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Distribution and release of 2,4,5-trichlorobiphenyl in ice

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Abstract

The distribution of persistent organic pollutants (POPs) in ice and the release of POPs from ice during ice melting have an important influence on the eco-environment and water quality of a river. Through laboratory simulation experiments, the distribution and release of 2,4,5-trichlorobiphenyl (PCB29) in ice and the partition coefficients of PCB29 in ice water at different temperatures, concentrations, and pH levels were studied. The results showed that, at different temperatures and concentrations, the concentration of PCB29 in ice increased progressively with depth. The modes of release of different concentrations of PCB29 from ice were obtained. A large amount of PCB29 was released rapidly in the first melting period, and then the remaining PCB29 was released uniformly. The pH value dominated both the distribution and late release of PCB29 in ice. In ice water, at different temperatures, concentrations, and pH levels, the majority of PCB29 entered the water, and a lesser amount remained in the ice. Finally, laboratory experiment results were verified with field investigations. A theoretical framework is provided by this research of the behavior of POPs in ice under different environmental conditions, but a more quantitative understanding of the behavior of POPs in ice will need to be developed through further laboratory studies combined with field investigations.

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Keywords: Persistent organic pollutants; 2,4,5-trichlorobiphenyl; Ice; Distribution; Release; Partition coefficient

1. Introduction

The 5464 km-long Yellow River originates in the northern part of the Bayankala Mountains at an altitude of 4830 m on the Qinghai-Tibet Plateau, in China (Huang et al., 1992; Fu, 1998), and is the fifth longest river in the world. In recent years, the river has been significantly polluted by contaminants. According to water quality monitoring results of the Yellow River in Inner Mongolia, water pollutants include persistent organic pollutants (POPs), described in the *Stockholm Convention on Persistent Organic Pollutants* (Yuan et al.,

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2001), and the most typical POPs are organochlorine pesticides and polychlorinated biphenyls (PCBs) (Pei et al., 2010). POPs are a class of highly toxic substances with strong carcinogenicity, teratogenicity, and mutagenicity (Nicholas et al., 2001; Ricardo et al., 2005). There has already been a considerable amount of research on pollution of POPs in rivers (Fu et al., 2003; Rajendran et al., 2005; Fujii et al., 2007). As the Yellow River's freezing period in Inner Mongolia can last up to five months, some pollutants stranded in ice during the freezing period may cause secondary pollution in the river when ice starts to melt in the spring of the next year, in accordance with unique environmental chemical characteristics of rivers in the freezing period (Terry and Spyros, 2002). Therefore, study of the behavior of POPs in ice plays an important role in understanding the water quality problems of the Yellow River.

There have been some studies on organic contaminants in ice and snow. Melnikov et al. (2003) observed concentrations

of POPs in ice and snow in the Ob–Yenisey River Watershed and concluded that the spatial analysis results of data on POPs for the watershed are in most cases similar to measurements carried out in the far north of Canada. Gustafsson et al. (2005) provided a coherent and reliable set of observations on the concentrations of PCBs in particulate and dissolved forms in snow and ice, showing that ice is not a significant medium for long-range transport of POPs in the Arctic. Pucko et al. (2010) presented evidence that both geophysical and thermodynamic conditions in sea ice are important in determining pathways of accumulation or rejection of hexachlorocyclohexanes. Further study by Meyer and Wania (2008) focused on organic contaminant amplification during snowmelt, concluding that there are essentially two patterns of organic contaminant enrichment in snow meltwater: one leads to preferential elution with the early meltwater fractions, and the other leads to enrichment of particle-sorbed substances in late meltwater fractions. These results provide an important starting point for any in-depth discussion of POP behavior in ice. However, these findings relate only to POP behavior in ice and snow under specific environmental conditions. Also, the actual ice environment is constantly changing, so it is necessary to investigate POP behavior in ice under different environmental conditions.

