CHARACTERISATION OF MOLECULAR INTERACTIONS BETWEEN BROMINATED PERSISTENT POLLUTANS AND SOIL USING X-RAY ADSORPTION FINE STRUCURE (XAFS) SPECTROSCOPY

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Abstract

The interactions between pollutants in soil and constituents of the soil happen on a molecular level. For this reason techniques suitable for studies on a molecular scale have to be investigated. One such technique is X-ray absorption fine structure (XAFS) spectroscopy. In this study XAFS spectra were collected for three brominated persistent pollutants (Br-POPs): 6-Bromo-2,4,5-trichlorophenol (BrTriClP), Pentabromophenol (PentaBrP), and 3,3′,5,5′-Tetrabromobisphenol A (TBBA). The substances were selected to represent a range in the number of bromine, position of the bromine, and number of additional halogens. Furthermore, spectra for BrTriClP adsorbed to black carbon (BC) and natural organic material (NOM) were also collected. The studied substances displayed unique spectra, which indicate that other brominated organic persistent pollutants may be characterized by XAFS as well. Furthermore, the spectra for BrTriClP changed as it was adsorbed to BC and NOM, demonstrating that XAFS may be used to characterize how Br-POPs interact with different materials and surfaces present in soil.

Introduction

Once deposited on or released in soil, a compound's ability to be transported to other compartments of the environment is controlled by its availability. High availability indicates that the compound may spread and potentially pose a threat to other parts of the environment. The interactions between pollutants in soil and constituents of the soil happen on a molecular level and hence knowledge about these interactions is essential. Although brominated persistent pollutants (Br-POPs) are likely to adsorb to organic matter or similar material or phases present in soil due to the Br-POPs liphophilicity, the final processes limiting the availability of Br-POPs include intermolecular forces such as π-bonding, hydrogen bonding, and dipole-dipole interactions.[1] In order to study these intermolecular forces, a technique that is able to in describe the molecular structure of Br-POPs, as well as changes in the molecular structure caused by intermolecular forces, is needed. One such technique is X-ray absorption fine structure (XAFS) spectroscopy. The XAFS spectrum is often divided into two regions: X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy. The later, EXAFS, is more suitable for determining distances between central and neighboring atoms and the number of neighboring atoms, while XANES is suitable for observing changes in central-atom coordination with changes in experimental or environmental conditions.

The aim of the presented study was to assess in what detail XAFS spectroscopy could be used to describe the molecular interactions of Br-POPs with materials found in soil. Three substances differing in symmetry, number of bromine, number of other halides and their relative positions were included in the study (Fig. 1): 6-Bromo-2,4,5-trichlorophenol (BrTriClP), Pentabromophenol (PentaBrP), and 3,3′,5,5′-Tetrabromobisphenol A (TBBA). The bromophenols were selected as they may be related to existing knowledge concerning chlorophenols, a class of substances in the past used as fungicides and herbicides.[2] TBBA

was chosen as it represents a previously widely used a brominated flame retardant (BFR) with shown thyroid hormonal and estrogenic activity.[3] Black carbon (BC) and natural organic material (NOM) were used as analogues for materials present in soil. BC was included as it is a well now adsorbent of aromatic substances, including phenols, due to strong π-interactions between the aromatic structures in the carbon and aromatic rings of pollutants.[4] NOM was included as it represents a material that besides π-interactions may offer other ways of interacting with pollutants, e.g. through hydrogen bonding and dipole-dipole interactions.

