

CHARACTERIZATION OF ORGANIC HALOGENS IN PRECIPITATION IN BEIJING BY HYBRID NAA

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Abstract

The precipitation samples, collected from Beijing from 2006.5 to 2007.12, were studied by a hybrid neutron activation analysis (NAA) method for the concentrations and distribution of persistent extractable organic halogens (EPOX). The average concentrations of EPOCl, EPOBr and EPOI were 102, 0.18, and 0.31 $\mu\text{g/L}$, respectively. Most of EPOCl measured in the precipitation were unknown. Significant correlations between the logarithms of the concentrations of EPOCl and EPOBr ($r=0.65$, $p<0.0001$) or EPOI ($r=0.72$, $p<0.0001$) and between the concentrations of EPOBr and EPOI ($r=0.79$, $p<0.0001$) were observed, which suggested that EPOCl, EPOBr and EPOI in precipitation in Beijing might mainly come from the same sources. There were no clear seasonal trends for the concentrations of EPOX observed.

Introduction

Organic halogens, especially organic chlorinated compounds, such as polychlorinated biphenyls (PCBs), polychlorinated dibenzo-dioxins/furans (PCDD/Fs) and organochlorine pesticides (OCPs), listed as persistent organic pollutants (POPs) by the Stockholm Convention, are stable in the environment, undergo long-range atmospheric transport, and possess the ability of bioaccumulation through food chain and impose serious threat to human health and the environment. Over the past decades, thus, these compounds have been extensively investigated in various environmental matrices¹⁻³. However, due to the huge number of organic halogens with different chemical and physical properties, individual analysis of them would be impractical and presently also impossible. Recently, more and more studies indicated that traditional analytical methods such as gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) could not provided enough information to reflect the actual OCs contamination levels^{4,5}. Instrumental neutron activation analysis (INAA) is the most convenient and quick method, and is also the only analytical method currently available for simultaneously determining EOCl, extractable organobrominated (EOBr) and extractable organoiodinated compounds (EOI) in an extract⁶⁻⁸.

The atmosphere is one major pathway, where semi-volatile organic compounds of a persistent nature are cycling. In the last decades, these organic contaminants in the atmosphere and their deposition behaviors have been increasingly investigated in American and European countries. In particular, wet deposition has been monitored, as dry deposition only contributes to a minor extent to the total deposition of PCBs and OCPs. However, there are few papers available on study of the organic contaminants in wet deposition in China. In this study, precipitation samples collected from Beijing were analyzed by a hybrid NAA method to characterize the

persistent extractable organic halogens.

Material and methods

Precipitation samples for this investigation were collected on the rooftop of a building, about 10 m above the ground level. Precipitation was collected in stainless-steel funnels and then drained through a column containing cleaned XAD-2 resin. XAD-2 resin was then Soxhlet-extracted in acetone: hexane (1:1, v/v) for 24 h and the extracts were concentrated to about 10 mL. To measure extractable persistent organochlorinated (EPOCl), extractable persistent organobrominated (EPOBr), extractable persistent organoiodinated (EPOI), the extract was treated with concentrated sulfuric acid, followed by washing, drying and concentrated to 4 mL. One aliquot was taken for EPOX analysis and the other was left from the OCPs and PCBs analysis.

INAA was carried out at a neutron flux of $8.0 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$ for 15-min in a miniature neutron source reactor at China Institute of Atomic Energy, Beijing, China. The analyses were based on γ -peaks from ^{38}Cl ($t_{1/2} = 37.24$ min, $E_{\gamma} = 1642$ keV), ^{80}Br ($t_{1/2} = 17.68$ min, $E_{\gamma} = 617$ keV), and ^{128}I ($t_{1/2} = 24.99$ min, $E_{\gamma} = 443$ keV). The counting time was 15 min.

The blank values of Cl, Br, and I were corrected for the experimental values. ^{24}Na ($t_{1/2} = 15.0$ h, $E_{\gamma} = 2754$ keV) was simultaneously determined as a check for contamination caused by inorganic halogens⁹. The results indicated that ^{24}Na was not found in the sample and blank extracts, which meant that the contamination from inorganic halogens was negligible. The detection limits of NAA were 50 ng, 7.0 ng and 2.5 ng for Cl, Br and I, respectively.

