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Uptake of Bromide by Two Wetland Plants (*Typha latifolia* L. and *Phragmites australis* (Cav.) Trin. ex Steud)

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The successful use of bromide (Br^-) as a conservative tracer for hydrological tests in wetland systems requires minimal Br^- loss due to plant uptake. The uptake of Br^- by two wetland plants, cattail (*Typha latifolia L.*) and reed grass (*Phragmites australis* (Cav.) Trin. ex Steud), was investigated in greenhouse flow-through microcosms. Concentrations of Br^- and other pertinent constituents in sediment pore water were measured at 2 cm depth increments in the sediment column. The vertical Br^- concentration profiles in the sediments clearly revealed Br^- uptake by *T. latifolia* and by *P. australis*. X-ray spectroscopy studies of bromine in plant samples revealed the accumulation of Br^- in root and leaf tissues. Plant transpiration was found to significantly concentrate dissolved species in sediments and was accounted for in the calculations of Br^- uptake rates. Michaëlis−Menten kinetics satisfactorily describe Br^- uptake by *T. latifolia*. The uptake of Br^- by *P. australis*, however, showed unique features that could not be described using Michaëlis−Menten kinetics. The addition of chloride (Cl^-) effectively inhibited Br^- uptake, and the uptake of Cl^- and Br^- by *T. latifolia* was shown to follow dual-substrate Michaëlis−Menten kinetics. Results of this study indicate that the use of Br^- for tracer experiments in vegetated wetland systems should be evaluated with great caution.

Introduction

Accurate hydrological information is critical for the assessment of contaminant dynamics and the design of environmental remediation strategies. Contaminants are usually transported by surface and groundwater, and the direction and velocity of water flow thus affect their spatial distribution. Chemical tracers are employed in field experiments to determine the direction and velocity of water flow and to estimate key hydrogeological parameters such as porosity, dispersivity, and hydraulic conductivity (*1*). Ideal tracers should be nontoxic, inexpensive, easy to detect in trace amounts, conservative, and present at low background concentrations in nature (*1*).

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Bromide (Br^-) has traditionally been considered an ideal hydrological tracer due to its relatively nonreactive nature and low concentration in soils, having a worldwide average concentration of 0.85 mg/kg (*2*). Numerous experiments involving systems with growing plants, such as the assessment of nitrate dynamics in riparian forests (*3*), or tests of hydraulic conditions in wetland sediments (*4*−*6*) have used Br^- as a tracer. Several recent studies, however, have demonstrated the loss of this tracer under certain experimental conditions and postulated uptake of Br^- by plants as an explanation for its disappearance (*7*, *8*). Many plant species, including barley (*9*, *10*), alfalfa (*10*, *11*), corn (*12*), canola (*10*), sorghum (*13*), potato (*14*), lettuce (*15*), and tomato (*16*), have been implicated in active Br^- uptake.

Wetland systems are among the most productive ecosystems on Earth and perform important ecological, hydrological, and environmental functions. Recently, there has been growing interest in using natural as well as constructed wetlands for removing pollutants from surface runoff, groundwater discharge, or industrial and domestic wastewaters. The design of constructed wetlands and assessment of contaminant-removal capacities of existing wetlands usually requires hydrological information that may depend on the results of tracer tests. The applicability of Br^- as a conservative tracer in wetland environments is contingent on the extent of its uptake by plants. Unfortunately, a thorough understanding of Br^- uptake by common plant species in wetland systems is currently not available.

Rates of Br^- uptake by terrestrial plants have been generally found to be a function of Br^- concentrations (*9*, *11*, *13*, *15*, *16*). Working with excised barley roots, Epstein found that Br^- absorption rates obey Michaëlis kinetics (*9*). Other researchers have reported linear relationships between Br^- supplemented to soils and absorbed by plants (*11*, *13*, *15*, *16*). In studies that examined excised roots, at least two processes that are important to Br^- uptake by plants were overlooked, namely, the upward translocation of Br^- from roots toward shoots and plant transpiration with its effect of concentrating Br^- in the soil/sediment pore water. These processes may enhance ion transport toward roots. In past field and greenhouse experiments that have focused on Br^- uptake by plants, a uniform Br^- concentration throughout the rhizosphere has been generally assumed. The accuracy of such experiments is compromised because plant transpiration and uptake will almost certainly lead to nonuniform concentration profiles of Br^- in the sediments.

Chloride (Cl^-), which is chemically analogous to Br^- and more enriched in natural environments (*1*, *17*), is a probable inhibitor of Br^- uptake by plants (*9*). Therefore, the effect of Cl^- on Br^- uptake needs to be quantified to assess under what conditions Br^- can be used as a conservative tracer.

Halide ions absorbed by plants could remain in inorganic form or undergo transformations into organic species (*18*, *19*). Stable organohalides and inorganic halides that remain in plants could be detected by in situ X-ray spectroscopy technique (*19*), while volatile organic halides, such as methyl bromide, evolve easily from plant tissue into the atmosphere.

