland Sea and the Bohai Sea.
- (3) To explore the possible sources of CPs in the Seto Inland Sea.

Procedure:

- (1) Participate a cruise in the Seto inland sea, and collect water and sediment samples;
- (2) Discussion with Prof. Xinyu Guo about the comparison of POPs in the Bohai Sea and Seto Inland Sea.

Result:**Introduction**

CPs are complex mixtures of chlorinated n-paraffins with different carbon chain lengths and degrees of chlorination (Li et al., 2021). According to the carbon chain length, CPs can be subdivided into short-chain chlorinated paraffins (SCCPs, C₁₀-C₁₃), medium-chain chlorinated paraffins (MCCPs, C₁₄-C₁₇) and long-chain chlorinated paraffins (LCCPs, C₁₈-C₃₀). Since the first synthesis of CPs in the 1930s, they have good flame retardancy and electrical insulation, low volatility and high stability, and are inexpensive and readily available. CPs are used in flame retardants, plasticizers, metal cutting fluids and other product (Tomy et al., 1998). China has been producing CPs products since the 1950s and is currently the world's largest producer and a major exporter (Glüge et al., 2016). Shandong Peninsula and Liaodong Peninsula are important CPs producing areas in China. SCCPs are of particular interest to researchers because of their long-distance transport potential, persistence, bioaccumulation, high toxicity to aquatic organisms, and possible carcinogenic effects in humans. In May 2017, the Stockholm Convention Persistent Organic Pollutants Review Committee decided at its Eighth Conference of the Parties to list SCCPs in Annex A as a new group of persistent organic pollutants to limit their production and emissions (Castro et al., 2019).

Affected by population use emissions and emissions from CPs production areas, there is a high level of CPs pollution in the rivers and atmosphere in the Bohai Rim region. As the most important

sink for pollutants in the Bohai Rim region, a large amount of CPs pollutants enter the Bohai Sea. The long-term existence in water bodies and sediments threatens the ecological environment of the Bohai Sea and further causes health risks to humans through the enrichment of marine food webs.

In this study, we have carried out sample preparation and instrumental analysis on the surface seawater samples of the Bohai Sea in April, August, and November-December 2018 (Fig. 1), obtained experimental data, and preliminarily analyzed the concentrations and distribution of SCCPs.

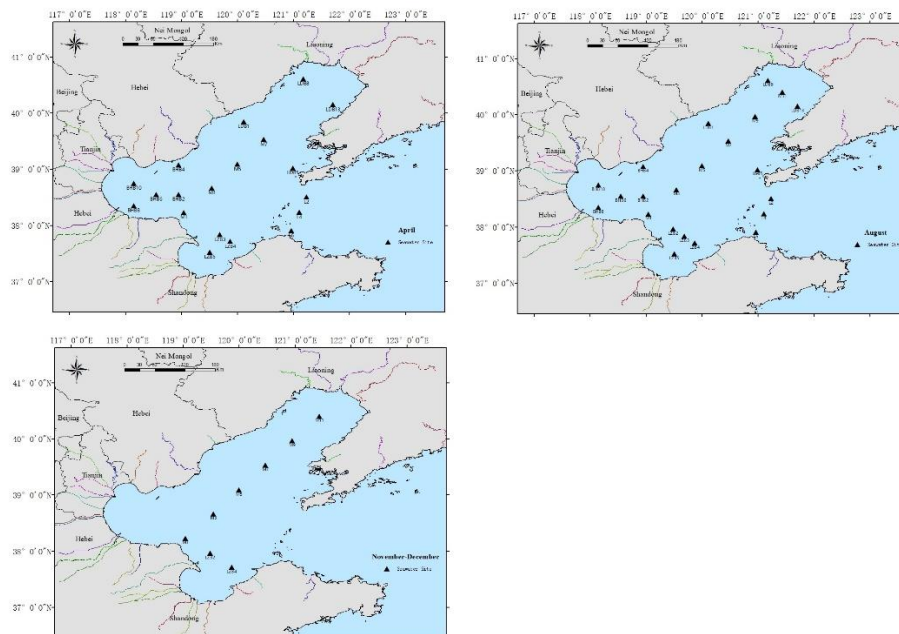


Fig.1 The sampling sites of surface seawater in the Bohai Sea in 2018.