Material and Methods

Brominated organic substances: 6-Bromo-2,4,5-trichlorophenol (BrTriClP), 98 %; Pentabromophenol (PentaBrP), 96 %; and 3,3′,5,5′-Tetrabromobisphenol A (TBBA), 97% from Sigma Aldrich (Stockholm, Sweden) were mixed with BN using a mortar prior to analysis to suitable concentration. BrTriClP dissolved in MeOH was evaporated into NORIT SA4 (NORIT, Amesfort, The nertherlands) activated black carbon (BC) and Suwannee River aquatic natural organic material (NOM), resulting in concentrations of 8000 ppm BrTriClP in both matrixes. The BrTriClP was then allowed to equilibrate with the matrixes during further evaporation for 14 days. Data were collected at the superconducting multi-pole wiggler beam line i811 at MAX-lab (Lund University, Sweden) with 1.5 GeV beam energy and 100-200 mA electron current. Br K-edge (13.474 keV, calibrated with PentaBrP) spectra were recorded at room temperature at ambient atmospheric pressure in fluorescence mode using a double crystal monochromator (Si [111]). The fluorescence signal was detected with a Lytle detector filled with Ar with samples positioned at 45° to the incident beam. The monochromator was detuned 25% to remove higher order harmonics. XAFS data (If/I0 against energy) were collected at an exposure time of 2-4 s for each data point with 5 eV steps from 150 eV to 50 eV before the edge, 0.25 eV steps from 45 eV before the edge to 30 eV after the edge, 0.5 eV steps from 30 eV to 100 eV after the edge, 1eV steps from 100 to 200 eV after the edge, and 3 eV from 200 eV to 800 eV after the edge. Data were aligned, normalized and averaged using the Athena software.[5] Each XAFS spectrum represents the average of 3 scans. For reduction and fitting of EXAFS data, the software WinXAS 2.3 was used. Above the absorption edge, a cubic spline fit was used to remove the background and the data were k^3-weighted to enhance data at higher k-values.[6] Possible backscattering from atoms in other molecules, including interactions with BN, were assumed to be small and were therefore not considered in the modeling. The BrTriClP model used for the final fits to EXAFS data included single scattering (SS) paths for first, second, third and fourth shell contributions. During the fitting procedure, the coordination number (CN) for all FEFF paths were fixed to the theoretical value, and the amplitude reduction factor (S_0^2) was determined to be 1.0, which is equal to previous reports [7]. The edge energy (ΔE_0) was allowed to vary, but kept internally constant for all shells in a sample.

Results and Discussion

The X-ray absorption near edge structure (XANES) spectra for BrTriClP, TBBA, and PentaBrP are compared in Fig. 1. As can be seen, the edge energy (A) and the height and position of the minor peak (B) are different for all three substances. Spectra for BrTriClP and TBBA have similar major peaks (C) and the spectra in the post-edge region (D) largely overlap. The factors influencing differences in the XANES region could not be assessed, but likely the number of bromine, total number of halogens, and number of phenyl rings are of importance. However, XANES spectra of additional substances are needed in order to verify this. Previous studies on organohalogen compounds using X-ray spectroscopy has shown that the pre-edge spectral features of halides are caused mainly by low-energy features corresponding to the $1s \rightarrow \pi^*$ and $1s \rightarrow \sigma^*$ transitions of the halogen–carbon bonds.[8]

The XANES spectra for BrTriClP mixed with BN, adsorbed to BC, and adsorbed to NOM are shown in Fig 2. As can be seen, the edge energy (A) is similar for all spectra, with a slightly higher energy for BrTriClP adsorbed to NOM. The height of the minor peak (B) is similar but the positions are different for all three spectra. Similar differences can be observed for the major peaks (C), although the peak for BrTriClP mixed with BN is slightly higher. The spectra for BrTriClP adsorbed to BC and NOM largely overlap in the post-edge

region (D). The factors influencing the differences in the XANES spectra of BrTriClP adsorbed to BC and NOM could not be assessed in detail, but the BC spectra was assumed to be more influenced by π-interactions between the aromatic structures in BC and BrTriClP in comparison to the NOM spectra. The spectra for BrTriClP mixed with BN was assumed to influenced by hydrogen bonds, as this constitutes the major interactions present in crystal phenol.[9] The spectra displayed in Fig. 2 may also represent the spatial distribution of the BrTriClP molecules with BrTriClP mixed with BN having an crystaline ordered spatial distribution, followed by BrTriClP adsorbed to BC which also may display ordered spatial distribution. BrTriClP adsorbed to NOM is likely to display a more disordered spatial distribution in comparison to the other two spectra.

The spectra displayed in Fig 2. clearly shows that the interactions between Br-POPs and soil materials may be observed by XANES. However, in order to determine the kind of interactions the molecular structure and molecule distortions of BrTriClP has to be determined in great detail, both for a single compound and when adsorbed to different surfaces or materials. By observing how molecular structure and molecule distortions change for different regions of the BrTriClP molecule during adsorption, the type of interactions can be deduced. Both the molecular structure and molecule distortions can be calculated using the EXAFS portion of the XAFS spectra.
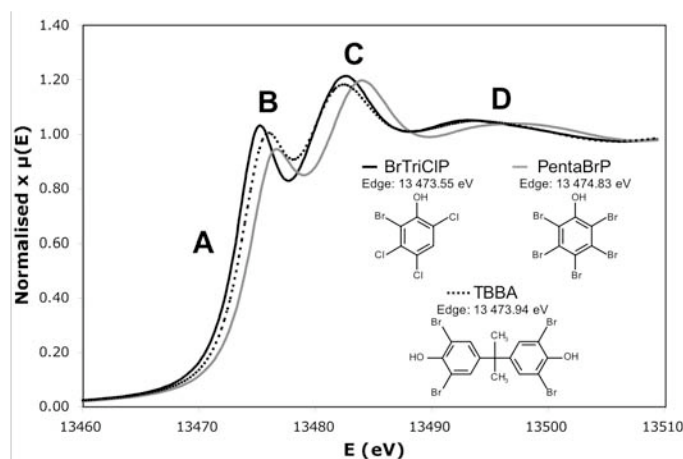