The principal objective of this study was to examine Br^- uptake by *Typha latifolia* and *Phragmites australis*, and the effect of Cl^- on Br^- uptake, with the aim to help design and interpret Br^- tracer experiments in wetland sediments. *T. latifolia* and *P. australis* were selected for this study because they represent some of the major plant species in many natural wetlands and are commonly planted in constructed wastewater treatment wetland systems (e.g., refs *20*−*22*) and because the expanding distribution of the invasive *P. australis*

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has raised concerns about the ecological and environmental consequences (*23*). The effect of evapotranspiration on the Br^- concentration profile in sediments, and hence on its uptake kinetics, was highlighted in this research. X-ray absorption spectroscopy data obtained for the root, stem, and leaf tissues were used to confirm the uptake of bromide by both plant species and to determine if stable organobromine chemicals were produced in the plants.

Materials and Methods

Experimental Setup. The experiment was conducted under well-controlled conditions with custom-built microcosms and clean silica sand. Three flow-through microcosms were constructed from plastic buckets (inner diameter: 26 cm; height: 30 cm) by adding a drainage outlet (diameter: ~1 cm) at the center of the bottom. In August of 2002, ASTM standard 20/30 silicon sand (from U.S. Silica) with an average porosity of 0.38 was added to a depth of about 20 cm, and one shoot of *T. latifolia* or *P. australis* was transplanted into each of two different microcosms. The third microcosm was maintained as a control in the absence of plants. A nutrient solution was pumped into the top of the microcosms, which had a drain to discard excess solution and maintain a constant water level above the sediments. Removing water at a constant rate from the bottom of the microcosms with a peristaltic pump achieved a constant infiltration rate into the sediments. The nutrient solution was a modified Hoagland solution and contained 1 mM KH_2PO_4, 2 mM KNO_3, 1.5 mM $Ca(NO_3)_2$, 2 mM $MgSO_4$, 0.5 mM $(NH_4)_2SO_4$, 10 μM $Fe(NO_3)_3$, 9.07 μM $MnSO_4$, 46.3 μM H_3BO_3, 0.73 μM $ZnSO_4$, 0.089 μM $NaMoO_4$, 0.38 μM $CuSO_4$, and 62.5 μM KBr. Solutions for the control and *P. australis* microcosms also contained 2 mM sodium acetate. The water level above the sediments was kept at approximately 3 cm to mimic the constantly flooded nature of wetland systems, and the drainage rate was maintained at 350 mL per day, resulting in a hydraulic retention time, without correcting for evapotranspiration, of about one week (*20*). By late November of 2002, 133 μM KCl was added to the nutrient solutions for all microcosms to study the impacts of Cl^- on the uptake of Br^- by both plant species. Given that the growth of several crops has been shown to remain unaffected by the application of Br^- at levels up to 1250 μM/L (*10*), it was assumed that the effect of Br^- on the growth of both plant species in this study was negligible.

Collection and Analysis of Pore Water Samples. Pore water samples were collected in October and November of 2002 (to determine Br^- uptake) and in May of 2003 (to determine the impact of Cl^- on Br^- uptake). Sampling at 2 cm increments from the sediment−water interface to a depth of up to 20 cm was conducted. About 10 mL of the water sample was needed to measure all relevant chemical species. Therefore, at each depth, pore−water samples were collected from five different locations, 5−10 cm apart from each other. Two milliliter aliquots of water were slowly collected from each location with long stainless needles and syringes. Water samples collected at each depth were then mixed before being passed through 0.45 μm nylon filters (Fisher Scientific). Since the size of the microcosms used in the experiment was relatively large and many plants were growing in a single microcosm, this sampling strategy was implemented to help account for possible variations in the horizontal dimension that might be a concern for pot experiment carried out with single plant.

A Dionex Ion Chromatograph (IC) (model LC20) with a conductivity detector (Dionex CD25) was used to quantify the concentrations of Br^-, Cl^-, and sulfate. The injection loop was 25 μL, and the columns were Dionex IonPak AS-14 and AG14, both with a diameter of 4 mm. The eluent contained 3.5 mM Na_2CO_3 and 1 mM $NaHCO_3$, and the flow rate was 1 mL/min. Standard samples run for quality control purposes showed that the relative standard deviation of chromatographic analysis was usually less than 5%.

X-ray Spectroscopy of Br in Plant and Sediment Samples. Bromine in plant and sediment samples was probed directly using element-specific X-ray absorption spectroscopy (XAS), specifically near-edge measurements at the Br K-edge (13 474 eV). The K-absorption edge of Br and its features in the near-edge region correspond to electronic transitions from the inner shell Br-1s orbitals to vacant atomic and molecular orbitals of Br-4p character. Leaf, stem, and root materials from *T. latifolia* and *P. australis* and portions of a sediment core from the *T. latifolia* pot were sampled in March 2003 and analyzed directly by X-ray spectroscopy. The samples were neither treated with chemicals nor dried or pulverized before their examination. X-ray spectra were acquired at the Stanford Synchrotron Radiation Laboratory (SSRL) on beamline 2−3 using a Si (220) double crystal monochromator and an internal KBr (s) standard. Slit openings were set to 1.0 × 1.8 mm upstream and downstream of the monochromator. All X-ray absorption spectra were collected using sample fluorescence, which was measured using a 13-element Germanium detector. X-ray absorption spectra of Br model compounds (compounds with known Br coordination chemistry) were also acquired to identify the chemical state of Br in plants and sediments.