Based on laboratory simulation experiments, this study was meant to provide results on distribution and release of 2,4,5-trichlorobiphenyl (PCB29) in ice and partition coefficients of PCB29 in ice water at different temperatures, concentrations, and pH levels, and to verify these results with field investigations. It is hoped that this paper will provide a theoretical basis for studies on the impact of distribution and release of POPs in ice on water environments under different environmental conditions.

2. Materials and methods

2.1. Experimental methods

The PCB29 solution was prepared with distilled water and a PCB29 standard solution (0.005 mg/mL, with acetone as the solvent) after a long period of shaking. We then put the stainless steel barrel filled with PCB29 solution in the device (Fig. 1), which can create experimental conditions close to the freezing condition of natural rivers: freezing from top to bottom. Finally, the solution was frozen in a cryostat, which can control the temperature.

The experiment was organized as follows:

(1) Distribution experiment: One liter of PCB29 solution with a certain concentration and pH value (regulated with NaOH and HCl) was prepared, and completely frozen at a certain temperature. Then, the ice core was cut to three layers from top to bottom, melted, and analyzed.

(2) Release experiment: One liter of PCB29 solution with a certain concentration and pH value was prepared, and completely frozen at -25°C , then melted in the laboratory. Two hundred milliliter of meltwater was collected for every sample during melting and five water samples were analyzed.

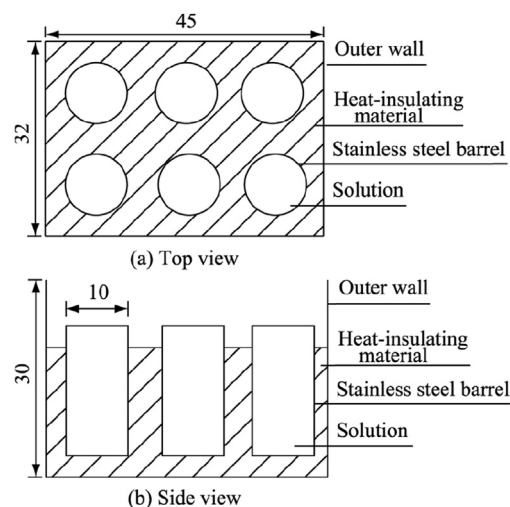


Fig. 1. Sketch of experimental device (units: cm).

(3) Determination of ice-water partition coefficient: One liter of PCB29 solution with a certain concentration and pH value was prepared, and frozen at a certain temperature. The ice-to-water volume ratio was kept at about 1:1. Then ice and water were separated for analysis.

According to these methods, the distribution and release of PCB29 in ice and partition coefficients of PCB29 in ice water at different temperatures, concentrations, and pH levels were investigated.

2.2. Field sample collection

From January 4, 2012 to February 21, 2012 (the freezing period), ice and water samples were collected in the Toudaoguai section of the Yellow River. During the sampling period, the average temperature was -5°C , the average pH value of ice was 7.6, and the average thickness of ice was 46 cm. Ice samples at 20 cm from the surface and 20 cm from the bottom were collected, and then placed in clean stainless steel barrels. Two-liter water samples under the ice were collected and put in brown glass bottles.

The river ice began to melt between February 22 and February 24, 2012 (the average temperature was 3°C). Three two-liter water samples were collected from the shore on February 24, March 13, and March 31.

All samples were transported to the laboratory for analysis.

2.3. Concentration analysis

2.3.1. Extraction of PCB29

This experiment used the solid phase extraction (SPE) method to extract PCB29 from the solution. The specific steps were activating the SPE column, solution-adding, drying, and eluting.

Activating the SPE column consisted of leaching the C18 column at a rate of 1 mL/min with 5 mL acetone, 5 mL hexane, and 5 mL distilled water in turn, to keep the column moist when adding solution. Solution-adding occurred when

the PCB29 solution was allowed to flow through the activated C18 column at a rate of 5 mL/min. Drying occurred after the completion of solution-adding. The column was dried for 12 min with pure nitrogen to remove residual moisture in the column. The samples were then eluted with PCB29 with 5 mL acetone and 10 mL hexane in turn. Then, the eluent was collected.

