Screening of 102 Organic Pollutants in Groundwater along the Beijing-Hangzhou Grand Canal in China By GC×GC-TOFMS

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Abstract
Screening of 102 organic pollutants in groundwater along the Beijing-Hangzhou Grand Canal in China by GC×GC-TOFMS. A total of 45 samples were collected. The targets of the investigation involve multiple types of organic pollutants such as Polycyclic aromatic hydrocarbons (PAHs) and their derivatives, phthalates (PAEs), phenols, anilines, polychlorinated naphthalenes (PCNs), polychlorinated biphenyls (PCBs) et al. The results showed that naphthalene, fluoranthene and phthalates are commonly detected compounds. There are 8 categories of organic pollutants detected. The highest concentration of 4-nitrobiphenyl is as high as 430 μg/L, and other targets were detected at the higher concentration in the sample. It means groundwater in the sites have been polluted by micro organic pollutant.

Keywords: Organic pollutants, Groundwater, GC×GC-TOFMS, Screening

1. Introduction
Groundwater plays a pivotal role in sustaining human activities, especially in arid environments with scarce surface water resources (Lezzaik et al., 2018). It is a limited ecological resource representing a small percentage of the total water distribution. Groundwater is also an important source of drinking water (Bei et al., 2019) and industrial and agricultural water (Lamastra et al., 2016). The safe use of water for human consumption is well known to be affected by typical toxic algae bloom that can even lead to the shutdown of drinking water networks (Balest et al., 2016). The contribution from groundwater is vital; perhaps as many as two billion people depend directly upon aquifers for drinking water, and 40% of the world’s food is produced by irrigated agriculture that relies largely on groundwater. While the pollution of groundwater is also getting worse. Such as pesticides, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and other organic pollutants (Arias-Estève et al., 2008; F. J. et al, 2013; Lamastra et al., 2016). And the groundwater pollution risk is also very high. In general, groundwater pollution is less polluted than surface water. However, with the development of social economy, the content and type of organic pollutants in groundwater are gradually increasing, and the situation of groundwater pollution is becoming more and more severe. There are many sources of pollution in groundwater, such as sewage from factories, untreated wastewater discharge, and agricultural activities. This paper mainly conducts screening of micro organic pollutants in several major cities along the Grand Canal and rural groundwater.

2. Methods and Materials

2.1 Sample collection and pretreatment
Groundwater samples (n=45) from 4 provinces including Hebei, Shandong, Jiangsu and Zhejiang along the Beijing-Hangzhou route in China were collected during September 14 to 25, 2017. The samples are mainly derived from groundwater supply sources, irrigation wells, factory sewage rivers and drinking water wells. The collected samples were stored in a 1L clean brown bottle in a cryogenic incubator filled with ice and transported back to the laboratory for testing as soon as possible. Liquid-liquid extraction (LLE) was used as pretreatment because it has advantages of non-selectivity, versatility, and high recovery. Samples were extracted by three steps: neutral, basic and acidic, the extracted organic phase were dehydrated with anhydrous sodium sulfate and concentrated to 1mL by rotary evaporation, nitrogen gas purging for GC×GC-TOFMS analysis. The 102 pollutant standards include PAEs, PAHs and PCBs mixed standards and 59 individual standards (AccuStandard, USA).

2.2 Instrumental analysis
All experiments were performed using time-of-flight mass-spectrometer Pegasus (LECO Corporation, USA) coupled with an Agilent 7890B Gas Chromatograph GC×GC-TOFMS (Agilent, Palo Alto, CA, USA). The 1D column was a DB-5MS (30m×0.25 mm×0.25 μm, Agilent Technologies, USA), and the 2D column was a Rxi-17Sil MS with dimensions of 10m×0.1mm×0.10 μm film thickness, similar to 50% phenyl/50% dimethyl polysiloxane (Restek, USA).
3. Results and Discussion

The concentration of compounds in each province is shown in Figure 1. There are 41 samples of at least one organic pollutant detected in 45 groundwater samples. The total sample detection rate was 91.1%; A total of 41 species of 102 organic pollutants were detected, and the detection rate of the components was 40.2%. Among all of groundwater samples, the samples came from Dezhou, Shandong Province in China have the most types of pollutants, and 26 of organic pollutants were detected, with sample detection rate of 65%. Followed by Jiaxing, Zhejiang Province, a total of 19 organic pollutants were detected, the sample detection rate was 47.5%; There are 16 organic substances detected in Cangzhou, Hebei Province, with sample detection rate of 40%.

Among the organic pollutants detected, the top four in the concentration detection are naphtalene, fluoranthen, diisobutyl phthalate and dibutyl phthalate respectively. The detection frequency rates are 56%, 34%, 27%, and 27%, respectively. This is related to the prevalence of these organic pollutants in the environment. Eight kinds of polycyclic aromatic hydrocarbons, phthalates, phenols, sulfates, anilines, polychlorinated naphtalenes, chlorobenzenes and nitrobenzenes were detected in samples. Among them, polycyclic aromatic hydrocarbons have the highest detection rate, which is related to the widespread use of fossil fuels.

The concentration of micro organic pollutants detected in groundwater samples along the Beijing-Hangzhou Grand Canal in China ranges from 0.41-430 μg/L. Among the detected organic pollutants, the concentration of 4-nitrophenyl in the Dezhou area of Shandong Province was the highest, reaching 430 μg/L; Followed by aniline in the region at a concentration of 241 μg/L. This may be related to local factory sewage. 4-Nitrophenyl and aniline are carcinogenic, and were listed in World Health Organization International Agency for Research on Cancer's list of cancers (1987). It was shown that the groundwater in Shandong Dezhou in China has a certain degree of pollution. It is necessary to further trace its pollution source for the safety of the groundwater.

4. Conclusion

The micro organic pollutants were generally detected in groundwater samples taken along the Beijing-Hangzhou Canal in China, but the overall concentration is not high in addition to Dezhou sample. The micro pollutants detected mainly involve 8 kinds of polycyclic aromatic hydrocarbons and phthalates et al and 4-nitrophenyl was detected at the highest concentration of 430 μg/L. It is necessary to strengthen the investigation and evaluation of organic pollution in groundwater to ensure water quality safety.

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