

## Increases in mercury emissions from desert soils in response to rainfall and irrigation

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**Abstract.** As part of an international Hg flux intercomparison at the Steamboat Springs, Nevada, geothermal area, several dynamic soil flux chambers and micrometeorological gradient systems were operated over desert soils in early September 1997. A series of unanticipated convective rain cells impacted the site with the first rainfall in ~90 days, and the initial 4-cm rainfall increased soil moisture from ~0.01 to 0.06% (vol/vol). Several chambers were operating prior to the events, and two were deployed over wet soils following rainfall. Rainfall resulted in an immediate and steep rise in ambient air Hg concentrations and soil Hg emissions which persisted for 12–24 hours. Fluxes increased most quickly and to a greater degree over the wettest soils, and the rate of increase was related to chamber design and flushing rate. The flux response was also apparent in the micrometeorological data. In general, soil emissions increased by an order of magnitude following the rain, and reached levels ~6 times above those at the same time the previous day. These fluxes were significantly correlated with temperature, radiation, humidity, wind speed, and soil moisture. After drying for ~40 hours, selected soil plots were manually irrigated with low-Hg-distilled water. Mercury emissions responded similarly across the three treated sites, uniformly increasing from ~60 ng m<sup>-2</sup> h<sup>-1</sup> pretreatment to ~650 ng m<sup>-2</sup> h<sup>-1</sup> posttreatment, which was a factor of ~6 higher than adjacent control soils. Possible causes of the increases in flux include soil gas displacement, desorption of Hg<sup>0</sup> by water molecules, and desorption of Hg(II) and subsequent reduction in solution. The kinetics of the flux response, combined with local soil and climatic conditions, suggest that Hg emissions were responding primarily to soil moisture and solar radiation. These data have interesting implications for the role of changing regional climates on biogeochemical cycling of Hg.

### 1. Introduction

The ability of Hg to volatilize from soils has long been known [e.g., *McCarthy et al.*, 1969], and the natural emission of Hg from soils is an important contributor to the global Hg cycle [*Carpi and Lindberg*, 1998]. Mercury exists in soils in several forms, many of which (particularly Hg<sup>0</sup>) exhibit relatively high elevated vapor pressures at background temperature. The primary sources of Hg in soils which have not been directly contaminated (e.g., by mining activities) include parent and weathered minerals, geothermal precipitates, and atmospheric deposition. Soils enriched in mercury by natural geologic processes may contain concentrations of the order of 10<sup>0</sup>–10<sup>2</sup> μg/g [e.g., *Gustin et al.*, 1994], while background soils are generally considered to contain Hg at levels <0.5 μg/g.

The factors influencing Hg emissions from soils range from the apparent (soil temperature and mercury speciation) to the unexpected (humidity and solar radiation [e.g., *Poissant and Casimir*, 1998; *Carpi and Lindberg*, 1997]). The effect of temperature has been most widely reported and quantitatively studied. The vapor pressure of Hg<sup>0</sup> increases exponentially

with temperature, and many studies have reported exponential relationships between temperature and emission rates for background, contaminated, and geologically enriched soils as well as buried wastes [e.g., *Lindberg and Turner*, 1977; *Lindberg et al.*, 1979; *Xiao et al.*, 1991; *Lindberg et al.*, 1995; *Gustin et al.*, 1996]. Because of the strong temperature effect, few other relationships have been as well documented, and the recent suggestions of a direct effect of solar radiation on fluxes are complicated by indirect temperature effects from soil heating [*Gustin et al.*, 1996; *Carpi and Lindberg*, 1998].

Among the “other” factors, soil moisture and rainfall effects have been mentioned in recent studies, often anecdotally via their influence on air concentrations. *Wallschläger* [1996] and *Schmolke et al.* [1999] have measured increased Hg concentrations in air immediately above the ground following rain events, while *Carpi and Lindberg* [1998] reported a strong increase in Hg emissions from background field soils following the first rain after a 2-month drought. In the only known soil moisture manipulation study, Hg fluxes were found to change significantly over soils which were deprived of natural rainfall for several weeks. Although adjacent control soils showed no trends, the treated soils went from being a net Hg source prior to drying (>30% moisture), to a Hg sink while dry (i.e., dry deposition was measured to soils of <10% moisture), and back

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Paper number 1999JD900202.  
0148-0227/99/1999JD900202\$09.00

to a net source after rewatering with distilled water to 25% moisture [Advokaat and Lindberg, 1996].

The development of field-portable teflon flux chambers [Kim and Lindberg, 1995] operated with automated analyzers for Hg<sup>0</sup> [e.g., Poissant and Casimir, 1998; Lindberg and Price, 1999] has increased research on soil fluxes, and an intercomparison of field methods was an important research need [Iverfeldt et al., 1996]. From September 1–4, 1997, an international team of researchers descended on the Steamboat Springs desert geothermal area for a 4-day Hg flux intercomparison over soils geologically enriched with Hg (the Nevada Study and Tests of the Release of Mercury From Soils (STORMS) campaign [Gustin et al., this issue (a)]. One objective of the study was to determine the climatic factors influencing Hg fluxes over enriched soils, including soil temperature and solar radiation. An unexpected factor for this desert setting was rain-induced effects on soil moisture. This paper reports results of flux chamber measurements under prerairfall and postrainfall moisture regimes, and of the response to manual irrigation of several treatment plots for comparison with controls. Limited micrometeorological data are included for comparison, but these data and their relationship with the flux chamber data are described in detail elsewhere in this volume [e.g., Gustin et al., this issue (a)].