2.3.2. Detection of PCB29

A gas chromatograph equipped with an electron capture detector was used to determine the concentration of PCB29 based on the retention time and the peak area.

(1) Gas chromatographic conditions

At the inlet, the temperature was 300°C, the pressure was 0.12 MPa, and the carrier gas flowed at a rate of 2 mL/min. At the gas chromatography-electron capture detector (GC-ECD, 63Ni), the temperature was 300°C. The dimensions of the SPB-1 chromatographic column were 30 m × 0.32 mm × 0.25 μm. The temperature elevation program of the column was as follows: the initial temperature was 120°C and remained so for 18 min. The temperature was then increased to 180°C at a rate of 5°C/min, and remained constant for 5 min. The temperature finally reached 240°C at a rate of 10°C/min and remained at 240°C for 20 min.

Other conditions were as follows: the carrier gas was high-purity nitrogen, with a flow rate of 56 mL/min; the split ratio of the split injection was 6; the injection volume was 1 μL; and the quantitative method was the external standard method.

(2) Standard chromatogram of PCB29

PCB29 standard solutions (0.005 mg/mL) were respectively diluted with acetone to 5.0, 4.0, 3.0, 2.0, and 1.0 μg/mL. PCB29 was then detected according to the gas chromatographic conditions described above. The standard curve of PCB29 is shown in Fig. 2.

(3) Calculation of PCB29 concentration

The PCB29 concentration was calculated with the following equation:

$$C_2 = \frac{M_2 C_1 Q_1}{M_1 Q_2} \quad (1)$$

where C_2 is the concentration of PCB29 in the sample (μg/L), C_1 is the concentration of PCB29 in the standard solution (μg/mL), M_1 is the peak area of PCB29 in the standard solution, M_2 is the peak area of PCB29 in the sample, Q_1 is the

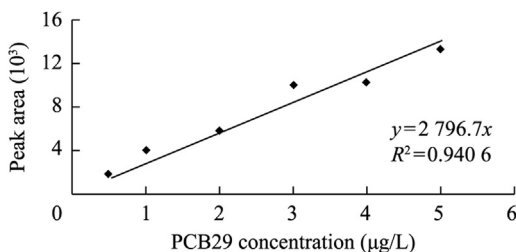


Fig. 2. Standard curve of PCB29.

extracted solution volume of the sample (1 mL), and Q_2 is the sample volume (L).

2.4. Quality control

The equipment and tools that were in contact with PCB29 solution were all made with stainless steel or glass, so as to prevent PCB29 from being absorbed by organic material. The following measures were adopted to control the quality of analysis of PCB29 concentration: After the PCB29 solution was ultrasonic-cleaned using deionized water, the glassware was heated at 250°C for 5 h in a muffle furnace to remove organic pollutants. Recovery rate tests for about 10% of the samples were conducted, and the recovery rate was between 76% and 80%, which met the requirements of control. Parallel experiments for about 10% of the samples were conducted, and the relative standard deviation was less than 15%.

3. Results and discussion

3.1. Distribution of PCB29 in ice

After PCB29 solutions (with a concentration of 20 μg/L and pH value of 6.9) were completely frozen at different temperatures, the concentrations of PCB29 in ice all presented a tendency to increase progressively with depth (Fig. 3). When solution was freezing from top to bottom, the freezing process could actually be characterized as the process of water purification (Döppenschmidt and Butt, 2000). When the solution froze, PCB29 was discharged into lower ice continuously, and then froze at the bottom before the solution froze completely. Because of the rapid freezing process, some PCB29 remained in the upper ice. Therefore, PCB29 contents were lowest in the upper ice and highest in the lower ice. This distribution pattern is similar to that of typical phenolic compounds in ice, with phenolic compound concentration being lowest in the earlier-freezing outer ice and highest in the later-freezing inner ice (Gao, 2009).

Fig. 4 describes the distribution of PCB29 in upper and middle-layer ice in Fig. 3. It can be seen that for PCB29 solutions with the same concentration, along with the reduction of the freezing temperature, PCB29 concentrations increased gradually in the early-freezing upper and middle-layer ice.

