



## Atmospheric bromine flux from the coastal Abu Dhabi sabkhat: A ground-water mass-balance investigation

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[1] A solute mass-balance study of ground water of the 3000 km<sup>2</sup> coastal sabkhat (salt flats) of the Emirate of Abu Dhabi, United Arab Emirates, documents an annual bromide loss of approximately 255 metric tons (0.0032 Gmoles), or 85 kg/km<sup>2</sup>. This value is an order of magnitude greater than previously published direct measurements from the atmosphere over an evaporative environment of a salar in Bolivia. Laboratory evidence, consistent with published reports, suggests that this loss is by vapor transport to the atmosphere. If this bromine flux to the atmosphere is representative of the total earth area of active salt flats then it is a significant, and generally under recognized, input to the global atmospheric bromide flux. **Citation:** Wood, W. W., and W. E. Sanford (2007), Atmospheric bromine flux from the coastal Abu Dhabi sabkhat: A ground-water mass-balance investigation, *Geophys. Res. Lett.*, *34*, L14405, doi:10.1029/2007GL029922.

### 1. Introduction

[2] A regional ground-water resource evaluation in the coastal sabkha in the Emirate of Abu Dhabi (Figure 1) indicated that the solute Cl/Br mass ratio in the sabkha aquifer was unusually large (mean 7250 based on 172 samples) relative to analyses of input of ground water solutes (mean 4080 based on 7 samples) (Table 1). This difference appears to have resulted from a relative loss of bromide rather than a relative gain in chloride. This observation is interesting in that bromide in many ground water systems is normally considered conservative and is often used as both an environmental and artificial tracer as a result of this property [Davis *et al.*, 1998]. There have, however, been speculations of apparent bromine loss from coastal wetland environments [Rhew *et al.*, 2000; Yokouchi *et al.*, 2000; Keppler *et al.*, 2000]. More relevant to this study area are reports in which bromide appears to have been lost from evaporite environments [Levy, 1977; Ericksen, 1981]. Consistent with these later speculations are measurements of elevated concentration of atmospheric bromine over a saltpan area of the Dead Sea [Hebestreit *et al.*, 1999; Matveev *et al.*, 2001], Great Salt Lake [Stutz *et al.*, 2002], and Salar de Uyuni, Bolivia [Hönninger *et al.*, 2004]. The first quantitative estimate of flux from a salt flat (not brine) surface was based on direct MAX-DOAS atmospheric measurements above Salar de Uyuni, Bolivia over an interval

of four days in the fall of 2002 [Hönninger *et al.*, 2004], and suggested a bromine flux of approximately 7 kg/km<sup>2</sup>/yr. This value was later found to be consistent with an independent geochemical ratio approach [Risacher *et al.*, 2006] although both studies suggest this value was probably a minimum. Our study on the coastal sabkhat of Abu Dhabi used an indirect mass-balance approach that integrated measurements of loss over seven thousand years, allowing for a robust estimate that averages small annual changes. Analysis from this geohydrologically uncomplicated system suggests a loss of approximately 85 kg/km<sup>2</sup>/yr, an order of magnitude greater than calculated from the salar in Bolivia [Risacher *et al.*, 2006; Hönninger *et al.*, 2004].

### 2. Hydrogeologic Setting

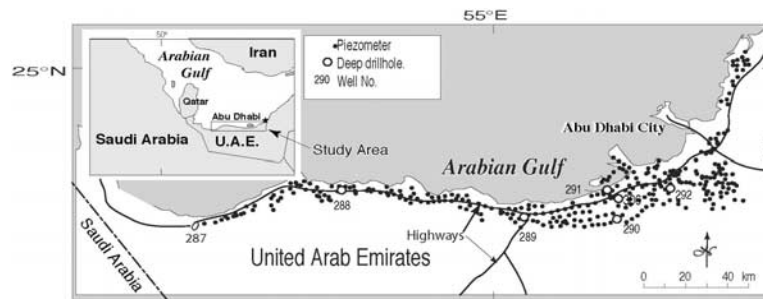
[3] The Holocene-age (7000 BP) (Abu Dhabi Formation), upon which the coastal salt flat forms, occupies a region approximately 300 km by 10 km, with an average thickness of 10 m [Wood *et al.*, 2002]. The Abu Dhabi formation consists of uncemented reworked sand dunes of uniform grain size (0.18 to 0.22 mm) exhibiting a porosity of approximately 0.38 and consequent spatially uniform hydraulic conductivity of approximately 1 m/d  $\pm$  20% [Wood *et al.*, 2002]. The water table and eolian processes of this coastal sabkha are in dynamic equilibrium, resulting in the flat topographic surface sloping gradually toward the Arabian Gulf. The water table surface, approximately a meter below the surface, mirrors that of the topographic gradient. The capillary zone intersects the land surface and thus transports both solute and water to it in response to evaporation from the surface. Retrograde minerals including calcite, dolomite, gypsum, and anhydrite precipitate in the capillary zone as the water is warmed approaching the surface [Wood *et al.*, 2005]. Normally soluble minerals (halite, carnallite, sylvite, niter, and others) precipitate on the sabkha surface in response to water evaporation.

