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X-Ray Absorption Spectroscopic Studies of As-Humic Substances in the Ground Water of the Taiwan Blackfoot Disease Area

H.-C. Wang,[1] H. P. Wang,[2] C.-Y. Peng,[2] H.-L. Liu,[3] H.-L. Huang[2]

[1] Division of Chest Medicine, Department of Medicine, Veterans General Hospital-Kaoshiung, Kaoshiung, Taiwan, Republic of China
[2] Department of Environmental Engineering, National Cheng Kung University, Tainan City, Taiwan, Republic of China
[3] School of Health Science, Kaoshiung Medical University, Kaoshiung, Taiwan, Republic of China

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Arsenic (As) in aquatic systems has a complex chemistry with oxidation-reduction, ligand exchange, precipitation and adsorption reactions (Ferguson and Gavis 1972; Cullen et al. 1989). Human activities, such as burning of fossil fuels and the mining processing of sulfide minerals can increase the concentration of As in soil and ground water (Ferguson and Gavis 1972). As being prevalent in the ground water are considered carcinogenic. During 1962-72, a blackfoot endemic peripheral vascular disease occurred at the southwest coast of Taiwan. Over 90% of blackfoot disease victims settled in Chai-Yi (Pu-Tai and I-Chu) and Tainan (Shiao-Chia and Pei-Men) counties. The possible etiology factor of the blackfoot disease was thought to be associated with the ground water that was drunk by local inhabitants. For many years, it is generally thought that As in artesian wells was the main cause of the fatal disease (Tseng 1977; Chen et al. 1992; Chen et al. 1994). Animal tests of As, however, have proved unsuccessful to induce cancer (Ferguson and Gavis 1972). On the contrary, humic substances (HS) in ground water were found leading to the blackfoot disease (Lu 1990; Lu et al. 1990; Lu et al. 1994). The debate for the cause of the blackfoot disease in Taiwan is still under controversy. Studies of the blackfoot disease in Taiwan have focused attention on the epidemiology and animal tests (Lu et al. 1994; Chiou et al. 1995). Chemical structure of the toxic As species in ground water in the blackfoot disease area is still not well understood. Speciation information such as bond distance and coordination number of select excited atoms can be determined by extended X-ray absorption fine structural (EXAFS) spectroscopy. X-ray absorption near-edge structural (XANES) spectra can also provide information about the oxidation state and coordination geometry of the excited atoms. Thus, the main objective of this work was to study the speciation of As in the ground water, that might cause the blackfoot disease. Specifically, we have reopened two sealed wells and sampled the As contained ground water in the balkfoot disease area and investigated the speciation of As by EXAFS and XANES spectroscopies.

MATERIALS AND METHODS

Representative ground water samples were obtained from the old sealed wells located at Pu-Tai (Chai-Yi county) and Pei-Men (Tainan county) in the southwest coast of Taiwan. Concentrations of As in well waters were measured by ICP-MS

Correspondence to: H.-C. Wang

(ELAN, Model 5000). The measurements of pH values, D.O. (dissolved oxygen) and temperatures of the well water samples were conducted on site during sampling (Table 1). Arsenic species in each well water (30L) was uptaken onto high purity γ-Al_2O_3 (Merk) (about two grams) in a column (od 1 inch) adsorber at 298 K for about 24 hours. The As species concentrated (on Al_2O_3) samples were dried in vacuum for about two hours and ground to <200 mesh for X-ray absorption (EXAFS and XANES) studies.

Table 1. Concentrations (ppb) of toxic metals in ground water of the blackfoot disease area in the southwest coast of Taiwan.

Well Location	Pu-Tai	Pei-Men	
D.O. (mg/L)	0.5	1.5	
Temperature (K)	300	299	
pH	7.3	7.5	
Toxic Metal Concentration (ppb)			Limit
As	529	633	50
Cr	2.7	0.9	50
Ni	3.3	0.9	100
Cu	7.4	1.8	1000
Hg	1.8	0.3	2
Pb	3.9	1.8	50

XANES and EXAFS spectra were collected on the Wiggler beamline at the Taiwan Synchrotron Radiation Research Center (SRRC). Data were measured in the fluorescence mode in the region of the As K edge (11867 eV) at 298 K. EXAFS spectra were analyzed on the measured oscillatory structure, which appears at 50-1000 eV above the absorption edge. The raw absorption data in the region of 50 to 200 eV below the edge position were fit to a straight line by the least-square algorithms. The fitted pre-edge background curves were extrapolated throughout all data range and subtracted and normalized to minimize the effect of sample thickness. The isolated EXAFS data was normalized to the edge jump and converted to the wavenumber scale. Fourier transformation of the scattering curve yielded a radial structure function (RSF). The k^2-weighted EXAFS spectra were Fourier transformed to R space over the range between 2.7 and 11.5 $Å^{-1}$. The multiple-scattering X-ray absorption modeling program FEFF 8 was used in the RSF calculation for the model structure. The EXAFS data were also analyzed using the UWXAFS 3.0.

