Loss of Bromide in a Wetland Tracer Experiment

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Abstract

Bromide recovery during tracer tests conducted in 12 wetland research cells averaged 48%. Loss of water by infiltration, analytical biases, and inadequate measurement period were rejected as causes of low bromide recovery. The nonconservative behavior of bromide was probably caused by plant uptake. Investigators conducting bromide tracer studies in wetlands should recognize that bromide may be not be conservative in wetlands, particularly during periods of rapid plant growth.

Bromide is generally regarded as one of the best hydrologic tracers because it (i) is nonreactive (conservative) in most environments, (ii) is found at low background concentrations, (iii) is easy to analyze, and (iv) has low toxicity (Bowman, 1984; Davis et al., 1980). We conducted bromide tracer tests in 12 wetland research cells at the Tres Rios Wetland Demonstration Project (Phoenix, AZ) to determine the effect of design variations on hydraulic characteristics and unexpectedly found low bromide recovery. This paper addresses the question, Does bromide behave conservatively in wetlands?

Study Site

Each of 12 wetland research cells had a surface area of 1200 m^2 (50 m long × 24 m wide). Earthen dikes approximately 3 m wide separated the wetland cells. Shallow areas were planted with two species of bulrush, soft-stem bulrush [*Schoenoplectus tabernaemontani* (K.C. Gmel.) Palla] and three-square bulrush [*Schoenoplectus americanus* (Pers.) Volk. ex Schinz & R. Keller], in mid-1995. Each cell was transected by a deep zone (1 m in depth) at each end (Fig. 1). The cells varied with respect to the number of internal deep zones (zero to three), with each design represented in triplicate. During the tracer experiments, the hydraulic loading rate (HLR = outflow/surface area) was 83 mm d^{-1} for all cells. Nominal hydraulic detention times (HDT = outflow/porosity-corrected volume; with an assumed porosity of 0.7 to account for plant volume; Kadlec and Knight, 1996) were 4.1 to 5.1 d, depending upon the number of deep zones.

Constant flow to each of the 12 cells was maintained by routing inflow water through two splitter boxes. Flow to each cell passed over a 22.5° V-notch weir, into a small mixing box, and from there into an 8-inch (~203 mm) pipe that intersected a perforated 8-inch pipe laid perpendicular to the main axis of the wetland (Fig. 1). This design distributed water evenly across the front of the wetland. Inflow was measured at the inlet weirs using a fixed stage gauge.

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Methods

Bromide tracer was added to each wetland cell by mixing 5 to 6 kg reagent-grade NaBr with about 100 L of water in a large barrel. After careful mixing, the concentrated bromide solution was poured quickly (within 30 s) into the mixing box below the inlet weir. Water samples were collected at the outlet weir using an ISCO (Lincoln, NE) 3700 automatic sampler over a period of 15 d (1997 experiment) or 29 d (1998 experiment), with samples collected at intervals of 1 to 6 h. In total, 4100 samples were collected. Inlet water samples were collected manually once a day. Outflow was measured daily at the outlet of each wetland cell using a stage gauge and weir.

Bromide and chloride were analyzed by ion chromatography (Dionex [Sunnyvale, CA] DX500). The method detection limits (MDL) were 0.045 mg L^{-1} for Br^- and 0.18 mg L^{-1} for Cl^- and the practical limits of quantification (POQ = 5 × MDL) were 0.23 mg L^{-1} for Br^- and 0.90 mg L^{-1} for Cl^-. All of our samples had Br^- and Cl^- concentrations well above these levels. Analytical bias was evaluated using external quality assurance standards (SPEX [Metuchen, NJ] IC standard).

Mass balances were determined for bromide and chloride. The mass of bromide recovered was computed from the zeroeth moment of the tracer curve:

$$M_0 = \int_0^\infty QC(t)dt \qquad [1]$$

where M_0 = the zeroeth moment of the curve, mg; Q = daily averaged outflow, L d^{-1}; $C(t)$ = concentration of tracer at time (t), mg L^{-1}; and t = time, d.

Recovery of bromide was determined by the difference between the mass added and the mass recovery (M_0). Chloride mass input was computed as the product of a single daily Cl^- measurement and measured flow. Chloride was not added in the tracer experiment, but the water contained fairly high chloride concentrations (~350 mg L^{-1}). Average daily chloride output was computed as the product of the average concentration of all samples collected by the automated sampler and flow.

The first experiment was conducted between 26 June and 11 July (Cells 1–6) and between 31 July and 14 Aug. 1997 (Cells 7–12). A second experiment was conducted in two of the cells (R2 and R5) the following spring using a longer sample collection period. Further experimental details are provided in Whitmer (1998).