X-ray data were processed using SixPACK version 0.43 (*24*) and WinXAS version 2.0 (*25*). SixPACK was used for energy calibration and averaging of scans. Averaged fluorescence scans were imported into WinXAS for background correction, normalization, and further spectral analysis. A smooth background was obtained by fitting a first-order polynomial to the preedge region and another first-order polynomial fit to the postedge region normalized the edge jump to 1.0 at 13,540 eV. WinXAS was also used for linear least-squares fitting of experimental data with spectra of model chemical compounds to establish the speciation of Br in the natural samples.

Results

Effects of Plant Transpiration on the Vertical Chemical Species Concentration Profile. In vegetated sediments, evapotranspiration transfers water from the sediments to the atmosphere. If the transpiration rate is either higher or similar to the drainage rate, this process could significantly concentrate the dissolved compounds in the rhizosphere as illustrated by Figure 1.

Evaluation of the loss rate of any reactive species in the rhizosphere under strong plant transpiration requires the aid of a conservative tracer. A detailed profile of a conservative tracer allows for calculation of the fraction of water that a specific layer contributes to the overall plant transpiration, and therefore also the steady-state loss rate of a reactive species in the same sediment layer. In this experiment, sulfate represents a good tracer candidate. There are three pathways that could lead to the loss of sulfate in the microcosm sediments: dissimilatory sulfate reduction, precipitation or adsorption, and plant uptake. Since nitrate was present at millimolar levels in the pore water throughout the domain and denitrification is energetically favorable over sulfate reduction, sulfate reduction should not occur nor was it detected. The fact that sulfate concentrations remained constant in the control microcosm (Figure 2) suggests that no significant amount of sulfate was precipitated or adsorbed to the solid matrix. Sulfur is an essential nutrient and its content in dry plant materials usually ranges from 0.1 to 0.5% (*24*). Given that the loading of sulfate applied to the microcosms was greater than 42 mg day^{-1}, loss of sulfate due to plant uptake was also negligible. The sulfate profiles measured in October and November of 2002 for the

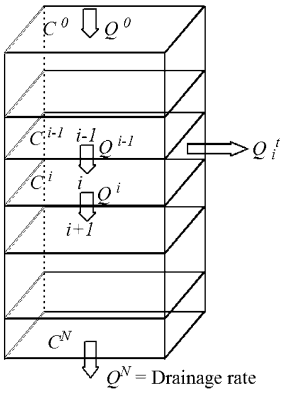

FIGURE 1. Mechanism by which plant transpiration concentrates dissolved species. For cell *i* with a water loss due to transpiration of Q_i^t; an inflow Q_{i-1} with concentration of C_{i-1}; and an outflow $Q_i = Q_{i-1} - Q_i^t$; the concentration in cell *i* at steady state is $(C_{i-1}Q_{i-1})/Q_i$. The outflow rate for the last cell (cell *N*) is the drainage rate. With the known drainage rate and the vertical concentration profile of the conservative species, the transpiration and inflow rates in each cell can be estimated: $Q_{N-1} = C_{N-1}Q_N/C_N$; $Q_{N-1}^t = Q_{N-1} - Q_N$; $Q_{i-1} = C_{i-1}Q_i/C_i$; $Q_{i-1}^t = Q_{i-1} - Q_i$.

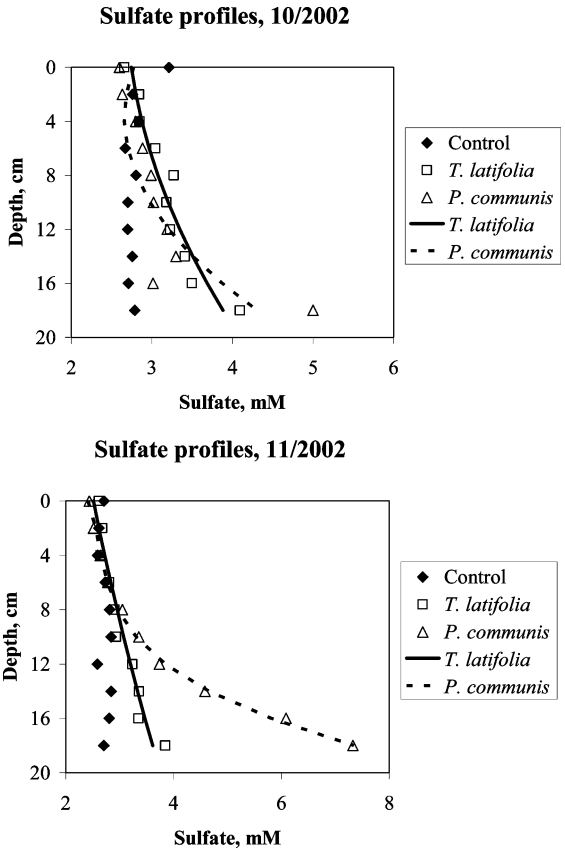

FIGURE 2. Pore water sulfate concentrations in October and November of 2002. Trend lines are the best-fit regression curves. Because of limited sample volume, only one sample was measured. Triple control standards over similar concentration ranges run in parallel indicated that the relative standard deviation was less than 5%.