Influenced by global pandemic of COVID-19 and also due to the new policies for international travelling in China and Japan, we cancelled the exchange and study plan at Ehime University in Japan in 2021. We were not able to participate a cruise in the Seto Inland Sea, so we did not collect water and sediment samples from the Seto Inland Sea.

SCCPs Concentrations in Surface Seawater

Table 1 lists the concentrations of SCCPs in the surface seawater of the Bohai Sea at different time periods. For Σ SCCPs, it was detected in all seawater samples. In the three time periods, the detection rate of SCCPs in the dissolved phase was higher than 60%, and the detection rate in the particulate phase was 100%. Overall, the concentrations of Σ SCCPs ranged from 20.47 ng/L to 5751.97 ng/L (median concentration: 208.2 ng/L). Compared with other studies in China, the concentrations of Σ SCCPs in the seawater of the Bohai Sea was lower than the concentrations of Σ SCCPs in the seawater of the Pearl River Estuary in southern China (270±66 ng/L) (Huang et al., 2019), and also lower than the concentrations of Σ SCCPs in the river system of Shanghai (278 ng/L) (Wang et al., 2019). But it was higher than the concentrations in the seawater of the East China Sea (122±73 ng/L) (Hu et al., 2021). SCCPs in the Bohai Sea are at a moderate pollution level in China.

Table 1**Concentrations of SCCPs in the surface seawater of the Bohai Sea.**

seawater		Dissolved-phase SCCPs(ng/L)	Particulate-phase SCCPs(ng/L)	Σ SCCPs(ng/L)
2018.04	detection rate	0.63	1	1
	mean	35.1	252.03	287.13
	standard deviation	41.19	531.09	524.67
	min	n.d.	20.47	20.47
	max	145.16	2465.9	2465.9
	median	30.19	120.3	142.83
	2018.08	detection rate	0.91	1
mean		628.36	230.82	859.18
standard deviation		1399.68	529.24	1439.6
min		n.d.	37.76	61.26
max		5680.92	2560.39	5751.97
median		86.81	77.55	201.09
2018.11- 12		detection rate	0.88	1
	mean	113.69	503.59	617.28
	standard deviation	164.41	502.23	453.25
	min	n.d.	34.35	64.75
	max	533.98	1451.76	1478.24
	median	40.95	296.54	566.31
	total	detection rate	0.8	1
mean		314.3	283.58	597.87
standard deviation		982.73	534.64	1067.21
min		n.d.	20.47	20.47
max		5680.92	2560.39	5751.97
median		42.63	94.47	208.2

Perspectives in future:

Since SCCPs were added as POPs by the Stockholm Convention, the production and use of SCCPs were restricted worldwide (Castro et al., 2019), and the production of MCCPs and LCCPs as substitutes increased (van Mourik et al., 2016). The chemical structure, environmental behavior and toxicity of MCCPs are similar to those of SCCPs; some studies have found that MCCPs with a chlorination degree of more than 46% are persistent and toxic; the production and application of MCCPs may have similar side effects to the environment and biosphere as SCCPs, and bring about

new environmental issues and health risks. Environmental impacts and potential endocrine disrupting effects of MCCPs and LCCPs have been included in the EU priority list. However, there is less information about the concentration levels of MCCPs and LCCPs in the environment compared to SCCPs. SCCPs, MCCPs and LCCPs deserve equal attention in the environment.

At present, the most common analytical method for CPs is gas chromatography, mainly for SCCPs and MCCPs (Gao et al., 2016). LCCPs have high melting and boiling points and are difficult to volatilize, so it is difficult to analyze by gas chromatography (Koh et al., 2002). Some researchers have established a method for simultaneous determination of SCCPs, MCCPs and LCCPs based on reversed ultrahigh-pressure liquid chromatography (UPLC) coupled with chlorine-enhanced electron spray ionization/atmospheric pressure ionization (ESI/API) quadrupole time-of-flight mass spectrometer (QTOF-MS) (Li et al., 2017), the results are remarkable. This study expects the follow-up work to develop a CPs analysis method using high performance liquid chromatography to analyze the concentration level and distribution of SCCPs, MCCPs and LCCPs in the Bohai Sea.

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