[4] Low values of hydraulic gradient (slope of the water table) (between 0.0033 and 0.00025) and low values of hydraulic conductivity of approximately 1 m/d result in a seepage rate of approximately 0.2 m/y. Thus, less than 5% of mass of solutes entering the system from ground water have been discharged to the Arabian Gulf over the 7000-year life of the sabkha [Wood *et al.*, 2002, 2005]. There is, however, a selected solute loss resulting from overland runoff. In general, the winter rain dissolves the surface salts and returns the solutes to the Abu Dhabi Fm. This surface generated brine has high density, and as it descends mixes with the less dense water in the aquifer and water entering the Abu Dhabi Fm. from underlying aquifers. The mixed water is raised to the surface by capillary action, water is lost by evaporation, and the solutes again form as salts on

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**Figure 1.** Map showing the sampling locations of 172 shallow (less than 4 m) piezometers finished in the sabkha and 7 deep wells (~100 m) finished in the underlying Tertiary carbonate-evaporite formations.

the surface in preparation for the next recharge cycle. This process is repeated, increasing the solute concentrations with time. If the rainfall flux is small, there is sufficient storage volume in the capillary zone and all the solutes are recharged. If, however, rainfall flux is larger than storage volume, chemical differentiation occurs where only ions from the most kinetically rapid mineral solution (carnallite, sylvite, niter, antarctite, etc.) are recharged whereas ions from the less soluble minerals with slower kinetic solution, such as halite, are rejected and become part of the overland runoff to the Gulf. Approximately half of total sodium and chloride input in this system has been lost by surface runoff to the Gulf [Wood *et al.*, 2005]. Salt crusts on the sabkha surface have the same Cl/Br ratio (7000) as the solute analyses [Wood *et al.*, 2005].

### 3. Bromide Mass Balance

[5] Upward groundwater flux from the underlying formations is believed to be between 3 and 4 mm/y, determined from a vertical gradient of approximately 0.1 and vertical hydraulic conductivity of approximately  $1 \times 10^{-4}$  m/d [Sanford and Wood, 2001]. Combining this with the observed thickness of 10 m and a porosity of 0.38 suggest that during the 7000 years of the existence of the sabkha, between six and seven pore volumes of brines have entered from underlying formations [Wood *et al.*, 2002]. A pore volume  $P_v$  is defined as

$$P_v = v \emptyset \quad (1)$$

where  $P_v$  is the volume of fluid ( $L^3$ ) in the interstitial pores of the saturated aquifer ( $L^3$ );  $v$  is the volume of saturated aquifer ( $L^3$ );  $\emptyset$  is porosity ( $L^3/L^3$ , dimensionless); and  $L$  is

length. An analogous value to pore volume is the mass ratio (MR), (the number of masses of input of a given conservative ion relative to those observed in the system) can be calculated from a closed system, in which the original pore fluid was seawater using the following equation;