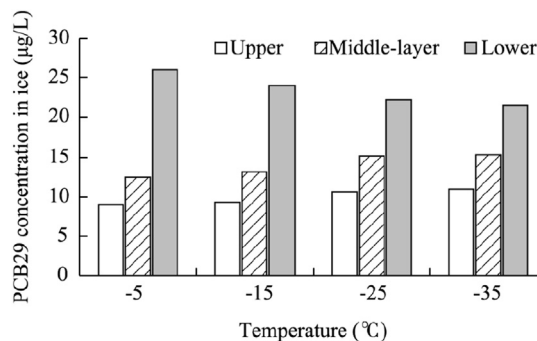


Fig. 3. Distribution of PCB29 in ice at different temperatures.

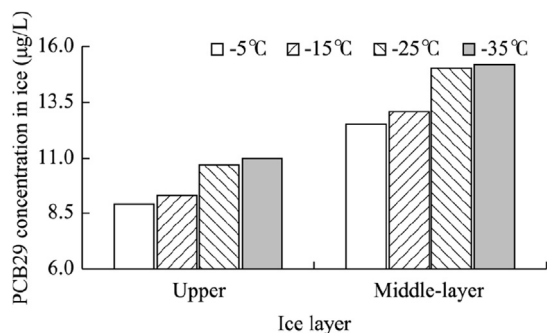


Fig. 4. Distribution of PCB29 in upper and middle-layer ice at different temperatures.

This is due to the fact that the branching shape and nucleation number that ice generated at different temperatures were not the same. At a lower temperature, a larger area is required by the solution to release the latent heat. Thus, the solution produces more branches when the freezing temperature is lower. The branches capture impurities and the impurity concentration increases in ice (Chen et al., 2010). Therefore, as the freezing temperature decreased, the PCB29 concentrations in the early-freezing upper and middle-layer ice increased gradually.

Similarly, when different concentrations of PCB29 solutions (pH = 6.9) were completely frozen at -25°C , the PCB29 concentrations in ice all increased from top to bottom (Fig. 5). These are also the result of solution freezing from top to bottom, with the freezing being the process of water purification (Döppenschmidt and Butt, 2000). In addition, when solution concentration increased, there was more PCB29 in the upper ice. Thus, during the freezing process, the higher the PCB29 concentration was, the worse the effect of freezing purification. This result is in accordance with the distribution law of phenolic compounds in ice: when the solution concentration increases, more phenolic compounds are found in earlier-freezing outer ice (Gao, 2009).

After PCB29 solutions (20 µg/L) with different pH values were completely frozen at -25°C , the distribution of PCB29 in ice was varied (Fig. 6). As shown in Fig. 6, under the acidic condition, the PCB29 concentration in the middle-layer ice was higher than that in the upper and lower ice. Under the neutral condition, the PCB29 concentration increased

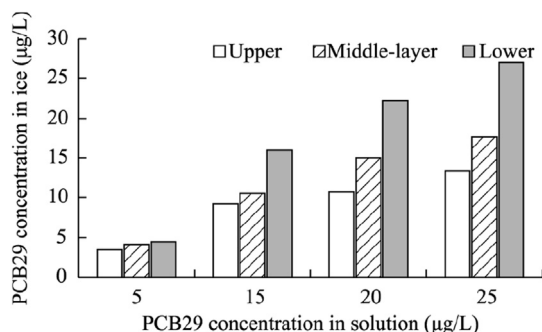


Fig. 5. Distribution of PCB29 in ice with different PCB29 concentrations in solution.