microcosms are shown in Figure 2. On the basis of the increasing sulfate concentration with depth, it is clear that *T. latifolia* as well as *P. australis* transpired a significant amount of water relative to the drainage rate. Regression lines corresponding to the sulfate profiles were used in the calculation of the evapotranspiration rates to minimize the impact of experimental variations. On the basis of these

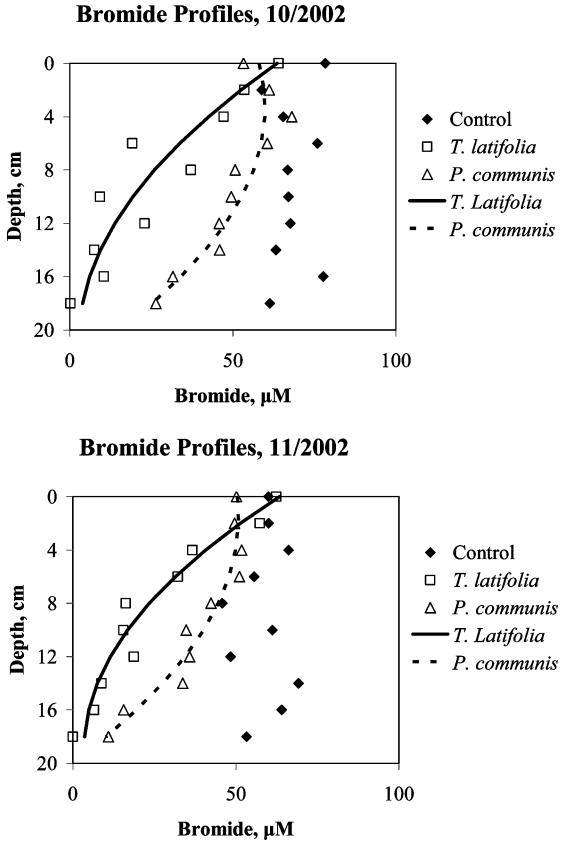

FIGURE 3. Pore−water profiles of Br^- in the absence of Cl^-. Lines represent regression curves against depth (*z*). Because of limited sample volume, only one sample was measured at each depth. Parallel control standards over similar concentration ranges indicated that relative standard deviation was less than 5%.

profiles, water transpired by *T. latifolia* amounted to ~40% of the drainage water for both months. For *P. australis,* this value went from 50% in October to 200% in November.

Uptake of Bromide. Br^- profiles measured during October and November of 2002, shown in Figure 3, suggest an active uptake of Br^- by both *T. latifolia* and *P. australis*. If no uptake occurred, the Br^- profiles would mirror those of sulfate shown in Figure 2. If the uptake of Br^- was a passive process (i.e., Br^- only entered the roots with the water transpired by the plants), the vertical concentration profile of Br^- would remain constant in all three microcosms.

Br^- uptake rates were calculated using eq 1, and a regression of the Br^- concentration against depth (*z*) to obtain smoothened Br^- profiles was used.

$$\mu_i = (Q_{i-1}C_{i-1} - Q_iC_i)/V_i \ (\mu\text{M day}^{-1}\ \text{L}^{-1}) \qquad (1)$$

Here, μ_i represents the Br^- uptake rate in cell *i* in units of μM day^{-1} L^{-1}. Q_i, the vertical flow rates, are derived from the sulfate profiles and the drainage rates, accounting for the effect of the evapotranspiration. The volume of liquid in each cell is about 0.38 L (porosity is about 0.38, and the total volume is about 1 L).

The relationship between the Br^- uptake rate and its smoothened pore water concentration is shown in Figure 4. For *T. latifolia*, a higher Br^- concentration enhanced the Br^- uptake rate monotonically. These uptake rates could be described satisfactorily using the Michaëlis−Menten model (eq 2):

$$\mu_i = 50.2\frac{C_{\text{Br}}}{123 + C_{\text{Br}}} \ (\mu\text{M day}^{-1}\ \text{L}^{-1}) \ (R^2 = 0.99) \qquad (2)$$