## 2. Experimental Design, Methods, and Sites

Details on the Steamboat Springs, Nevada, site, measurement locations, and methods used by each group, including the flux chamber designs, are presented elsewhere in this volume [e.g., Gustin et al., this issue (a)]. Each group operated either or both flux chambers (FC) and micrometeorological systems to quantify air/surface exchange rates for Hg; however, this paper primarily describes the flux chamber data because the artificial moisture manipulations were only possible over the limited surface areas afforded by the FC. Although several FC designs were used in the intercomparison, all groups used automated mercury analyzers to measure Hg<sup>0</sup> levels continuously at the inlet and outlet of each FC, with a 5-min resolution [e.g., Lindberg and Price, 1999]. All but the Goteborg University (GU) group used a Tekran 2537A analyzer (GU used a Gardis analyzer [see Gustin et al., this issue (a)]. The FC data were derived from four clusters of sites (FC within clusters were located <5 m apart): (1) Frontier Geosciences (FG), Goteborg University (GU), and GKSS Institute (GKSS); (2) Oak Ridge National Laboratory (ORNL) and University of Michigan (UM); (3) Environment Canada, Atmospheric Environment Service (EC); and (4) University of Guelph (UG) (detailed locations of all measurement sites are shown by Gustin et al. [this issue (a)]. Briefly, there were four basic FC designs: the ORNL all-teflon rectangular “box” (deployed by GKSS, GU, UM, and ORNL [e.g., Carpi and Lindberg, 1998], a low rectangular polycarbonate pastry cover (FG), a square plexiglass box lined with teflon (UG), and an opaque teflon-lined aluminum hemisphere (EC [Poissant and Casimir, 1998]). The latter two designs employed small internal circulation fans. The FC differed in surface area, volume, and air exchange rate, which influenced their response times, as discussed below. An extensive discussion of FC blank methods and results for the ORNL and EC FC are published (blanks are generally <1% of the mean daytime fluxes reported in this paper [Poissant and Casimir, 1998; Carpi and Lindberg, 1998]). Total Hg levels in the soils at each plot were as follows (in  $\mu\text{g/g}$ ): FG/UG/GKSS

equal to 1.4–2.9; ORNL/UM equal to 3.6–4.1; EC equal to 4.6–4.7; UG equal to 2.8–4.0 [see Gustin et al., this issue (a)].

### 2.1. Uncontrolled Irrigation (Rain Event)

Although “it never rains in the desert” (M. S. Gustin, personal communication, 1996), it became apparent by 1100 hours (local time) on September 2 that storms were approaching, and a rain event of ~2 cm occurred from ~1220–1240. All FC were in place and operating over soils by ~0930–1000, prior to rain. However, after some initial soil measurements, three of these systems (ORNL, UG, UM) were removed from soils for several hours of blank measurements. Because of the approaching rain, the ORNL and UM FC were not again deployed until some time after the rain event, over wet soils (1330 for ORNL, 1530 for UM), while the UG FC was again operating over still dry soils by 1130. Hence, when the rain began, five FC were already in place over dry soils (FG, UG, EC, GU, GKSS), while two FC were deployed over wet soils after the event (ORNL, UM). Once underway, all FC ran undisturbed for ~20 hours, which included a second rain period after sunset of ~1 cm, from 1900 to 1945. Visual inspection of the surrounding soils indicated that the wetting front from the first event was isolated to the upper 2–3 cm, and all soils were still clearly wet the following morning but quickly dried under full Sun by midafternoon (by visual inspection).

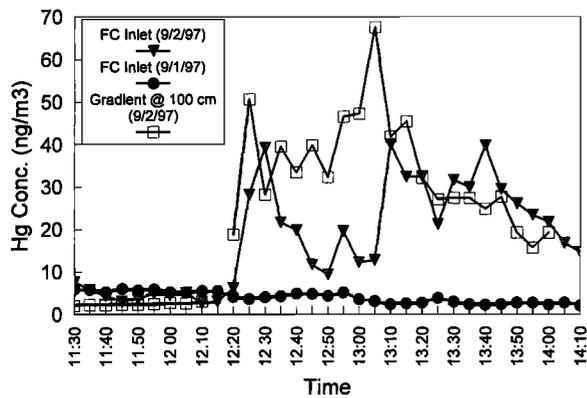
### 2.2. Controlled Irrigation

Because of the response seen in the FC data after the first rain event, a controlled soil wetting experiment was performed on the final day, ~40 hours after both rain events and when soils were again thoroughly dry. This experiment was designed in part to test the hypothesis that the Hg flux was due to reduction of Hg<sup>2+</sup> delivered in the rain event itself. After ~20 hours of undisturbed operation, and beginning at 1000 on September 4, four of the FC plots were rapidly watered by hand with low-Hg (<0.5 ng/L) distilled water to simulate the moisture delivered by a 1-cm rain event (using the same watering device, plots were watered between 1000 and 1015 in this order: UM, UG, EC, GKSS). Each FC was carefully lifted from the soil, and water was applied uniformly for ~1 min followed by sealing of the FC over the wet soil surface. The ORNL plot immediately adjacent to the UM plot was left unwatered as a control. All FC were then operated without further disturbance for 2–3 hours in full sunlight. Adjacent open soil plots were watered similarly and monitored visually for drying rate. Visible moisture was still apparent after 2 hours at a depth of 1 cm. Inspection of the original plots below the FC prior to watering indicated that all visible traces of soil moisture from the events on September 2, 1997, were gone.

## 3. Results

### 3.1. Response of Hg Fluxes to Precipitation Events

From the onset of the first rain event it was apparent from the mercury analyzer readouts that precipitation was having an effect on airborne Hg at the Steamboat Springs field site. The effect was initially manifested in rising air concentrations as illustrated in Figure 1a which shows the 5-min Tekran data for two sites ~20 m apart. Trends in local climatology during the rainfall events are shown in Figure 1b. Each research group at five different locations observed similar responses during and immediately following the initial rain event, and Hg levels in air remained above those measured during the prerair period



**Figure 1a.** Trends in ambient air concentrations of Hg before and after the rain event at ~1220 on September 2, 1997. Flux chamber (FC) data provided by the UG were measured 15 cm above the soil at the FC inlet on September 1 prior to the rain event and on September 2. Gradient data from EC were measured at 100 cm above the soil on September 2 (also at 245 cm, not shown).