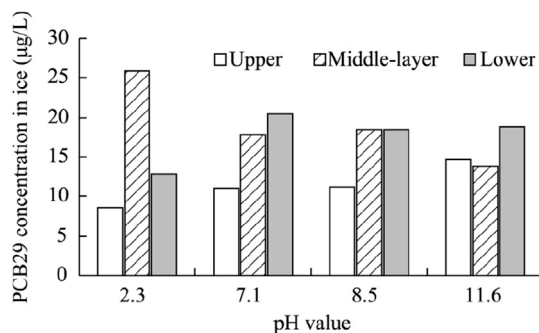


Fig. 6. Distribution of PCB29 in ice with different pH values.

progressively with depth. Under the weak alkaline condition, the PCB29 concentration in the upper ice was minimal and concentrations in middle-layer and lower ice were close to one another. Under the alkaline condition, PCB29 concentrations were about the same in upper and middle-layer ice, and concentrations in lower ice were the highest. These facts show that strong acidic and alkaline conditions have some effect on the distribution of PCB29 in ice. In the upper ice the PCB29 concentration remained low, but in the lower ice the PCB29 concentration was not necessarily at its highest level. The reason is that the variation of pH affected the structure and properties of the ice and changed the charge of the PCB29, leading to changes in distribution.

3.2. Release of PCB29 from ice

After different concentrations of PCB29 solutions (pH = 6.9) were completely frozen at -25°C , the pattern of release of PCB29 during ice melting period at room temperature was basically consistent: on average 41.6% of PCB29 was released rapidly in the early meltwater, and then the remaining PCB29 was released uniformly (Fig. 7). This is

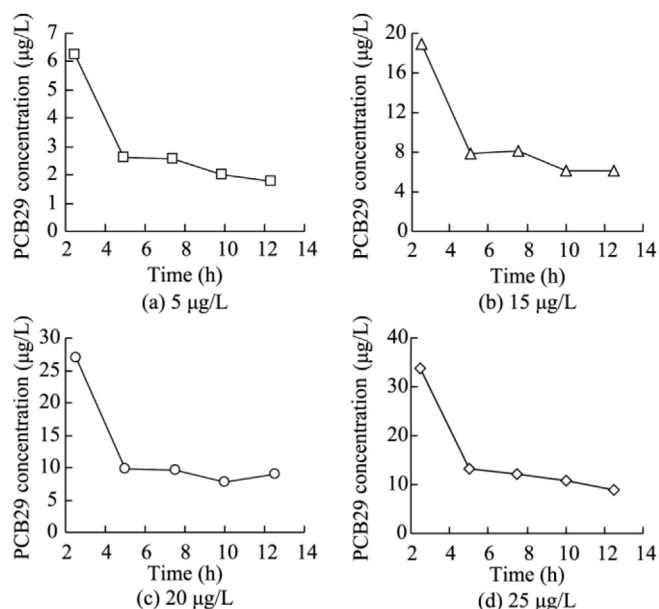


Fig. 7. Effect of PCB29 concentration in solution on release of PCB29 from ice.

because of the fact that, during the freezing process, some PCB29 accumulated on the ice edge and did not enter internal ice (Cho et al., 2002; Klanova et al., 2003). Once ice started to melt, the PCB29 was quickly released. Meanwhile, the PCB29 that was entrapped in ice crystals during ice growth—the entrapment procedure of PCB29 was similar to brine expulsion from sea water (Weeks and Ackley, 1989)—was released during late melting. This release pattern resembles that of organic contaminants from snow (Meyer and Wania, 2008).

When PCB29 solutions (20 µg/L) with different pH values were completely frozen at -25°C, the maximum release of PCB29 during ice melting period at room temperature all occurred during the first period, while the release trend was different during late melting. Under the acidic condition the release showed a tendency to increase. There was a uniform release under the neutral condition. Under the alkaline condition, the rate of release first increased and then decreased (Fig. 8). Thus, pH has a certain influence on the late release. According to the effect of pH on the distribution of PCB29 in ice, it can be inferred that the variation of pH affected the structure and properties of the ice and changed the charge of PCB29, resulting in changes in late release.