The near-edge structure in an absorption spectrum covered the range between the threshold and the point at which the EXAFS began. Semi-quantitative analyses of the XANES spectra were conducted by the least-square fitting of linear combinations of standard spectra to the spectrum of the sample. XANES spectra of As model compounds such as $NaAsO_2$ (Sigma), As_2O_3 (Sigma), Na_2HAsO_4 (Fluka), As_2O_5 (ACROS), As(III)-HS and As(V)-HS were also measured on the Wiggler beamline. The As(III) and As(V)-HS complexes were prepared by chelation of 5% $NaAsO_2$ and Na_2HAsO_4 with humic acid (Fluka) at 300 K for one hour and dried at 380 K for eight hours.

RESULTS AND DISCUSSION

Concentrations of toxic metals in ground waters in the blackfoot disease area are shown in Table 1. It is very clear that the concentration of As in the ground waters exceeded the limits of the EPA water quality (50 ppb) by at least ten times. In 1960s, for instance, the average concentration of As in that ground water was 460 ppb at Pu-Tai (Chia-Yi County, Taiwan).

The derivatives of XANES spectra can reveal more detailed information, which cannot be clearly observed in XANES spectra. The As K-edge XANES spectra and their first derivatives of As model compounds and As uptaken on Al_2O_3 are shown in Figure 1. The first derivative feature of XANES spectra appeared at 11870 eV and 11874 eV indicated the existence of As(III) and As(V), respectively. The first derivative feature for As(III) was well separated from As(V) by about 3-4 eV. XANES spectra of As in ground water (uptaken on Al_2O_3) in the blackfoot disease area are also shown in Figure 1 . Mainly As(V) was observed at 11874-11875 eV.

The XANES spectra were also expressed mathematically in a LC XANES fit vectors, using the absorption data within the energy range of 11860-11890 eV. XANES spectra of As model compounds such as $NaAsO_2$, As_2O_3, Na_2HAsO_4, As_2O_5, As(III)-HS and As(V)-HS were also measured on the Wiggler beamline. We found that As_2O_5 and As(V)-HS were the main As species in the ground water of the blackfoot disease area. A small amount of As(III)-HS was also observed. Relative contents of the As species in the ground water of the blackfoot disease area with an over 90% reliability in the fitting process are shown in Table 2. Interestingly, we found that in the Pei-Men ground water, the amount of the As(III)-HS species was relatively abundant (a fraction of about 0.13). Generally, the toxicity and mobility of As(III) in the environment is much greater than that of As(V) by at least ten times (Foster et al. 1998). Accordingly, in 1962, the blackfoot disease cases for the inhabitants using the Pei-Men well water were found significantly.

Basic understanding of As in the blackfoot disease area at the molecular scale is essential for determining the toxic As species that may cause blackfoot disease. Information on the atomic arrangement in terms of bond distance, coordinate number and kind of near neighbors, thermal and static disorder can generally be obtained by EXAFS spectroscopy. The EXAFS spectra were recorded and analyzed in the k^2 range between 2.7 and 11.5 $Å^{-1}$. An over 99 % reliability of the EXAFS data fitting for As species was obtained. In all EXAFS data analyzed, the Debye-Waller factors (σ^2) were less than 0.012 $Å^2$. The Debye-Waller factor is the root-mean-square distribution (RMSD) of the internuclear distances and represents both dynamic and static disorder. The structural parameters obtained from the best fit to the EXAFS data are shown in Table 3. EXAFS of As model compounds