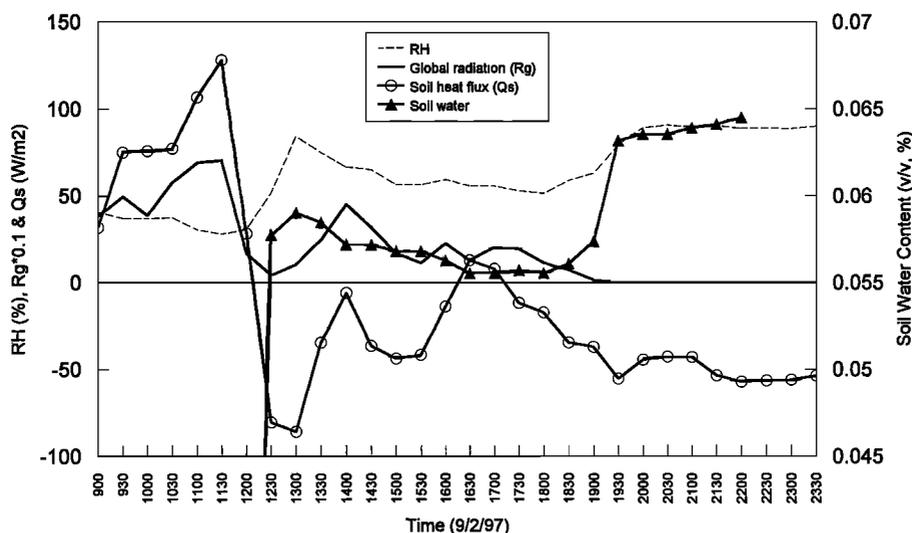
for at least 30 hours following the second rain event. The mean air concentration measured throughout the Steamboat Springs area by eight different systems increased from  $7.6 \pm 9.3 \text{ ng/m}^3$  at 1200 prior to the event, to  $31 \pm 25 \text{ ng/m}^3$  at 1630. There was not a similar consistent increase in air concentrations following the second rain event which fell on already wet soils after sunset (mean  $\text{Hg}^0$  equals to  $32 \pm 20 \text{ ng/m}^3$ ). By 1830 the following day the area mean air concentration had decreased to  $13 \pm 14 \text{ ng/m}^3$ , but concentrations did not return to pre-rain levels until ~1200 of the final day (September 4). Although other climatic variables also varied over this period (Figure 1b), it is clear that the rain event was at least partially responsible for the measured increase in ambient Hg concentrations.

As reflected in the concentration data, Hg emissions from these desert soils responded rapidly to the initial rain event. Figure 2 illustrates the trends measured with six different flux

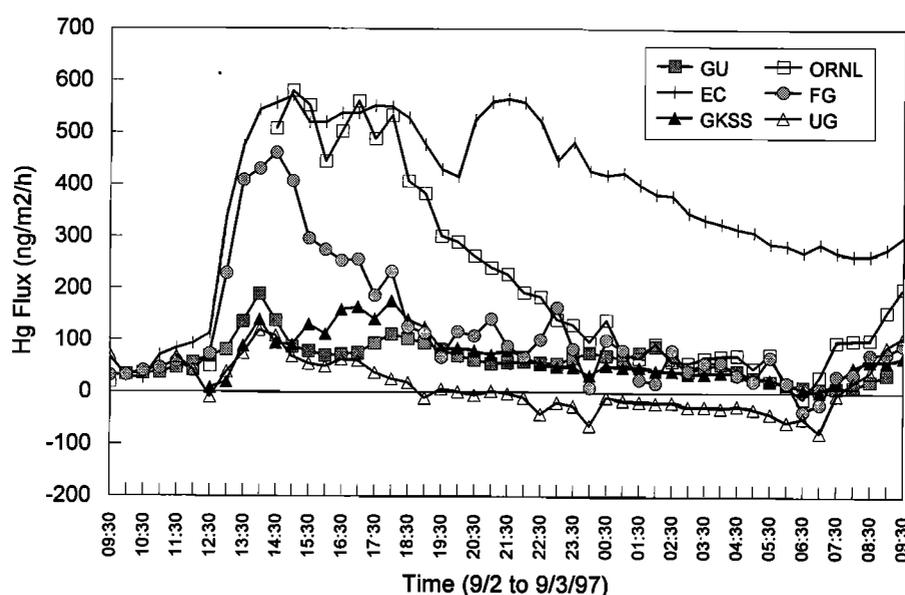
chambers, showing a remarkably similar pattern in the timing of the fluxes following rain; a sharp increase then two or three generally smaller peaks, followed by a gradual decline at night to fluxes comparable to pre-rain values, and a slower increase after sunrise the following day. Beginning at comparable pre-rain fluxes throughout the site (overall mean  $47 \pm 19 \text{ ng m}^{-2} \text{ h}^{-1}$ ,  $n = 27$ , for the period 0930–1200, see Table 1), soil Hg emissions measured by all FC increased dramatically over the next 2–3 hours beginning at ~1230. The mean post-rain flux measured across the area was  $\sim 290 \text{ ng m}^{-2} \text{ h}^{-1}$  ( $\pm 250$ ,  $n = 86$  for the period 1300–2000), but some sites responded more dramatically. The responses fell into two groups: three FC at three different sites (FG, EC, ORNL) exhibited peak fluxes of  $\sim 500\text{--}600 \text{ ng m}^{-2} \text{ h}^{-1}$ , while the other three FC (GU, GK, UG) reached peak fluxes of  $\sim 100\text{--}200 \text{ ng m}^{-2} \text{ h}^{-1}$  over the same period. The UM FC (not shown) operated only from 1530 to 1800 but measured a peak flux of  $\sim 1000 \text{ ng m}^{-2} \text{ h}^{-1}$  at 1530. These initial peaks were all followed by variable but generally decreasing fluxes throughout the day. Following sunset at 1815, the fluxes all decreased during the night, but the EC and FG FC exhibited an additional peak following the second rain event at ~1930 (Figure 2).

As suggested by the peak fluxes, the overall means for the 7-hour post-rain period of elevated fluxes differed significantly between two groups of sites, with one group around  $300\text{--}500 \text{ ng m}^{-2} \text{ h}^{-1}$  and the second around  $50\text{--}120 \text{ ng m}^{-2} \text{ h}^{-1}$  ( $p < 0.01$ ). The afternoon fluxes on September 2, 1997, were about sixfold higher on average compared to the same period on the previous day for the same sites (only GU, GKSS, and FG operated on September 1; mean equal to  $29 \pm 19$ ,  $n = 34$  for 1300–2000). The moisture effect appeared to extend into the following day as well, with the mean flux across the area still well above that before the rain event (mean equal to  $190 \pm 180$ ,  $n = 64$  for 1300–2000 on September 3, 1997). The soils retained a wet appearance until midday on September 3, 1997.