3.3. Distribution of PCB29 in ice water

The experiments on the distribution of PCB29 in ice water show that, at different concentrations, temperatures, and pH levels, PCB29 concentrations in the water phase were all higher than those in ice, and partition coefficients (ice/water) of PCB29 were 0.37–0.55, 0.43–0.55, and 0.42–0.55, respectively (Fig. 9). That means that, on average, 32% of PCB29 entered the ice when the solution froze, and most of the PCB29 was still in the water phase. This can be explained by two theories: one is that freezing is the process of water purification (Döppenschmidt and Butt, 2000), and PCB29 was discharged continuously from ice and entered the unfrozen solution; the other is the liquid-solid phase equilibrium theory that eutectic transformation occurred when the solution froze, causing precipitation of PCB29 from ice (Olivier et al., 2001). Thus, in ice water, the majority of PCB29 entered the water phase, and a lesser amount remained in the ice.

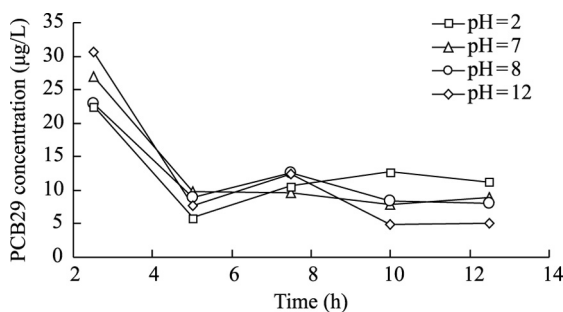


Fig. 8. Effect of pH value on release of PCB29 from ice.

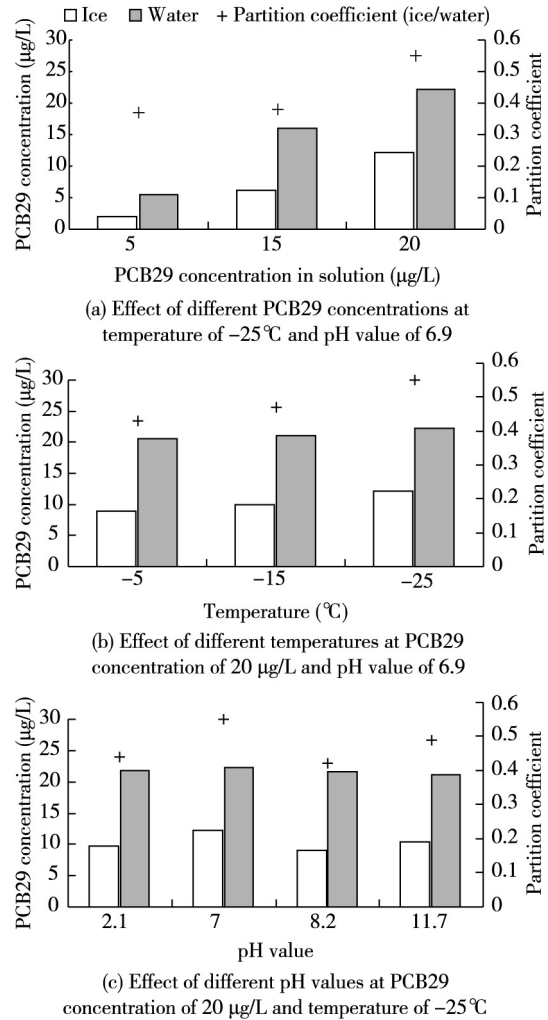


Fig. 9. Concentrations and partition coefficients of PCB29 under different conditions.

3.4. Field investigations

In order to verify the reliability of laboratory experiment results, a field study was carried out.

In the freezing period, PCB29 concentrations in the lower ice were all higher than in the upper ice in the Toudaoguai section of the Yellow River (Fig. 10). This result coincides

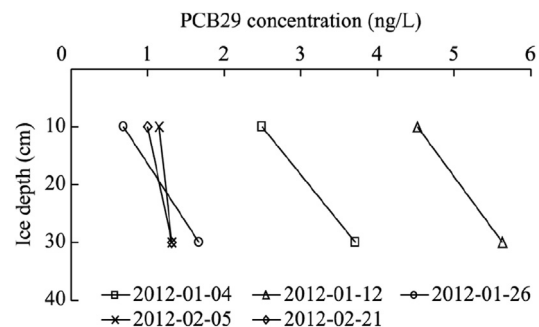


Fig. 10. Vertical distribution of PCB29 in ice of Toudaoguai section of Yellow River in freezing period.