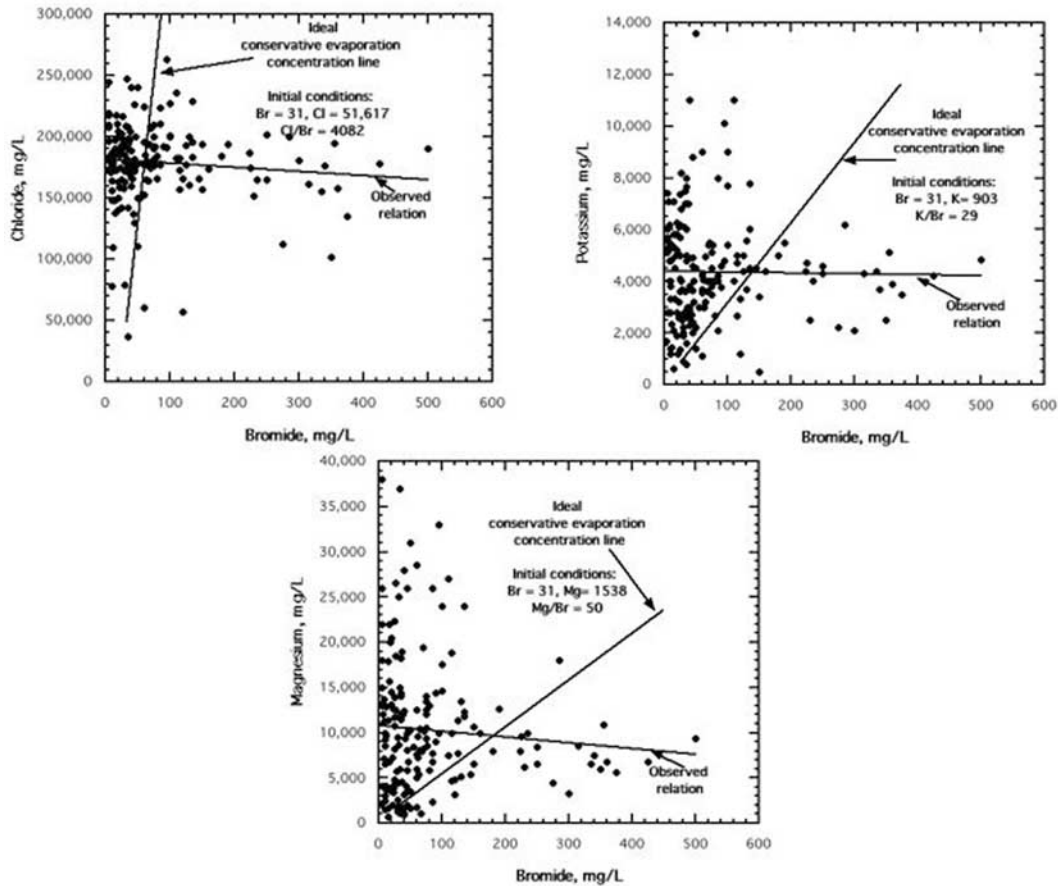
$$MR = [C_o - C_s]/C_i \quad (2)$$

where; MR is the mass ratio (dimensionless),  $C_o$  is the observed concentration of the ion in groundwater in the aquifer ( $M/L^3$ ),  $C_s$  is the concentration of the ion in seawater ( $M/L^3$ ),  $C_i$  is the concentration of the ion in the groundwater input to the aquifer ( $M/L^3$ ), and  $M$  is mass. Using the concentration of magnesium, believed to be conservative in this system (1454 mg/L input groundwater; 10,003 mg/L aquifer groundwater: Table 1), and recalling that the concentration of magnesium in seawater is 1290 mg/L, suggests that approximately 6 masses of magnesium have been added to the aquifer, a value consistent with the 6 to 7 pore volumes calculated from flux and head measurements. As no significant mass of magnesium mineral is found in or on the aquifer, and less than 5% of the mass has escaped to the Gulf in ground water discharge, the assumptions required for equation 2 are generally met.

[6] The average input bromide concentration from seven spatially distributed wells is approximately  $28 \pm 45$  mg/L (Table 1 and Figure 2). If bromide were conservative, the concentration in the sabkha would be approximately 235 mg/L, including 68 mg/L from the seawater that initially filled the first pore volume. Analyses of 172 spatially distributed samples (Figure 1) indicate an average bromide concentration of  $78 \pm 92$  mg/L (Table 1), an apparent loss of approximately 157 mg/L bromide from

**Table 1.** Chemical Analyses of Solute From Input and the Sabkha of Abu Dhabi

Source Aquifer	Identification	UTM East	UTM North	UTM Zone	Depth, meters BLS	Date Sampled	Mg, mg/L	K, mg/L	Cl, mg/L	Br, mg/L	Cl/Br	Number of Samples
Tertiary brine	GWP-287A	600 328	2 647 191	39	121	Jan-98	2600	1300	69,500	130	535	1
Tertiary brine	GWP-288A	687 801	2 666 649	39	89	Jan-98	950	300	19,700	11	1790	1
Tertiary brine	GWP-289	777 587	2 655 712	39	119	Jan-98	675	120	10,300	5	2060	1
Tertiary brine	GWP-290A	210 989	2 655 365	40	88	Feb-98	950	450	25,000	15	1667	1
Tertiary brine	GWP-291A	205 481	2 670 574	40	142	Feb-98	1350	950	55,100	20	2755	1
Tertiary brine	GWP-292	236 909	2 671 579	40	119	Feb-98	2400	1500	87,300	6	14,550	1
Tertiary brine	GWP-306A	208 465	2 668 318	40	129	Mar-99	1250	1100	62,500	12	5208	1
Tertiary brine (mean)					7		1454	817	47,057	28	4081	
Sabkhat brine (mean)					2	97-99	10,003	4239	176,346	78	7248	172