Given the differences in sampling locations, FC design, soil Hg levels, and flux measurement approaches, the similarity in trends after the rain event are a strong indication of a common



**Figure 1b.** Trends in climatologic variables measured at the Steamboat Springs site by several groups (post-rain soil moisture data measured at EC site and pre-rain data estimated from Gustin *et al.* [1996], atmospheric variables recorded at UM/ORNL site). Unfortunately, no group thought to operate a recording rain gage in the desert. Soil moisture from L. Poissant (personal communication, 1997).



**Figure 2.** The response of Hg emission from soils to rainfall recorded by six flux chambers on different soil plots at the Steamboat Springs geothermal area on September 2, 1997 (see text for site codes). For comparison, mean fluxes during the previous day were  $\sim 30 \text{ ng m}^{-2} \text{ h}^{-1}$  (during  $\sim 1300\text{--}2000$ ) at the GU, GKSS, and FG plots.

**Table 1.** Statistical Summary of Fluxes Measured in Response to Increased Soil Moisture Resulting From Natural Rainfall Events ( $\sim 3 \text{ cm}$  on September 2, 1997, at  $\sim 1215$ , See Text) and Manual Irrigation ( $\sim 2 \text{ cm}$  Equivalent Precipitation on September 4, 1997, at 1000)

Data	Event	Hg Flux, $\text{ng m}^{-2} \text{ h}^{-1}$				
		Preevent Mean ( $\pm$ s.d.)	Postevent Mean ( $\pm$ s.d.)	N	Peak Flux	Time of Peak
<b>Data from flux chambers</b>						
EC	Rain <sup>a</sup> (Sept. 2, 1997)	62 (28)	516 (60)	13	570	1500
GKSS	Rain <sup>a</sup> (Sept. 2, 1997)	...	122 (42)	13	131	1530
ORNL	Rain <sup>a</sup> (Sept. 2, 1997)	35 (...	496 (66)	10	580	1500
UM <sup>b</sup>	Rain <sup>a</sup> (Sept. 2, 1997)	...	1058 (151)	4	988	1530
FG	Rain <sup>a</sup> (Sept. 2, 1997)	42 (10)	283 (114)	13	461	1430
UG	Rain <sup>a</sup> (Sept. 2, 1997)	61 (16)	54 (35)	13	119	1400
GU	Rain <sup>a</sup> (Sept. 2, 1997)	42 (10)	103 (34)	13	189	1400
<b>Micrometeorological data</b>						
EC <sup>c</sup>	Rain <sup>a</sup> (Sept. 2, 1997)	...	1033 (685)	6	2364	1530
UNR/USGS	Rain <sup>a</sup> (Sept. 2, 1997)	340 (810)	1400 (1782)	13	2028	1430
UG	Rain <sup>a</sup> (Sept. 2, 1997)	340 (360)	831 (402)	9	637	1500
<b>Data from flux chambers</b>						
EC	Irrigation <sup>a</sup> (Sept. 4, 1997)	160 (13)	768 (122)	5	842	1130
GKSS	Irrigation <sup>a</sup> (Sept. 4, 1997)	19 (15)	670 (196)	4	812	1130
UM	Irrigation <sup>a</sup> (Sept. 4, 1997)	50 (20)	602 (72)	5	590	1100
UG <sup>d</sup>	Irrigation <sup>a</sup> (Sept. 4, 1997)	15 (...	582 (305)	2	797	1100
ORNL	Irrigation <sup>a</sup> (Sept. 4, 1997) (control) <sup>e</sup>	21 (7)	114 (17)	5	132	1230
GU	Irrigation <sup>a</sup> (Sept. 4, 1997) (control)	15 (13)	85 (44)	5	147	1100
<b>Micrometeorological data</b>						
ORNL	Irrigation <sup>a</sup> (Sept. 4, 1997) (control)	250 (130)	439 (184)	4	670	1200
UG	Irrigation <sup>a</sup> (Sept. 4, 1997) (control)	570 (220)	692 (450)	4	1240	1200

The preevent data represent the period 0930–1200 on September 2, 1997. Values should be considered accurate to two significant figures only and are derived from 30-min mean fluxes.

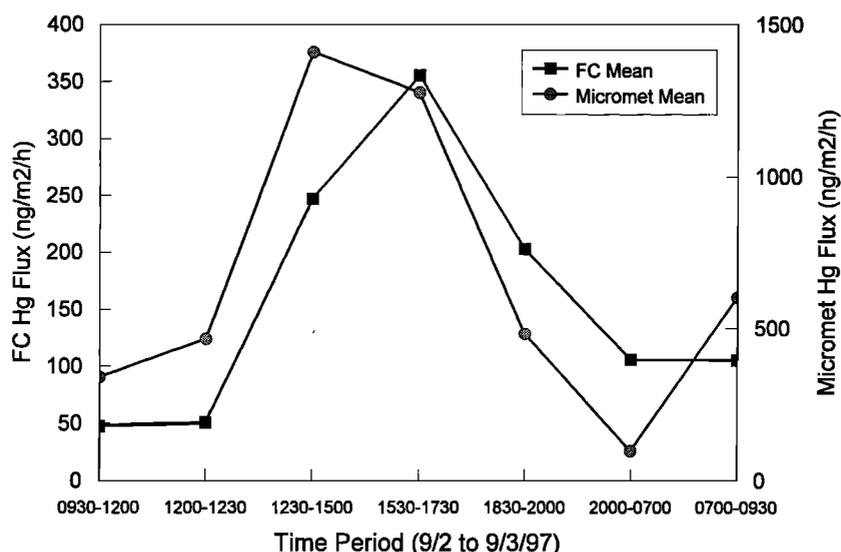
<sup>a</sup>Rain response (postevent) period is 1300–2000 on September 2, 1997; irrigation postevent period is 1030–1230 on September 4, 1997.

<sup>b</sup>UM sampled from 1530 to 1700 only.

<sup>c</sup>EC sampled from 1530 to 1800 only.

<sup>d</sup>UG sampled from 1030 to 1100 only.

<sup>e</sup>Controls received no irrigation (ORNL adjacent to MU; GU adjacent to GKSS).