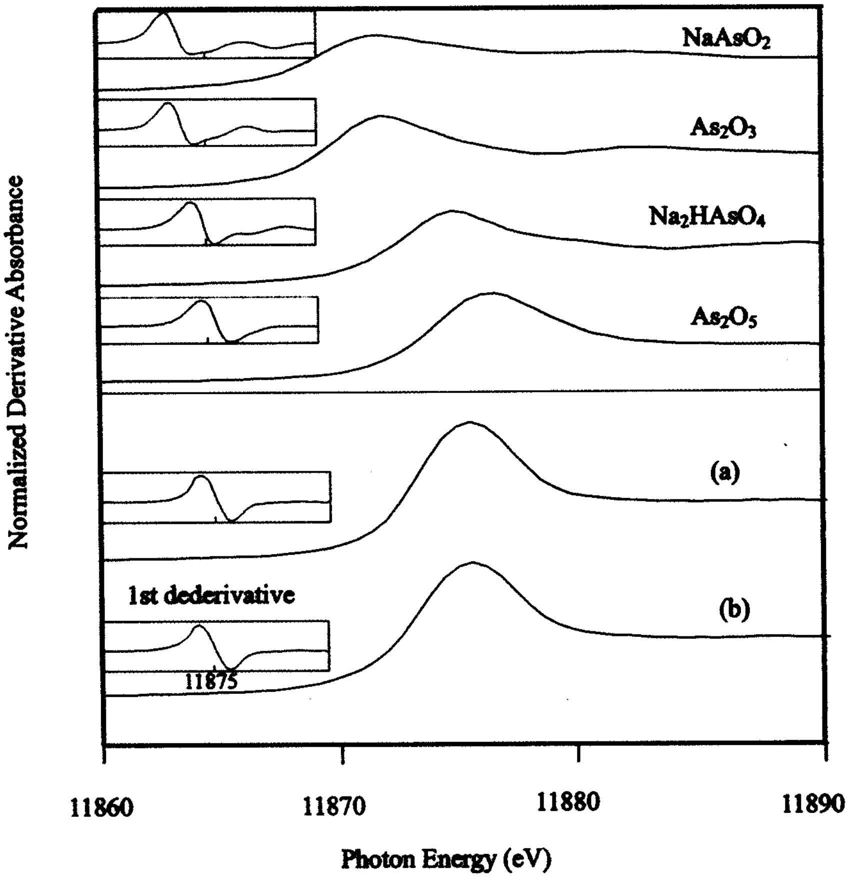

Figure 1. Normalized As K-edge XANES spectra (and their 1st derivatives all shown in the corner) of As model compounds ($NaAsO_2$, As_2O_3, Na_2HasO_4, As_2O_5) and As in the (a) Pu-Tai and (b) Pei-Men ground waters (uptaken on Al_2O_3) in the blackfoot disease area.

($NaAsO_2$, As_2O_3, Na_2HAsO_4 and As_2O_5) were also measured. As(V) (As_2O_5) was the main As species in the blackfoot disease well water (uptaken on Al_2O_3). By EXAFS, we found that the bond distances of As-O (1st shell) in well water were 1.69-1.70 Å. However, in the second shells, the bond distances of As-(O)-As (3.18-3.29 Å) were less than the normal As(V) (As_2O_5) (3.73 Å).

In the natural water, HS is the abundant organic matter. The function groups (e.g., carboxyl and phenolic groups) of humic substances tend to involve in the complexation with metal ions. On average, more than 50% of the total acidity of humic substances is contributed by their carboxyl functional groups (Xia et al. 1997). In ground water, As might be chelated with natural occuring HS and formed complex species. In the second shells of As in well water, the bond distances of As-C and As-As were 2.84 Å and 3.18-3.29 Å, respectively.

Table 2. Fractions of arsenic species in ground water of the blackfoot disease area studied by XANES.

	Pu-Tai Ground Water	Pe-Mem Ground Water
As_2O_5	0.53	0.54
As(V)-HS[a]	0.44	0.33
As(III)-HS[b]	0.03	0.13

[a] As(V)-HS: complexation of As(V) with humic substances.

[b] As(III)-HS: complextaion of As(III) with humic substances.

Table 3. Speciation parameters of As species in ground waters of the blackfoot disease area.

	Bond Distance (Å)	Coordination Number	σ^2(Å^2)
As in Pu-Tai ground water			
As-O	1.69	7.16	0.005
As-C	2.84	6.49	0.007
As-As	3.29	1.07	0.007
As in Pe-Men ground water			
As-O	1.70	3.80	0.001
As-C	2.84	1.65	0.007
As-As	3.18	1.24	0.007

σ^2: Debye - Waller factor.

As(V) and humic substances generally form octahedral complexes. In contrast, As(III)-HS possesses a structure of tetrahedral complexes. The coordination numbers of As-O for the As(III)-HS rich well water (Pei-Men) was about four. The presence of As-C in the second shells may be caused by innersphere complexation of As and humic substances (Xia et al. 1997).

In summary, As_2O_5 and As(V)-HS were the main As species in ground water of the blackfoot disease area. The bond distance of As-O (1st shell) in well water was 1.69-1.70 Å. In the second shells, bond distances of As-C and As-As were 2.84 Å and 3.18-3.29 Å, respectively. About 46% of As were chelated with humic substances, that was evidenced by the presence of the As-O-C bonding (2.84 Å). Chelations of As(V) and As(III) with humic substances formed octahedral and tetrahedral complexes, respectively. This work illustrates the usefulness of EXAFS and XANES for revealing the speciation of toxic As species in ground water of the blackfoot disease area.

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