**Figure 2.** Solute concentrations of bromide with three major ions illustrating the lack of correlation with increasing concentration. The observed relation (best fit line) suggests a loss of bromide relative to each of these solutes. In the absence of other processes, one would expect the bromide concentrations to increase with increasing evaporation and follow the ideal evaporation concentration curve. Those higher bromide concentrations to the right of the evaporation line reflect recent surface input of chemically differentiated solutes.

solution. Bromide has a MR value of 0.4—suggesting a significant loss from the system.

[7] The total bromide mass loss per unit aquifer volume (1 m by 1 m by 10 m) can be approximated by the following generalized mass balance expression;

$$M_{loss} = (M_{initial} + M_{input}) - M_{sabkha}, \quad (3)$$

where  $M_{input}$  is equal to  $(C_{input}) \cdot (MR) \cdot (\emptyset)$ ;  $M_{initial}$  is equal to  $(C_{ocean}) \cdot (\emptyset)$  and  $M_{sabkha}$  is equal to  $(C_{obs}) \cdot (\emptyset)$ .  $M$  is mass of solute; and  $C$  is concentration ( $M/L^3$ ). Missing from this abbreviated mass balance equation are eolian addition or subtraction, atmospheric precipitation, bromide mineral precipitation, and overland input and output, all of which are assumed to be small in this system [Wood *et al.*, 2002]. As a result of the high solubility of the bromide it is one of the first ions to recharge in a rain event and thus, not thought to be lost in overland runoff.

[8] Each cubic meter of the sabkha aquifer has an observed average total bromide solute mass loss of 0.0596 kg; for an average thickness of 10 m the loss would be 0.596  $kg/m^2$ . The total area of 3000  $km^2$  results in  $1.79 \times 10^9$  kg total bromide solute loss from of the sabkha. Dividing total loss by 7,000 (years that the sabkha have been in existence)

yields an annual loss of approximately 255 metric tons (0.0032 Gmoles) of bromide, or approximately 85  $kg/km^2/yr$ . Published investigations [Hebestreit *et al.*, 1999; Matveev *et al.*, 2001; Stutz *et al.*, 2002; Hönninger *et al.*, 2004] and laboratory studies described below suggest this loss is by vapor transport to the atmosphere.

[9] To test the hypothesis of vapor loss a representative sample of brine from the sabkha aquifer was spiked with a solution of KBr to raise the Br concentration to 105  $mg/L$ . Subsamples of this solution were added to washed sabkha sand and evaporated to dryness in a vacuum oven using a heat lamp with a UV light at an evaporation temperature of 80°C. The sediment samples were re-hydrated with distilled water, the solutes analyzed, and found to have lost 83% of the bromide; the chloride concentration (176,000  $mg/L$ ), however, remained the same as the initial solution. Although we did not differentiate the form of the bromide lost, we were able to demonstrate that transfer of bromide to the air does occur under conditions similar to those on the sabkha and are consistent with observations of bromine oxide ( $BrO$ ) vapor above similar environments [Hebestreit *et al.*, 1999; Matveev *et al.*, 2001; Stutz *et al.*, 2002; Hönninger *et al.*, 2004].

[10] A small mass of bromide (3 mg/g) is sorbed on the iron and manganese oxides coating the grains. After rinsing a representative sample of sediment from the sabkha in distilled water and drying, three subsamples of 70 g each were placed in a solution of 0.25 M hydroxylamine (3 liquid to 1 sediment by weight) and stirred for 24 hours. An aliquot of the resulting solution was removed and analyzed for Br by ICP/MS methods. The average of the three samples gave a sorbed Br value of 3 mg/g of sediment or approximately 0.005 kg/m<sup>3</sup>.