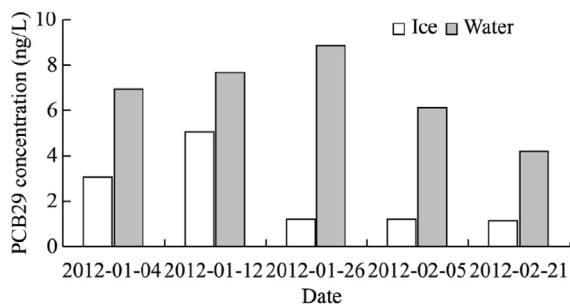


Fig. 11. PCB29 concentrations in ice and water of Toudaoguai section of Yellow River in freezing period.

with the results of laboratory experiments, and the concentration of PCB29 in ice increased progressively with depth. In addition, PCB29 contents in water were all greater than in ice (Fig. 11). Based on calculations, the average PCB29 concentration in water was three times that in ice. This also verifies the laboratory experiment results regarding the distribution law of PCB29 in ice water. The distribution of PCB29 in ice water suggests that water-body pollution is worse than that of ice in the freezing period. Thus, water quality problems during the freezing period cannot be ignored.

When the river ice started to melt, the PCB29 concentration in water increased significantly (Fig. 12). This further proves that a large amount of PCB29 in ice was released quickly in the first melting period, leading to temporary concentration maxima in water. Pronounced concentration peaks of organic contaminants, coinciding with the ice melting period, have also been observed in other places, such as river catchments on Cornwallis Island in Arctic Canada (Loseto et al., 2004), Bow Lake and its tributaries in the Canadian Rocky Mountains (Lafrenere et al., 2006), the St. Lawrence River and four of its tributaries in Canada (Quemerais et al., 1994; Pham et al., 2000), and the German Karst region (Simmleit et al., 1986). The potential for ice melting to cause temporary concentration maxima in water has been predicted using simulation models (Daly and Wania, 2004). It is also worth noting that the ice melting in temperate regions could pose a risk to the aquatic ecosystem during early spring, when many life forms are at a

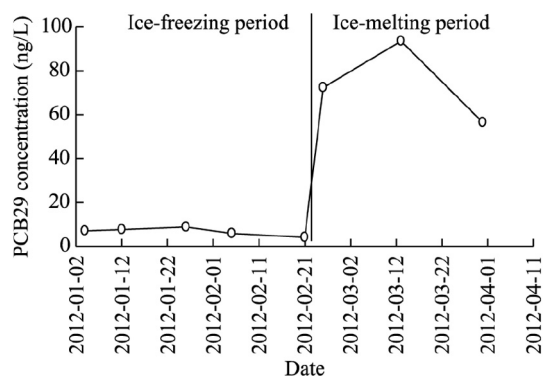


Fig. 12. PCB29 concentrations in water of Toudaoguai section of Yellow River.

vulnerable stage of development (Hickie et al., 1995; Vieites et al., 2004). Therefore, more attention should be paid to water quality and the ecosystem during ice melting.

4. Conclusions

(1) The concentration of PCB29 in ice increases progressively with depth at different temperatures and concentrations. This result aids in the understanding of the fate of PCB29 in ice. Strong acidic and alkaline conditions have some effect on the distribution of PCB29 in ice. In the upper ice, the PCB29 concentration remains low, but in the lower ice the PCB29 concentration is not necessarily at the highest level.

(2) At different concentrations and pH levels, a large amount of PCB29 will be released quickly at the early melting stage, resulting in water quality deterioration, which is likely to affect the water ecosystem. Therefore, more attention should be paid to water quality and the ecosystem during ice melting. The pH value has some effect on the late release of PCB29 from ice, and the late release is uneven and has no regularity.

(3) In ice water, at different temperatures, concentrations, and pH levels, the majority of PCB29 enters the water, with a lesser amount remaining in the ice, meaning that water-body pollution in the freezing period should not be ignored.

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