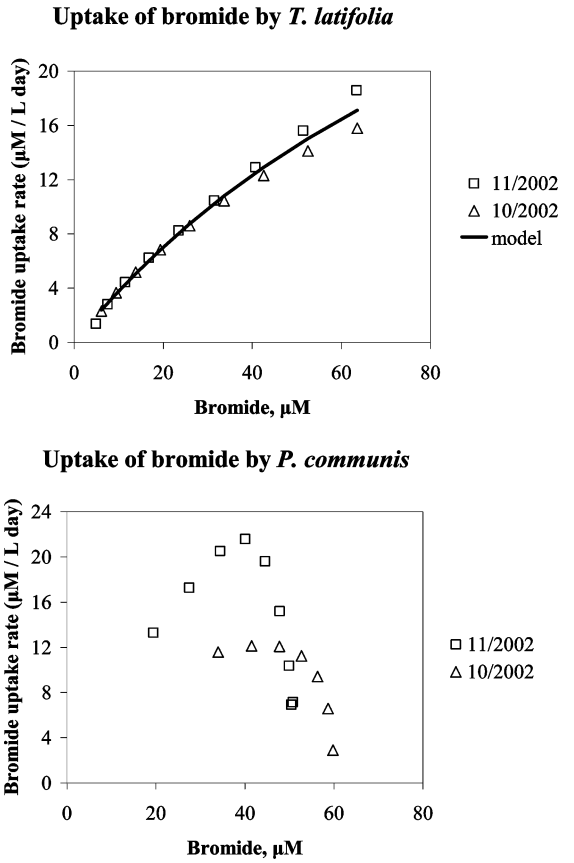

FIGURE 4. Relationships between Br^- concentrations in pore water and its uptake rate by *T. latifolia* and *P. australis*. Uptake of Br^- by *T. latifolia* is described well by the Michaëlis−Menten model (represented by the solid line).

where C_{Br} represents the pore water Br^- concentration. For the case of *P. australis*, this relationship is more complicated and shows less Br^- being taken up at higher pore water Br^- concentrations. As discussed later, there appears to exist a difference in the Br^- uptake rate by *P. australis* between its shallow and deep roots, and this effect needs a more thorough investigation.

Plant root distribution may affect the assessment of Br^- uptake since plant roots may alter the porosity and thus the volume of the liquid phase and since Br^- uptake rate is a function of root biomass. When the microcosms were dismantled in late July of 2003, it was observed that roots of *T. latifolia* and *P. australis* were distributed rather uniformly over the domain. Decomposition of some roots, especially the outer layers of the roots, was observed in both vegetated microcosms. The major portions of the roots appeared to be viable. The total mass of wet roots for the *T. latifolia* and *P. australis* microcosms was 645 and 815 g, respectively. Assuming that the density of the roots is 1 g mL^{-1} (*27*), the volume of roots in the *T. latifolia* and *P. australis* microcosms was 645 and 815 mL. Therefore, at the end of this experiment, the roots of *T. latifolia* and *P. australis* occupied less than 20% of the total void volume, and the results presented here were not corrected for their effect on the porosity.

Effects of Chloride on Bromide Uptake. Cl^- and Br^- are chemically analogous and usually coexist in natural environments, which generally show enrichment of Cl^- relative to Br^- (*1*). It has been reported that Cl^- inhibits Br^- uptake by barley roots (*9*). To investigate the interactions of Cl^- and Br^- during uptake by *T. latifolia* and by *P. australis*, 133 μM KCl was added to the nutrient solution for all three microcosms starting in late November of 2002. In May of

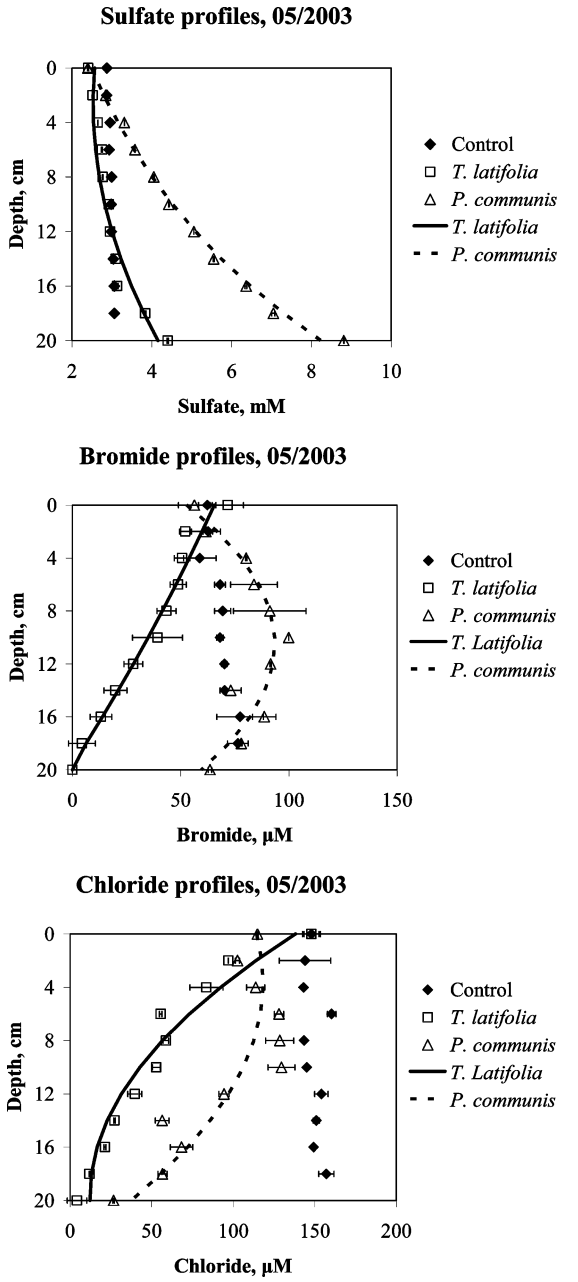

FIGURE 5. Pore−water profiles of sulfate, Cl^-, and Br^- measured in May of 2003. Lines represent regression curves against depth (*z*). Error bars reflect the standard deviation of duplicate measurements. For sulfate, the size of the bars is smaller than the symbol.