Results and Discussion

Following the slug input of bromide to the wetland inlets, bromide concentrations in the outlets peaked at around 5 d and then declined to background levels (~0.3 mg L^{-1}; Fig. 2). Average bromide recovery was 50% of bromide added (Fig. 3). A one-way t-test showed that average bromide recovery for the 12 cells tested in 1997 (50%) was significantly different ($p < 0.05$) from expected recovery (100%; i.e., no bromide loss). Several hypotheses were examined to explain poor bromide re-

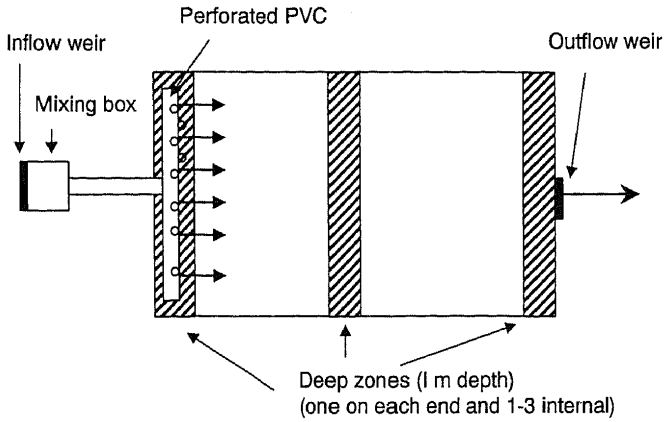

Fig. 1. Schematic of a wetland treatment cell. The main design variation was the number of internal deep zones, which varied from zero to three.

covery: (i) water infiltrated through the bottom of the wetland, carrying bromide downward; (ii) the measurement period was inadequate to recover all of the bromide added; (iii) analytical errors resulted in biased calculated recoveries; and (iv) bromide behaved nonconservatively.

Water and chloride balances showed that there was little infiltration in all but two cells (Cell 4, with 48% water loss and Cell 5, with 33% water loss). Average water loss was 14% of inflow (9% excluding these two cells). On an areal basis, average loss was about 14 mm d^{-1}. This was very close to the evaporation rate (12 mm d^{-1}) in a Class A evaporation pan located at Arizona State University during the time of this experiment, suggesting that computed water loss occurred mainly by evaporation. Furthermore, chloride was nearly conservative, with an average recovery of 94% (95% excluding Cells 4 and 5). Thus, water and chloride balances show that leakage from the wetland cells could not account for the observed bromide losses.

To test Hypothesis 2, the recovery period was doubled in the second experiment, conducted only in Cells 2 and 5. In Cell 2, bromide recovery was 39.0% at Day 16 and 41.7% at Day 29. Bromide recovery in Cell 5 was 23.4% at Day 16 and 24.6% at Day 29. Thus, bromide recovery at 16 d was 93% to 95% of bromide recovery at 29 d. This experiment showed that extending the duration of the experiment did not increase bromide recovery, allowing us to reject Hypothesis 2. The longer experimental observation period also gives some insight regarding the mechanism of bromide loss. If Br^- had been adsorbed, as suggested by Netter (1994), it would have been desorbed slowly after the Br^- peak declined, resulting in higher recovery over a longer observation period. The fact that this did not occur suggests that adsorption was not an important mechanism in bromide transport through this system.

Analytical errors could have biased calculated bromide recoveries (Hypothesis 3). However, average bias and relative standard deviation of analyses relative to the SPEX quality control standard was 2.5 ± 2.9% for Br^- and −0.4 ± 1.1% for Cl^- in the 1997 experiment and −0.3 ± 1.1% for Br^- and −0.6 ± 0.8% for Cl^- in the 1998 experiment. Other potential sources of error (e.g., inaccurate scales, chemical impurities) were found to be minimal. Thus, Hypothesis 3 was rejected.

The only reasonable explanation for the observed loss of bromide mass was its nonconservative behavior (Hypothesis 4). Although we did not measure uptake of bromide by plants, experiments using bromide tracers in agricultural systems have shown that bromide is readily taken up by plants (Chao, 1966; Owens et al., 1985; Kung, 1990; Jemison and Fox, 1991; Schnabel et al., 1995; Eckhardt et al., 1996). In these studies, bromide accumulation for a variety of crops ranged from 1 to 25 g Br kg^{-1} dry wt. plant and uptake rates ranged from 7 to 54 kg ha^{-1}. In these experiments, bromide recovery in harvested crops shows that plants actively took up bromide. In our experiment, 40 to 50 kg bromide was added per hectare and average loss was 50% (20–25 kg ha^{-1}). Bromide losses in our experiment are therefore

