

# Screening of polar pesticides in groundwater in Hebei Province, China

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## Abstract

As a big agricultural country, China has a relatively high pesticide usage in unit area, which is three times higher than developed countries. About 80% of pesticides directly enter the soil and the water through leaching or surface runoff during the usage of pesticides. In particular, some of the polar compounds are easier to migrate than other compounds, causing pollution of surface water and groundwater. The groundwater samples in Hebei Province, a major agriculture province in China, were screened by multi-residue liquid chromatography-tandem mass spectrometry for two consecutive years in 2014 and 2015. The results showed that among 44 polar compounds, 27 pesticides were detected in 2014 and 19 in 2015. Atrazine-desethyl-desisopropyl, 2,4-D and fomesafen were 434.3 ng/L, 711.5 ng/L and 508.2 ng/L respectively, which were significantly higher than those in other provinces in China. Atrazine and its metabolites were detected in both years. Except for Atrazine-desethyl-desisopropyl, other components were detected in high concentration in 2014. The detected concentrations of bentazone, hexaconazole, triadimenol, and triazolone were similar in the two years. Pesticides such as methomyl, isopropyl, diniconazole and imazethapyr were detected in 2014, but not in 2015, which is presumably related to the actual use of pesticides.

**Keywords:** Screening, polar pesticides, groundwater, liquid chromatography-tandem mass spectrometry.

## 1. Introduction

With the widely usage of pesticides in agriculture in China, the pollution of groundwater caused by pesticides is grown into one of the most critical environmental problems. Especially polar pesticides can easily enter the groundwater since they are easier to dissolve in water and migrate via leaching or surface runoff. Many countries have conducted researches on pesticide pollution of surface water and groundwater. In 1991, United States Geological Survey (USGS) started National Water-Quality Assessment Program (NAWQA), aiming at 75 pesticides and 8 degradation products. Owing to the limitation of analytical method and equipment, in China, researches on detection and screening of pesticide residues mainly focus on food and medicines. Relative

compounds in groundwater are needed to be fully investigated.

As one of the biggest major agriculture provinces in China, Hebei Province have highly representativeness. Therefore, we collected samples in Hebei Province for two consecutive years in 2014 and 2015. Using multi-residue liquid chromatography-tandem mass spectrometry, we screened samples for 44 pesticides.

## 2. Experimental Method

### 2.1. Sampling and sample pretreatment

The sampling sites included farmland, landfill, villages and cities. Using 1.0L brown sample bottle, we collected 47 groundwater samples in 2014 and 60 samples in 2015.

Each groundwater sample is added into a 1000mL brown glass bottle, mixed with BDMC and fluconazole-D (10 $\mu$ L, 1mg/L). HLB (500mg) column was activated by 5mL methanol and 5mL water. Then, samples were loaded with the speed up to 1mL/min. Following, 2mL water was required to purify the column, then pumping about 30min to ensure that there was no water exist. After that, the column was centrifuged 20min (2500r/min) and eluted by 6mL methanol which was collected in KD bottle. The eluent was concentrated to 0.5mL using nitrogen blow (35 $^{\circ}$ C). Finally, aldicarb-D<sub>3</sub>, carbaryl-D<sub>3</sub>, tebuconazole-D<sub>6</sub> (10 $\mu$ L, 1mg/L) were added into the bottle, and then the sample was transferred into 2mL sample bottle for LC/MS/MS.

### 2.2. HPLC-ESI-MS/MS

LC condition: kinetex C18 column (100 mm  $\times$  3.00 mm  $\times$  2.6 $\mu$ m, Phenomenex Ltd, USA); Mobile phase: 0.1% formic acid water (phase A) and acetonitrile (phase B). The separation of sample adopted gradient elution mode; column temperature was 40 $^{\circ}$ C; sample volume was 10  $\mu$ L.