**Figure 3.** Trends in mean fluxes for seven flux chambers (FC) and three micrometeorological systems operated during a period of rain. Shown are data for several sequential time intervals representing different behavior (in order: prerin, rain, initial peak, second peak, second rain event, dark, postsunrise). Sample  $N$  values are  $\sim 10$ – $100$  for FC data and  $\sim 5$ – $20$  for micrometeorological data. Relative standard errors of the mean fluxes are of the order of 20% (FC) to 40% (micrometeorological). The large difference in fluxes reported by the FC and micrometeorological approaches appears to be a function of the FC design, in particular the flushing rates used which caused FC to underestimate soil fluxes due to extended FC turnover times (H. Zhang and S. E. Lindberg, manuscript in preparation, 1999).

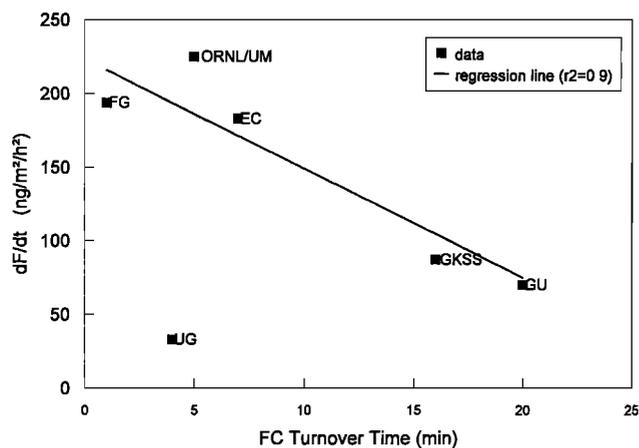
response of Hg flux to rainfall and the resulting increase in soil moisture in these desert soils. The responses of the different FC/soil plot combinations were significantly intercorrelated ( $p < 0.01$ ), with fluxes from the most complete data period (1430–0900,  $n = 38$ ) showing correlations among FC ranging from 0.44 (UG-EC, the two most different FC designs) to 0.92 (ORNL-GKSS, same FC design with two different flow rates). Overall, the mean  $r$  values for each FC with all five other FC ranged from 0.63 (UG) to 0.81 (ORNL) indicating that the FC were all responding in a qualitatively similar fashion to the effects of the rain event, despite the fact that the ORNL FC was placed on already wet soil, while the others were in place during the rain event.

Because of the similar behavior of the FC data, the possibility of an artifact must be considered. Flux chambers by their nature of being enclosed systems influence the exchange of gases over the surface, particularly for static designs. From the start it was readily apparent to the participants that the field FC and micrometeorological data were providing quantitatively different fluxes over these soils (FC fluxes were consistently lower, Figure 3). This is the subject of the accompanying paper by Gustin *et al.* [this issue (a)]. Despite the differences in magnitude, however, it is clear that both FC and micrometeorological measurement systems responded similarly over time to the rain event. Three of the FC designs showed significant but low correlations with the most complete micrometeorological data from the UNR/USGS site:  $r$  values ranged from 0.34 for ORNL ( $p < 0.05$ ) to  $\sim 0.47$  for FG and UG ( $p < 0.01$ ). The temporal patterns are basically the same, but the micrometeorological fluxes peaked before those measured by the FC, probably as a result of the delayed response times of the FC (turnover times ranged from 0.02 to 0.33 hours). However, the magnitudes of the fluxes are clearly different, with the FC yielding mean fluxes generally 15–20% of the micrometeo-

logical fluxes during daylight periods and 40–100% after dark. Recent chamber experiments in our laboratory have demonstrated a strong dependence of measured fluxes on FC flushing rates. Fluxes over these same soils in our laboratory increased in proportion to flushing rate suggesting that FC underestimate actual fluxes at low turnover frequencies (H. Zhang and S. E. Lindberg, manuscript in preparation, 1999). These differences are discussed in detail elsewhere [Gustin *et al.*, this issue (a)]. Despite these differences, the drastic effect of the rain event on Hg fluxes is real and apparently occurred across the entire Steamboat Springs sampling area, increasing mean Hg fluxes by an average of 4–8 times, and persisting for several hours. This is somewhat surprising considering that the soil depth visibly affected by the initial rainfall was limited to the upper few centimeters.

Although the trends in FC responses to the rain event were similar, there were important differences in the magnitudes of fluxes measured by the chambers, as well as in the rate of flux increase following rainfall,  $dF/dt$ . These differences could be the result of soil chemistry and Hg content, but our data suggest they are not. We have previously noted that the response of a FC to an outside stimulus (e.g., solar radiation) is limited by the FC flushing rate and that systems with a slow turnover time exhibit a delayed response [Carpi and Lindberg, 1997]. The computed values of  $dF/dt$  for the initial peak seen by each chamber are strongly related to turnover time ( $t = \text{FC volume}/\text{flushing rate}$ ). Excluding the UG FC which suffered blank problems, the variance in turnover time among FC explains over 80% of the variance in  $dF/dt$  (Figure 4). In this regression the ORNL, GKSS, and GU FC illustrate this trend particularly well, as they are each of identical design [Kim and Lindberg, 1995], but operated with different flushing rates (5, 16, and  $\sim 20$  Lpm, respectively).

Another important factor is the degree to which soil mois-



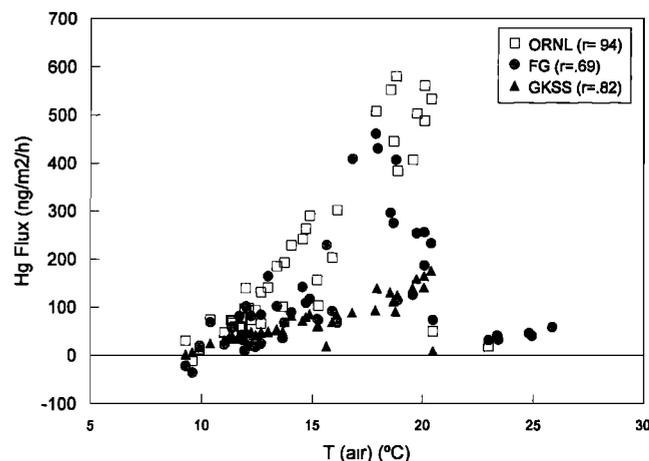
**Figure 4.** The rate of increase in soil flux following rain as measured by several flux chambers plotted as a function of FC turnover time (see text for site codes).