2003, pore water samples were collected, and contents of sulfate, Cl^-, and Br^- were determined. Again, the concentration profiles of these anions were fitted as a function of the depth to minimize the experimental variations on the calculation of transpiration and uptake rates (Figure 5).

The uptake of Br^- and Cl^- by *T. latifolia* and Cl^- by *P. australis* is clearly manifest by these profiles. The concentration of Br^- in the *P. australis* microcosm increased with depth in the top 10 cm, presumably due to an enhanced transpiration, as well as an inhibition of its uptake rate by Cl^-. Figure 6 shows the relationships between pore water Br^- and Cl^- concentrations and their respective uptake rates.

Relationships between Cl^- concentration and Cl^- uptake rate for *T. latifolia* and for *P. australis* are very similar and follow the pattern of Br^- uptake by *T. latifolia* (Figures 4 and 6). The simultaneous uptake of Br^- and Cl^- by *T. latifolia*

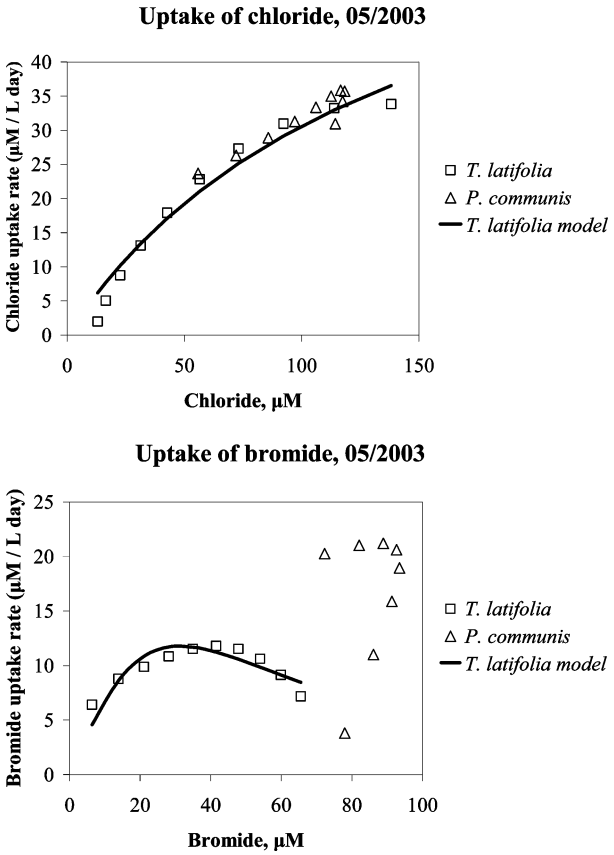

FIGURE 6. Relationships between Br^- and Cl^- concentrations in pore water and their uptake rates by *T. latifolia* and *P. australis*. The lines represent the dual-species uptake model (eq 3) (for *T. latifolia*).

could be described accurately using the dual-substrate Michaëlis−Menten model (*28*)

$$\mu_1 = \mu_{1,\max}\frac{C_1}{K_1\left(1+\frac{C_2}{K_{21}}\right)+C_1} \quad (3)$$

where μ_1 represents the uptake rate of species 1 in the presence of species 2, $\mu_{1,\max}$ is the maximum uptake rate of species 1 under optimal conditions, K_1 and K_{21} are fitted parameters, and C_1 and C_2 are concentrations of species 1 and 2, respectively. K_{21} represents the strength of the inhibition by species 2 on the uptake of species 1. The smaller K_{21}, the stronger the inhibition by species 2 is on the uptake of species 1. Br^- and Cl^- uptake kinetics were modeled for *T. latifolia* only, due to the complexity of the uptake dynamics with *P. australis*. The parameter K_{Br} for Br^- uptake was set to the value calculated earlier for the Br^- uptake in the absence of Cl^-. The results (shown in Figure 6) are

$$\mu_{Br} = 168.4\frac{C_{Br}}{123\left(1+\frac{C_{Cl}}{15.2}\right)+C_{Br}} \quad (R^2 = 0.73) \quad (4)$$

$$\mu_{Cl} = 74.4\frac{C_{Cl}}{143.1\left(1+\frac{C_{Br}}{3.3\times10^9}\right)+C_{Cl}} \quad (R^2 = 0.96) \quad (5)$$

Comparison of $K_{Cl,\ Br}$ (15.2 μM) and $K_{Br,\ Cl}$ (3.3×10^9 μM) suggests that the uptake of Br^- by *T. latifolia* is inhibited by Cl^-, whereas the inhibitory effects of Br^- on Cl^- uptake are negligible.