Fig. 1. X-ray absorption near edge structure (XANES) region, molecular structure, and edge energy of 6-Bromo-2,4,5-trichlorophenol (BrTriClP, solid black); 3,3′,5,5′-Tetrabromobisphenol A (TBBA, dashed); and Pentabromophenol (PentaBrP, solid grey). A: Edge region; B: Minor peak; C: Major peak; and D: post edge region.
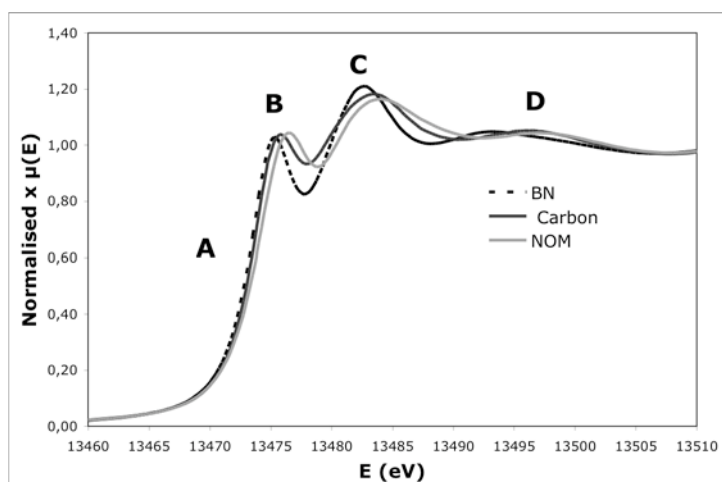

Fig. 2. X-ray absorption near edge structure (XANES) region of 6-Bromo-2,4,5-trichlorophenol (BrTriClP) mixed with BN (dashed black), adsorbed to black carbon (Carbon, dark grey), and adsorbed to natural organic matter (NOM, light grey). A: Edge region; B: Minor peak; C: Major peak; and D: post edge region.

The molecule structure and molecular distortions (σ^2) of BrTriClP mixed with BN, based on the EXAFS (spectra not shown) portion of the XAFS spectra, are given in Table 1 together with theoretical values. Theoretical distances were calculated using data from similar structures.[9-11] and calculated parameters were in good agreement with both the theoretical values and literature data.[11] In general, atoms in *ortho* position were the most difficult to assess properly, especially the oxygen atom. The σ^2 of this atom was fixed to the σ^2 of corresponding halogen in *ortho* position during the fist iterations in order to find an acceptable R (Å) value. Once a reasonable R value was found, this was fixed and a new σ^2 value for the oxygen was calculated. Similar calculations should be carried out for BrTriClP adsorbed to BC and NOM and be compared to the values presented in Table 1 in order to deduce the type of interactions between BrTriClP, BC and NOM.

Table 1. Final fits of distances (Å) and Debye-Waller factors (σ^2, with unit Å^2) between bromine (Br) and atoms present in 6-Bromo-2,4,5-trichlorophenol (BrTriClP). Calculations were based on the EXAFS spectra of BrTriClP. Theoretical distances were calculated using data from similar structures.[9-11]

	Calculated distance	Theoretical distance	Debye-Waller factor
Br - adjacent carbon	1.88	1.87	0.003
Br - *ortho* carbon	2.85	2.83	0.008
Br - OH	3.15	3.04	0.003
Br - *ortho* Cl	3.18	3.20	0.006
Br - *meta* carbon	4.14	4.134	0.003
Br - *meta* Cl	5.54	5.53	0.005
Br - *para* carbon	4.71	4.65	0.004

In conclusion, BrTriClP, TBBA, and PentaBrP, displayed unique XAFS spectra and differences in the spectra caused by interactions with soil materials could also be observed. Hence, our results support further characterization of other brominated organic persistent pollutants using XAFS. Future research should focus on providing detailed molecule structures, based on a combination of XANES and EXAFS, in order to better assess the type of interactions observed.

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