MS condition: ion source was ESI source, according to the characteristics of different compounds to choose positive mode or negative mode; electrospray voltage (IS) was 5000 V; ion source temperature was 600  $^{\circ}$ C; collision gas (CAD): 5psi; curtain gas (CUR): 20psi; GS1: 60psi; GS2:

**Table 1.** Concentration of identified compounds

| Target compound              | Year 2014                    | Year 2015                    |
|------------------------------|------------------------------|------------------------------|
|                              | Maximum concentration (ng/L) | Maximum concentration (ng/L) |
| Carbofuran                   | 4.41                         | 1.73                         |
| Carbaryl                     | 1.64                         |                              |
| Isoprocarb                   | 12.63                        |                              |
| Diniconazole                 | 4.33                         |                              |
| Tebuconazole                 | 2.80                         | 1.98                         |
| Propiconazole                | 4.37                         | 17.77                        |
| Propoxur                     | 5.68                         | 22.19                        |
| Fenobucarb                   | 4.74                         | 0.86                         |
| Methomyl                     | 26.64                        |                              |
| Hexaconazole                 | 0.51                         | 0.42                         |
| Triadimenol                  | 5.83                         | 4.19                         |
| Trihydroxy-Carbofuran        | 2.05                         | 12.86                        |
| Atrazine                     | 231.16                       | 107.75                       |
| Atrazine-desethyl            | 115.22                       | 106.00                       |
| Atrazine-desisopropyl        | 48.66                        | 41.38                        |
| Atrazin-desethyl-desisopropy | 233.53                       | 434.34                       |
| Bentazone                    | 10.77                        | 12.92                        |
| Dursban                      | 1.07                         |                              |
| Hexythiazox                  | 2.10                         |                              |
| Propamocarb                  | 9.36                         |                              |
| Imazethapyr                  | 68.81                        |                              |
| Prochloraz                   | 24.78                        | 1.31                         |
| Triazolone                   | 9.14                         | 1.68                         |
| Carbendazim                  | 219.40                       | 352.21                       |
| Isoproturon                  | 0.97                         |                              |
| Phoxim                       |                              | 3.87                         |
| 2,4-D                        | 22.21                        | 711.75                       |
| Fomesafen                    | 9.14                         | 508.24                       |

### 3. Acknowledgements

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60psi; scanning mode was multiple reaction monitoring (MRM).

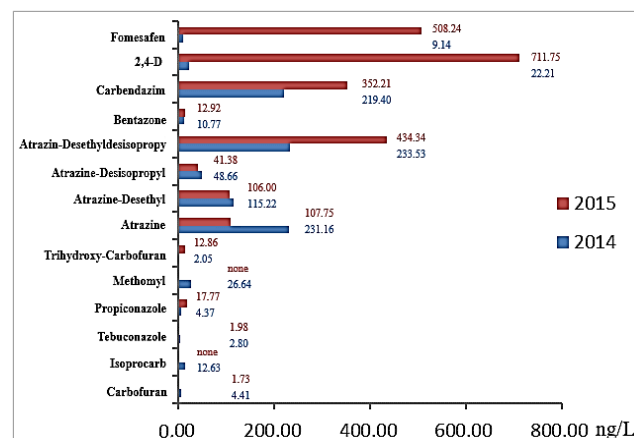
### 4. Results and Discussion

Among 44 target compounds, 27 compounds were identified in the samples for 2014 and 19 compounds identified in the samples for 2015. While aldicarb, Metolcarb, aldicarb-sulfone, aldicarb-sulfoxide, methiocarb, oxamyl, cymoxanil, ethoprophos, pymetrozine, dimethoate, diethofencarb, Pirimicarb, chlortoluron, molinate, iprobenfos and fluazinam were not found in both years. The maximum concentration of identified compounds are shown in Table 1.

### 5. Conclusion

Hebei was found a wider variety of pesticides with high concentration. For example, the maximum concentration of Atrazine-desethyl-desisopropyl (434.34 ng/L), Fomesafen (508.24 ng/L) and 2,4-D (711.75 ng/L) in Hebei are far over 0.1 µg/L which is the European ground water quality standard (EC, 2006 for pesticides).

The major differences of typical pesticides between the results from two years are shown in Figure 1. Carbaryl, isoprocarb, diniconazole, methomyl, chlorpyrifos, hexythiazox, propamocarb, imazethapyr and isoproturon were only detected in 2014, while the concentration of tebuconazole, triadimenol, hexaconazole and bentazone was similar in both two years. Which was speculated that is connected to the local usage of pesticides.



**Figure 1.** Main differences between 2014 and 2015

near an uncontrolled municipal solid waste landfill in Kolkata, India, *Global NEST Journal*, **19**, 367-376.

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