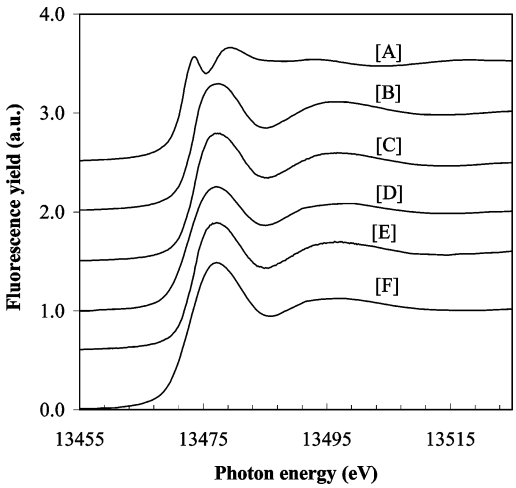

FIGURE 7. X-ray absorption spectra of Br in *T. latifolia* and *P. australis*. (A) 4-Bromophenol standard; (B) KBr (aq.) standard; (C) *T. latifolia* healthy green leaf; (D) *P. australis* healthy green leaf; (E) *T. latifolia* root; and (F) *P. australis* root. a.u. means arbitrary units.

It is important to note that the overall plant mass increased significantly over the duration of the experiment. The average growth rate of *T. latifolia* was estimated at 0.44 g/day, although from November to May, the growth rate might be lower than this average value. For this reason, one should not make a direct comparison of the magnitudes of the October/November and the May Br^- uptake rates since the uptake rates presented here are not normalized per unit plant biomass, which was only measured at the end of the experiment.

Regardless of the presence of Cl^-, the uptake rate of Br^- by *P. australis* follows a complex pattern in terms of the Br^- concentrations in the liquid phase. No simple formulation can describe the observed trends. As shown in Figure 5, due to a combined effect of evapotranspiration and Br^- uptake, the Br^- concentration first increased with depth and then decreased, resulting in identical concentrations of Br^- at different vertical positions in the *P australis* microcosms. When the Br^- uptake rates were then estimated based on these profiles, this resulted in different uptake rates for the same Br^- concentration by roots in shallow sediments (<10 cm) and deep sediments (>10 cm) and in the presence of different Cl^- concentrations, resulting in the Br^- uptake pattern shown in Figure 6, where the breakpoint is at a depth of 10 cm, with the higher uptake rates being depths >10 cm and the lower Cl^- concentrations.

Fate of Halides Absorbed by Plants. Bromine in *T. latifolia* and *P. australis* and in sediment from the *T. latifolia* microcosm was detected directly on the plant tissue and the sediment grains via XAS at the Br K-absorption edge. Because this technique is highly sensitive to the coordination environment and bonding state of halogens, it permits differentiation between inorganic halides and stable organobromine forms in heterogeneous natural samples. Compared with inorganic Br^- compounds, a C−Br bond in an organic molecule results in the appearance of lower-energy features corresponding to 1s → π^* or σ^* molecular orbital transitions. This contrast becomes evident in the spectra of the chemical compounds 4-bromophenol and aqueous KBr (Figure 7A,B).

Examination of healthy leaf, stem, and root samples from *T. latifolia* and *P. australis* revealed strong inorganic Br^- transitions resembling that of the KBr(aq) standard (Figure 7C−F). No significant conversion to stable organobromine was observed in healthy plant materials or in plant matter in the initial stages of degradation gathered from the sediment

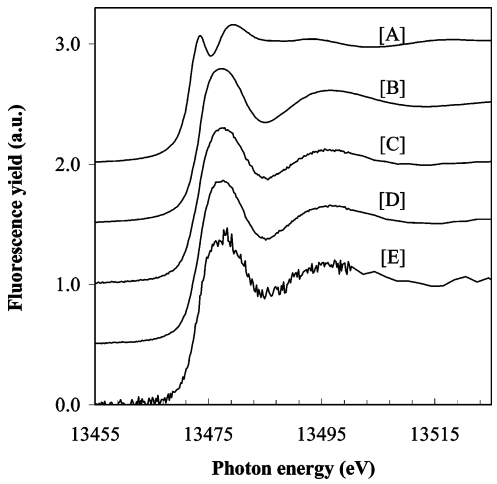

FIGURE 8. X-ray absorption spectra of Br in sediments of growing *T. latifolia*. (A) 4-Bromophenol standard; (B) KBr (aq) standard; (C) 1−2 cm below sediment surface (decaying organic material dominant); (D) 3−4 cm below sediment surface (decaying organic material dominant); and (E) 10 cm below sediment surface (heterogeneous mixture of sediment grains and organic material). a.u. means arbitrary units.

surface. The absolute intensity of the bromine signal in the spectra of the plant leaves was 2.5−4 times greater than that in the roots and stems, indicating that the leaves had the highest Br^- concentrations. However, the intrinsic heterogeneity of natural samples, with differences in density and thickness that are difficult to gauge, makes truly quantitative estimation of bromine concentration from these X-ray data problematic.