Results and Discussion

The average concentrations were 102.5 $\mu\text{g/L}$ (11.2~1641.8 $\mu\text{g/L}$) for EPOCl, 0.18 $\mu\text{g/L}$ (0.01~1.79 $\mu\text{g/L}$) for EPOBr, and 0.31 $\mu\text{g/L}$ (0.01~6.47 $\mu\text{g/L}$) for EPOI. It is obviously that EPOCl was the major fraction of the organic halogens in the precipitation, which accounted for more than 99 % of EPOX. Similar results have been reported for aerosols⁶ and pine needles^{10,11}. This distribution pattern is similar with each other because most of pollutants in the local atmosphere are present as organic chlorinated compounds. Laniewski et al. also found that most absorbable organic halogens in rain and snow were organic chlorinated compounds⁸. Further reason is that organic chlorinated compounds might be more difficult to be transformed and degraded than organic brominated and organic iodinated compounds in the environment¹⁰. Moreover, the relative proportions of the known organochlorines (84 PCB congeners+10 OCPs) analyzed by GC-ECD to total EPOCl were 0.03-1.44 %, which implied that most of EPOCl measured in rainwater were unknown.

As shown in Fig 1, significant correlations between the logarithms of the concentrations of EPOCl and EPOBr ($r=0.65$, $p<0.0001$) or EPOI ($r=0.72$, $p<0.0001$) and between the concentrations of EPOBr and EPOI ($r=0.79$, $p<0.0001$) (Fig. 1) were observed, which suggested that EPOCl, EPOBr and EPOI in rainwater might mainly come from the same sources.

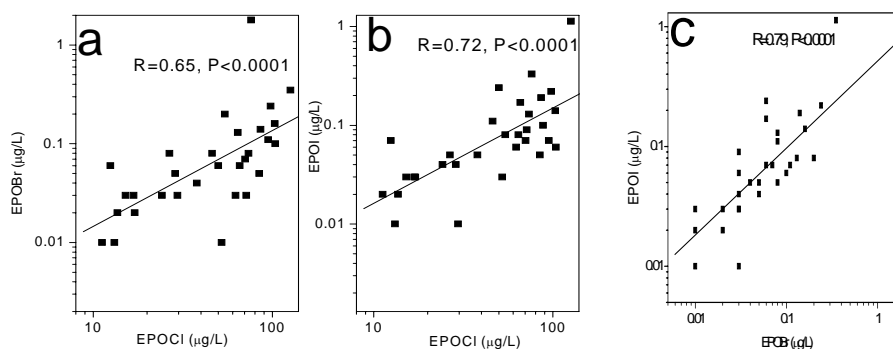


Fig 1 Relationship of EPOCI and EPOBr or EPOI, and EPOBr to EPOI in precipitation in Beijing

There were no clear seasonal trends for the concentrations of EPOX. This may be attributed to arid spring, autumn, winter and strong rainfall in summer 2006-2007. It was found that the concentrations of EPOCI, EPOBr, and EPOI were higher in May 2006, which likely attributed to agricultural activities, such as plowing and fertilizing in spring/early summer. The concentrations of EPOX reached the highest in May with very low rainfall, while the lowest in July in 2006 and 2007 with very high rainfall. It may be interpreted by the so-called 'dilution effect' for scavenging out the particles in air during the early phases of precipitation, with the subsequent 'clean' precipitation diluting the contaminant concentrations¹³. Therefore, smaller rainfall is expected to contain higher particles with plenty of organic halogens¹⁴.

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References

1. Chen J.S., GAO J.Q., *J Assoc Off Anal Chem* 1993; 76: 1193.
2. Kömp P., McLachlan M.S., *Environ Sci Technol* 1997; 31: 886.
3. Atlas E., Glam C.S., *Science* 1981; 211: 163.
4. Kiceniuk J.W., Holzbecher J., Chatt A., *Environ Pollut* 1997; 97: 205.
5. Watanabe I., Kashimono T., Kawzno M., *Chemosphere* 1987; 6: 847.
6. Xu D., Dan M., Chai Z., Zhuang G., *Atmos Environ* 2005 ; 39: 4119.
7. Gustavson K., Jonsson P., *Mar Pollut Bull* 1999; 38: 723.
8. Haynes D., Mosse P., Levay G., *Mar Pollut Bull* 1995; 30: 463.
9. Gether J., Lunde G., Steinnes E., *Anal Chimica Acta* 1979 ; 108: 137.
10. Xu D., Zhong W., Deng L., Chai Z., Mao X., *Environ Sci Technol* 2003 ; 37: 1.
11. Xu D., Deng L., Chai Z., Mao X., *Chemosphere* 2004; 57: 1343.

12. Laniewski K., Boren H., Grimvall A., *Chemosphere* 1999; 38: 393.
13. Ligocki M.P., Leuenberger C., Pankow J.F., *Atmos Environ* 1985; 19:1619.
14. Koester C.J., Hites R.A., *Environ Sci Technol* 1992; 26: 1375.