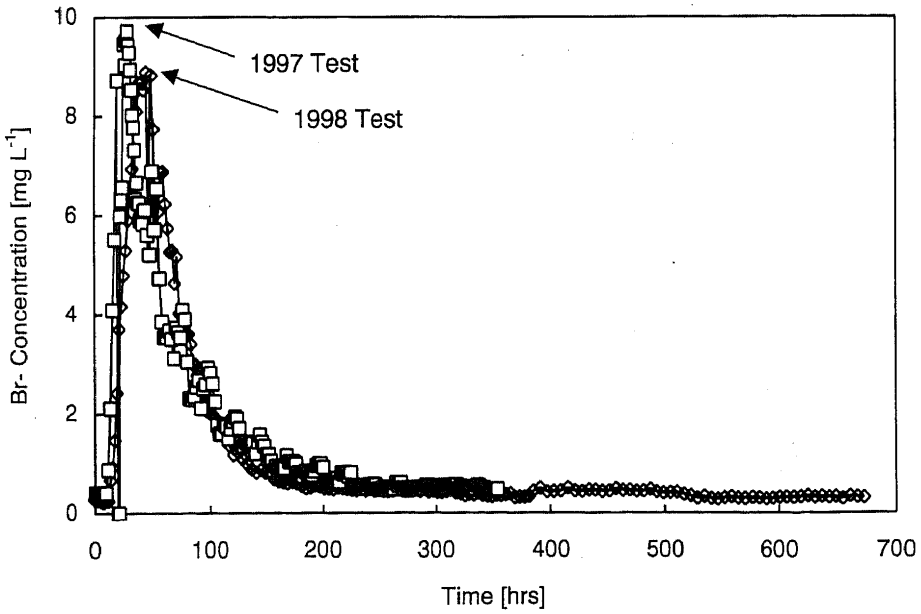

Fig. 2. Concentration of bromide in the outflow from Cell 2 following slug input (at time = 0). Results from 1997 and 1998 experiments are shown.

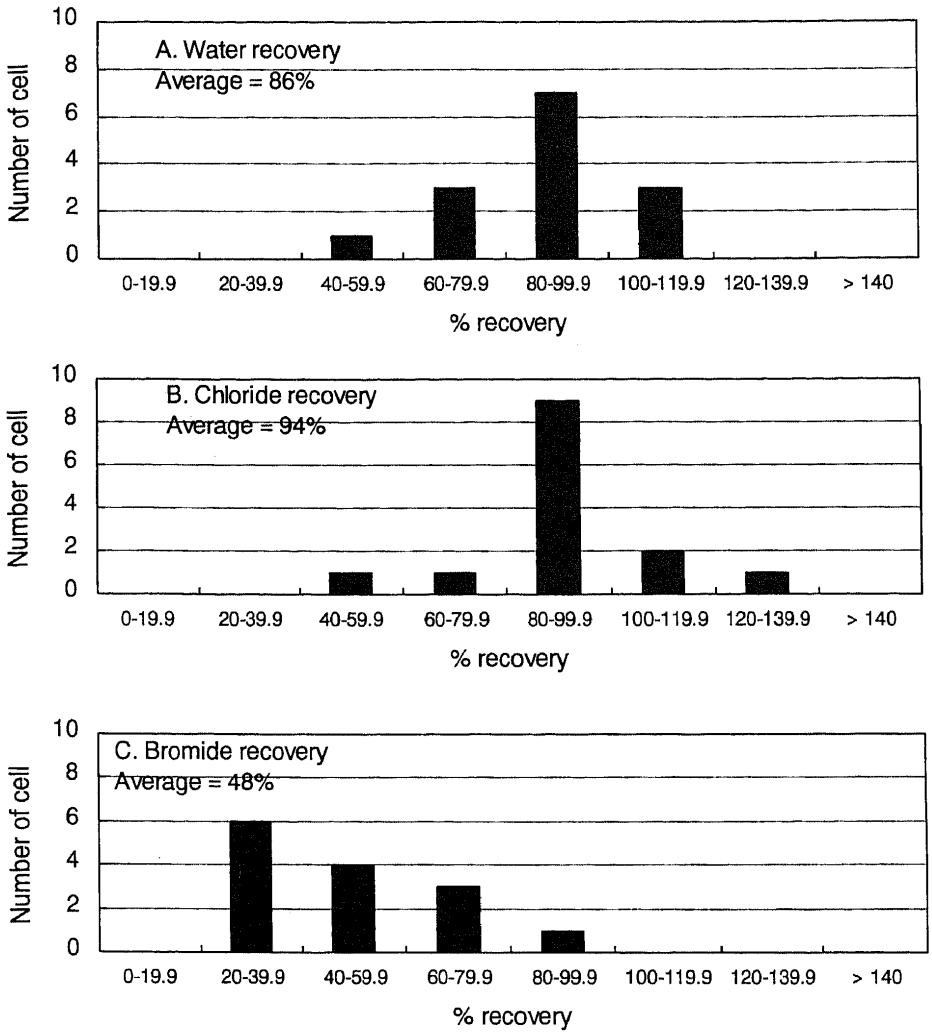

Fig. 3. Recovery of water, chloride, and bromide in the outflows of the research cells. Cells 2 and 5 were replicated, for a total of 14 individual tests in 12 cells.

well within the range of losses reported for agricultural crops. Furthermore, crop experiments show that bromide is taken up quickly, often within a few weeks. Thus, plant uptake is a plausible mechanism to explain the observed loss of bromide in our experiments.

Acknowledgments

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