The Br X-ray fluorescence signal of the sediment samples decreased with sediment column depth in the *T. latifolia* microcosm, reflecting a drop in Br^- concentration. Sediment samples collected between 1 and 2 cm and between 3 and 4 cm from the sediment surface were dominated by decaying plant matter with little mineral component and displayed intense bromine signals (Figure 8C,D). At 10 cm, where organic material appeared sparsely among the silica grains, the intensity of the signal dropped by approximately 90%, as evidenced by spectral noise (Figure 8E). At 15 cm and below, the sediment contained very little organic material and yielded no measurable bromine signal.

Discussion

Br^- has been widely used as a conservative tracer for the determination of hydrogeologic properties and flow in wetland systems. The success of using Br^- as a tracer in wetland sediments depends on the degree to which Br^- is taken up by wetland plants, which should ideally be negligible. Results of this study indicate that two prevalent wetland plants, *T. latifolia* and *P. australis*, take up significant quantities of Br^-. Therefore, the use of Br^- for tracer experiments in wetlands should be evaluated with caution or avoided altogether. Two important physiological processes have been overlooked in previous experiments (*9*) addressing Br^- uptake by plants: transpiration of water by plants and upward translocation of absorbed elements. Results of previous experiments on Br^- uptake by plants (*11*) have assumed a uniform concentration of Br^- throughout the sediment column. This study revealed that transpiration and Br^- uptake clearly lead to a heterogeneous Br^- distribution, making different portions of plant roots subject to different Br^- concentrations. Pore−water Br^- concentrations were determined here at 2 cm increments, and plant transpiration was accounted for in the evaluation of the Br^- uptake rates. Results indicate that uptake of Br^- by *T. latifolia* can be described by the Michaëlis−Menten formulation, as reported by Epstein (*9*). A linear relationship between the Br^- concentration in soil and its uptake by plants has frequently been reported (*11*, *13*, *15*, *16*). It seems likely that such a correlation is an approximation of Michaëlis−Menten uptake at low levels of Br $(15)^-$, while Br^- uptake by lettuce was found to display a linear behavior when Br^- concentration in soil was increased by 2 orders of magnitude (*15*). The values of saturation concentration are likely to be highly species-dependent.

Results showed that *T. latifolia* as well as *P. australis* take up Cl^- actively. For *T. latifolia*, the uptake of Cl^- and Br^- can be described by dual-substrate Michaëlis−Menten kinetics, with the uptake of Br^- strongly inhibited by Cl^-, whereas Br^- had only negligible inhibitory effects on the Cl^- uptake. Cl^- is essential for plant physiological processes, such as the water-splitting system of photosynthesis (*29*), which might explain the preference of Cl^- uptake over Br^- uptake. Since the uptake of Br^- and Cl^- by *T. latifolia* was described well by the dual-substrate Michaëlis−Menten formulation, and Br^- uptake was inhibited in the presence of Cl^-, it can be concluded that a saturable catalyzed transport mechanism accounts for the uptake of both of these anions by this common wetland plant. The molar Cl^-/Br^- ratio in this experiment is about 2. In the natural environment, this ratio is usually much higher (*1*). For instance, the average molar ratio between Cl^- and Br^- in seawater is about 650 (*30*). Therefore, in wetland systems where Cl^- is abundant, uptake of Br^- by plants may be strongly inhibited by Cl^-.

For the case of *P. australis*, the relationship between pore−water Br^- concentrations and root uptake rate does not follow the Michaëlis− Menten model, while Cl^- uptake does follow this model, which is consistent with the concept that Cl^- is an essential micronutrient. Further research is required to formulate a full description of this species-dependent behavior.

Upon entry into plant root systems, Br^- is subject to translocation within the plant tissues and possible chemical transformation. Our X-ray spectroscopy measurements demonstrated the accumulation of Br^- in the leaves, stems, and roots of *T. latifolia* and *P. australis*, substantiating the upward translocation of Br^- in the plant tissues. No significant conversion of Br^- into stable organobromine forms was observed in any plant samples at the detection limits of X-ray spectroscopy. These data do not preclude the possibility of MeBr formation and volatilization from the plant tissue. The demonstrated degree of halide uptake by wetland plants emphasizes the need for further research regarding halide methylation and release of greenhouse gases by these plants, which may account for the puzzling imbalances in the atmospheric methyl halide budget. In addition, the natural transformation of the Cl^- present in fresh plant material to stable organochlorine forms that may constitute portions of macromolecular structure has been shown to occur during the degradation of plant materials (*19*); thus, analysis of Br speciation after senescence and prolonged weathering of Br^--amended *T. latifolia* and *P. australis* tissues could reveal stable organobromine forms and shed light on the ultimate fate of absorbed halides in the soil.

In conclusion, this study has revealed spatial concentration distributions of Br^- as a function of sediment depth in planted microcosms, which are attributed to complex plant uptake and transpiration dynamics. The findings presented highlight the risk of relying on Br^- as a straightforward chemical tracer for hydrological studies in wetland systems and suggest the need for alternative tracers. Nevertheless, the observed inhibition of Cl^- on Br^- Br^- uptake shows that Br^- could be used as a tracer in settings with high Cl^- concentrations such as estuarine environments or salt

marshes. Expressions such as eq 5 can provide guidance on the conditions for which Br^- can be used as a tracer.

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