ture was increased. The OR FC falls above the regression line as a result of its deployment over already wet soils following the rainfall. The ORNL and UM chambers, which were placed on adjacent soil plots after rainfall had ceased, exhibited among the highest rates of increase and flux maxima (Figure 4 and Table 1). This suggests that the Hg response was related to the degree of increased soil moisture. Following rainfall, soil moisture in the upper 2 cm of open plots increased from extreme aridity (<1%, vol/vol) to ~5–6% (Figure 1b), but no data are available for the plots covered by FC. Since soil water appears to drive the increased fluxes, it is surprising that the other FC plots exhibited temporally similar responses to the ORNL and UM FC. However, the design of the various FC that were in place prior to the rain probably influenced the degree to which moisture penetrated the underlying soils. The EC FC, which exhibited the highest mean flux, and also a peak after the second rain event (unlike the other FC), was a 0.4 m diameter hemisphere, a design conducive to transporting falling rain into the immediate vicinity of the underlying soil. This site was also situated on a former stream outwash which exhibited a coarse and highly porous texture which was amenable to rapid diffusion of water into the soils beneath the chamber. The FG FC was situated near the EC site, on finer soils, but was of a design with a minimal footprint beyond the FC walls, while the GKSS and GU FC both had a teflon skirt for sealing the FC to the soil. These skirts reduce the transport of rainwater to soils below the FC surfaces (the ORNL and UM designs have the same skirts but were on already wet soils). The fact that all chambers did respond to moisture increases in the surrounding soils to some extent suggests that the effective “footprint” of these chambers may extend beyond their actual dimensions (this idea is also supported by reported correlations between flux and solar radiation for the EC FC which is opaque [Poissant and Casimir 1998]).

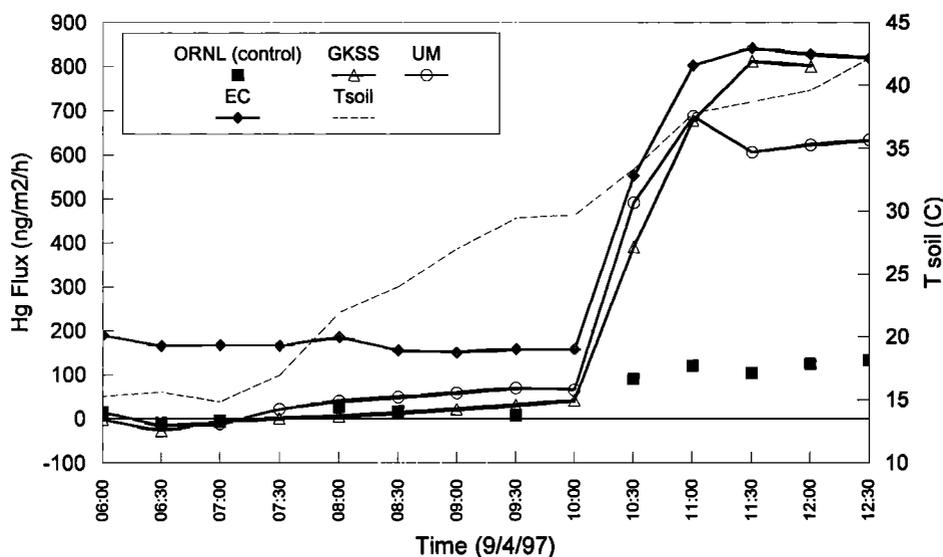
Once soil moisture was increased, the resulting fluxes may have been influenced by a number of variables. Soil Hg content was apparently not one of them. We found no significant relationships between total soil Hg or soil Hg<sup>o</sup> content and Hg flux (we regressed both the mean and maximum fluxes for the postrain period against soil concentrations for each plot; both  $r < 0.45$ ,  $p > 0.10$ ,  $N = 7$ ). However, for the 31-hour period following rainfall (1230–0930), the fluxes measured by

all but the EC FC showed significant correlations ( $p < 0.01$ ,  $N > 40$ ) with these variables: air temperature (mean  $r = 0.76$ ,  $N = 5$  FC), global radiation ( $r = 0.54$ ), wind speed ( $r = 0.61$ ), soil moisture ( $r = 0.75$ ), and relative humidity ( $r = 0.73$ ). The UNR/USGS micrometeorological data showed lower but still significant correlations with these variables, while the opaque EC FC exhibited a comparable correlation only with temperature ( $r = 0.49$ ). Of the parameters we measured, temperature is the one variable most often found to show a strong relationship with soil Hg emissions [e.g., Lindberg *et al.*, 1979; Poissant and Casimir, 1998], and air temperature consistently showed the best postrain correlations (soil temperatures were not recorded continuously, but the ORNL/UM soil plots were measured intermittently with a probe at 2 cm depth both inside and outside of the FC, and these temperatures exhibited a correlation coefficient of 0.99 with air temperature). Figure 5 shows the plot of soil flux versus temperature for selected plots and suggests that Hg may exhibit a hysteresis effect during this period (this effect is most apparent for the FC with the fastest turnover times: FG, ORNL, EC, and UG). Mercury flux over wet soils increases with rising soil temperatures along the upper curve (~1300 to 1530) but shows a different response to falling temperature along the lower curve (~1530 to 2000). This behavior suggests that there may be two different processes influencing the response to temperature, one during sunlight (rising limb) and one in the dark, or that the kinetics of one process are light sensitive.

It is also possible that these various correlations simply reflect similar diel cycles among the variables. When the daylight period (1230–1930,  $N = 14$ ) was examined alone, the correlations generally decreased, and were significant for fewer FC (primarily GKSS and ORNL); but those with solar radiation were most consistent (mean  $r = 0.66$ ,  $p < 0.01$ ,  $N = 5$ ). Flux increased in parallel with radiation after the first event (compare Figures 1b and 2), but the role of solar radiation in controlling flux in these soils is uncertain [see Gustin *et al.*, this issue (b)].