#### 4. Discussion

[11] We assume that the missing bromide is lost to the atmosphere in a manner similar to the other areas that have been investigated (Dead Sea, Great Salt Lake, and solar Uyuni), but we have not made direct measurements above the sabkha. It seems unlikely that a significant mass of bromide is lost by incorporation into the solid phase of halite, because only a small mass of bromide can fit into the halite lattice in substitution for chloride [Braitsch, 1971]. Furthermore, there is little halite on or in the system, as much of what forms on the surface is dissolved and reenters the aquifer with annual recharge. Consider the following: a 2-cm thick average covering of halite on the surface of the sabkha, a halite density of 2.165 g/cm<sup>3</sup>, and a Cl/Br ratio of 7000. One would expect to find a total mass of bromide in this surface halite to be 0.0037 kg/m<sup>2</sup> compared to a total loss of 0.596 kg/m<sup>2</sup>; thus, an insignificant amount of bromide is tied up with the current surface halite, and there is no significant halite observed below the surface of the sabkha. If one considers the total amount of halite lost from the system as 30 cm [Wood *et al.*, 2005] and assumes that the Cl/Br ratio was 7000, then the total amount of bromide lost by runoff would be approximately 0.056 kg/m<sup>2</sup> or less than one tenth of the missing bromide. Even if the Cl/Br ratio of the missing salt was equal to the input of 4080, it would only account for approximately 30 percent of the missing bromide mass.

[12] Mass ratio (MR) values less than 6 in this system represent a mass loss of that individual ion from the fluid in the system. Bromide has a MR value of 0.4, chloride 3.3, and potassium 4.7 (Table 1). These data suggest that significant loss of bromide mass has occurred relative to all three of these solutes even though potassium and chloride have clearly experienced losses. Loss of bromide relative to chloride, potassium, and magnesium is shown graphically in Figure 2. If bromide were conservative relative to these solutes, the concentration data would plot along the concentration line of increasing bromide concentration with increasing concentrations of the ions (Figure 2). In fact, most of data follow a different concentration relation indicating a significant loss of bromide relative to these solutes. None of the three solutes Cl, Mg, or K show a positive correlation with bromide concentration (Figure 2). The difference in slope between bromide and chloride, potassium, or magnesium in Figure 2 is a result of the difference in MR between the ions. Bromide concentrations to the right of the evaporation line represent chemically differentiated recharge from the surface. That is, the bromide ions in storage on the surface are not incorporated in minerals, and are thus preferentially recharged over other

ions at the initiation of recharge. The ionic ratio of the recharge event depends on storage space available for recharge and volume of water in the recharge event [Wood *et al.*, 2005]. Methods of data collection and analyses are described by Wood *et al.* [2002].

#### 5. Conclusions

[13] Based on published maps of the Earth, there are estimated to be on the order of  $1.5 \times 10^6$  km<sup>2</sup> of salt flats, or approximately 500 times the area of the Abu Dhabi salt flats. If the flux from salt flats worldwide can be assumed similar in magnitude to those from Abu Dhabi, then approximately 128 ktons (kilotons, 1.6 Gmoles) of bromide are lost annually. Bromine has been well documented as a significant factor in the loss of ozone from the atmosphere as shown by direct measurements [Matveev *et al.*, 2001]. Research on the natural global flux of bromine to the atmosphere has focused largely on sea spray on Arctic snow packs [Finlayson-Pitts *et al.*, 1990; Impey *et al.*, 1997; McConnell *et al.*, 1992; McElroy *et al.*, 1999] and on CH<sub>3</sub>Br from the oceans [Anbar *et al.*, 1996]. Our calculations suggest that approximately 128 ktons (1.6 Gmoles/y) of bromine may be added annually to the atmosphere from salt flat surfaces. This is approximately 12% of total estimated annual atmospheric bromine flux of 1100 ktons [Wofsy *et al.*, 1975]. Due to the aridity of typical evaporating environments and consequent lack of rainout, input to the atmosphere from evaporative environments may lead to a significant net flux of bromine to the atmosphere.

[14] Clearly additional work is needed to quantify vapor fluxes from this environment; however, if the contribution to the atmosphere on the whole is as large as it appears from this study, it would need to be addressed in studies of atmospheric ozone depletion. The loss of bromide relative to chloride also has important implications for low temperature geochemistry, where the Cl/Br ratio is often used to reconstruct paleoenvironments. As bromine loss from the sabkha appears to be in the form of a vapor, it is speculated that the isotopically heavier stable bromine, <sup>81</sup>Br, may exist in greater concentration in the evaporating environment. Bromide isotopic analyses thus might provide an interesting avenue for future investigation that may help constrain the estimates of bromide loss from this environment.

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