**Figure 5.** The relationship between soil flux and air temperature for three flux chambers (the correlations shown in the text were computed from all data for each FC; only three sites are illustrated here). The FG and ORNL data suggest a hysteresis effect. The low flux values along the x axis near 25°C are from the prerain period (see text for site codes).



**Figure 6.** The response of Hg emission from soils to manual irrigation with low-Hg distilled water ( $<0.5$  ng/L) recorded by three flux chambers on different soil plots, plus data from an adjacent control soil. The plots were irrigated at 1000 hours. Soil temperature ( $T_{\text{soil}}$ ) within the flux chamber at 2 cm depth is also shown (see text for site codes; the UG chamber reported a similar trend but did not operate continuously and is not shown).

### 3.2. Response of Fluxes to Controlled Soil Irrigation

It has been hypothesized that rain can deliver a fresh pool of reactive (e.g., easily reducible)  $\text{Hg}^{2+}$  to soils or surface waters which can be converted to  $\text{Hg}^0$  by organic matter (R. R. Turner, Frontier Geosciences, Seattle, personal communication, 1998), and increased Hg evasion from water surfaces has been noted after rain events in subtropical wetlands [Lindberg *et al.*, 1998]. To test the possibility that the composition of the rain itself influenced the measured Hg fluxes, a simple test was performed at several soil plots. On the final day of the inter-comparison ( $\sim 46$  hours postrain), four plots were irrigated with a volume of low-Hg distilled water ( $<0.5$  ng/L) comparable to the first rain event (UM, UG, GKSS, EC), while one plot was maintained as a control (ORNL, adjacent to UM), and fluxes were monitored for 2–3 hours. The response to irrigation was remarkably similar among the four plot/FC combinations (Figure 6) and paralleled that seen following the rain 2 days earlier. Within an hour of irrigation, fluxes in each plot increased by an order of magnitude and by a nearly identical factor over the control soil for the same period (treatment/control equal to  $6.1 \pm 0.6$ ). This observation is not consistent with a strong effect of rain chemistry and supports the concept that moisture addition alone significantly enhances Hg fluxes.

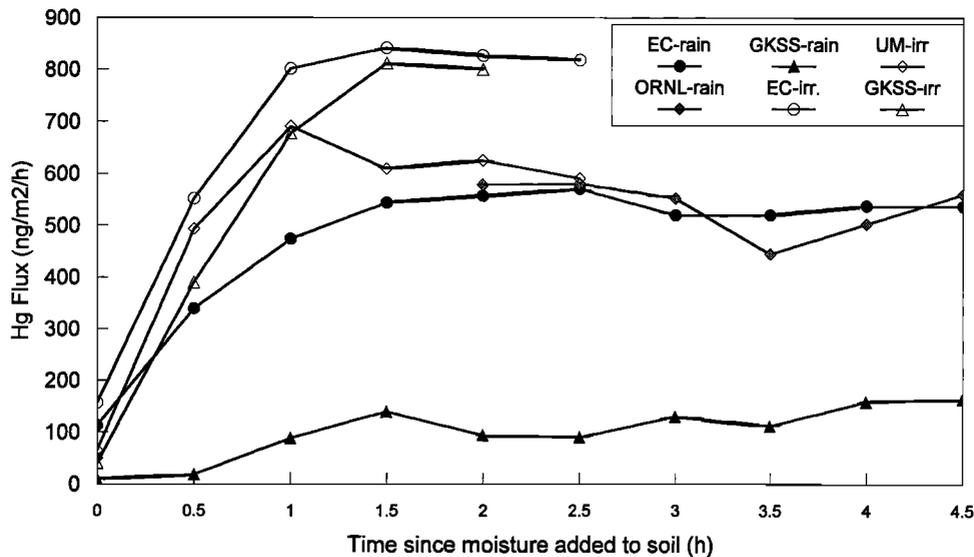
Figure 7 illustrates the response of Hg flux to both natural rainfall and artificial irrigation for three “matched” FC plots, two of which had FC over dry soils prior to the rain (GKSS, EC), and one which had the FC placed on wet soil after rain (ORNL/UM). For the GKSS and EC plots the data show that Hg flux over irrigated soils increases more rapidly and reaches a higher plateau compared to the response after rainfall. This difference is most dramatic for the GKSS plot and supports the idea that much of the variance in flux response after rainfall was related to the amount of moisture actually reaching the soils beneath the FC. Although the EC and GKSS FC remained over the same plots throughout the study, the design of the EC FC and greater soil porosity at that site combined to promote diffusion of the rainwater into the underlying soils, while the

GKSS FC design and soil texture were less conducive to this process, resulting in a much reduced response. However, upon direct irrigation, the Hg flux over both soils responded similarly. The ORNL and UM FC represent an interesting “pair” because the positions of these FC were exchanged on September 3 between the rain and irrigation events, meaning that the flux versus time response for each event (rain on September 2 and irrigation on September 4) represents the same soil plot. These curves are plotted together in Figure 7 where the response of Hg flux after irrigation (UM FC, 0 to 2.5 hours) matches surprisingly well with that after rain on the same plot (ORNL FC, 2 to 4.5 hours). This suggests that the delayed start of the ORNL FC after rainfall on September 2 probably missed the peak soil flux which occurred at most sites  $\sim 1.5$ – $2.5$  hours after the rain ended (Figure 2).

## 4. Discussion

There are several processes which could be responsible for the increase in Hg flux following the addition of water to these desert soils. The irrigation experiment with low-Hg-distilled water does not support the hypothesis that a form of easily reduced, reactive Hg is added to soils by rainfall in sufficient amounts to cause the response. Rather, the increase in flux appears to be related to soil physical or chemical interactions. The shapes of the response curves of flux versus time (Figures 2, 6, and 7) suggest that the initial response to moisture may exhibit first-order behavior. The 30-min mean fluxes suggest that the response plateaus within 30–60 min after water is added, but that most of the increase occurs in the first 30 min. However, these data were averaged from 5- or 10-min fluxes, and the 5-min raw data available to us for the irrigation experiments (EC, UM, GKSS) show that the fluxes plateau at  $\sim 20$  min and appear to follow a first-order function to that point (data not shown).

Table 2 summarizes rate constants from the initial flux response curves for the most complete data sets (EC (rain/



**Figure 7.** The relationship between Hg flux over soils and time since moisture was added to soils for both rain and irrigation events (all sites showed these trends; a subset of sites are shown for comparison; see text for site codes). Note that the fluxes for the 2 and 2.5 hour time periods from the UM-irr and ORNL-rain data sets represent the same soil plot (the UM and ORNL FC swapped positions between the rain and irrigation events; see text).

irrigation), GKSS (rain/irrigation), ORNL/UM (control/irrigation), and FG (rain); we used the highest time resolution data available to compute these values, generally 10-min fluxes). These coefficients fall into two general ranges (Table 2):  $k_2 < 0.04$  (mean  $0.033 \pm 0.007$ ) for plots where moisture was added indirectly by rain to soils surrounding the FC, and  $k_2 > 0.07$  (mean  $0.086 \pm 0.023$ ) for plots where water was added directly by irrigation of soils beneath the FC. The nonirrigated control soil exhibited a much lower rate constant of (0.005) for the response to increasing solar radiation and soil temperature. Given the initial fluxes ( $k_1$ ) measured at each site prior to increased soil moisture, we can compute flux doubling times for each response curve:

$$t_{2x} = [\ln(2F_0) - \ln(k_1)]/k_2.$$

Following direct irrigation, the soil fluxes doubled within 2 to 12 min (mean  $7 \pm 4$  min), compared to a much slower response for the dry control soils ( $t_{2x} \sim 90$  min). When rain wetted the soils indirectly outside of the FC footprint, fluxes doubled in  $\sim 20$ – $30$  min (Table 2).

Considering the rapid response time ( $\sim 10$  min) and its duration ( $> 12$  hours), both physical and chemical soil processes probably contributed to the observed fluxes. We will briefly consider the possible contributions of the following processes: (1) physical displacement of Hg-enriched soil gas by the percolating rain water front, (2) exchange of Hg(0) adsorbed on dry soil particle surfaces with (rain) water molecules, and (3) desorption of Hg(II) adsorbed on soil solid particle surfaces and its subsequent reduction. The hypothesis that Hg<sup>2+</sup> in rainwater was reduced to create the observed fluxes is not supported by the irrigation data.

Our data for Hg concentrations in ambient air showed two separate increases during the rain event (Figure 1a), a short (15 min) intense spike, followed by a second increase of longer duration (80 min). We hypothesize that the first is the signal of a physical displacement of Hg-enriched soil gas by the perco-

lating water front, while the second is the primary response to increased soil moisture and represents a different process. The transient nature of this initial spike make it difficult to measure the resulting flux, and the FC with the highest time resolution (FG) actually recorded a decreased flux during this spike (Figure 2). This decrease was probably an artifact of the rapid spike in the ambient air Hg concentration at the FC inlet compared to the slower FC turnover time.

We can, however, roughly approximate the flux that could have resulted from the physical displacement of soil gas during the initial spike. Concentrations of Hg<sup>0</sup> in soil gas were not measured in this study as there are no accepted field measurement methods, and few comparable data exist for comparison. Hence we estimated the contribution of the prerain soil gas Hg<sup>0</sup> using Fick's diffusion law [Hillel, 1982] as applied by Johnson and Lindberg [1995]. We assumed that meteorological effects are slight inside an enclosed flux chamber and estimated the contribution of the soil gas Hg<sup>0</sup> which was displaced by the rain water as follows:

**Table 2.** Rate Constants for the Increase of Hg Flux Over Wetted Soils

Soil Plot and Flux Chamber	Event	$k_1$	$k_2$	Flux Doubling Time, min
EC	rain	4.7	0.036	20
FG	rain	4.3	0.038	18
GKSS	rain	2.2	0.025	27
EC	irrigation	4.9	0.073	12
GKSS	irrigation	4.2	0.119	2
UM	irrigation	4.2	0.111	6
ORNL	control	4.4	0.0052	90

Constants were computed from the initial slope of  $\ln$  (flux) versus time response curves for both rain and irrigation events. The equation is of the form  $F = k_1 \times e^{k_2 t}$  (see text).

$$F = -0.66(p - s)D_0(C_{\text{Hg-air}} - C_{\text{Hg-soil gas}})/d$$

where  $F$  is the soil Hg flux ( $\text{ng m}^{-2} \text{h}^{-1}$ ),  $p$  is the soil porosity ( $V_{\text{pore}}/V_{\text{soil}}$ ),  $s$  is the soil moisture saturation,  $D_0$  is the Hg(0) diffusion coefficient in the ambient air ( $0.13 \text{ cm}^2 \text{ s}^{-1}$  or  $0.047 \text{ m}^2 \text{ h}^{-1}$  at  $25^\circ\text{C}$ ) [Thibodeaux, 1996],  $C_{\text{Hg-air}}$  is the Hg(0) concentration in the air immediately above the soil surface ( $\text{ng m}^{-3}$ ),  $C_{\text{Hg-soil gas}}$  is the Hg(0) concentration in soil gas ( $\text{ng m}^{-3}$ ), and  $d$  is the soil depth considered for the diffusion gradient (cm) (taken as the depth of the rain wetting front). The constant, 0.66, is a tortuosity coefficient, suggesting that the apparent path is about two thirds the length of the real average path of diffusion in the soil [Hillel, 1982]. Using pre-rain measured mean values of  $C_{\text{Hg-air}}$  (prerain) =  $5 \text{ ng m}^{-3}$  and  $F$  (prerain) =  $40 \text{ ng m}^{-2} \text{ h}^{-1}$ , and assuming  $p = 50\%$ ,  $s = 1\%$ , and  $d = 2 \text{ cm}$ , we estimate the  $C_{\text{Hg-soil gas}}$  (prerain) was  $\sim 60 \text{ ng m}^{-3}$ . The rain wetting front was seen to extend to  $\sim 2 \text{ cm}$  in depth, and we estimate that the Hg $^0$  concentration inside the flux chamber attributed to displaced soil gas ( $C_{\text{Hg-chamber}}$ ) was  $\sim 3 \text{ ng m}^{-3}$ , a small fraction of the initial measured spike ( $\sim 35 \text{ ng m}^{-3}$ , Figure 1a). These data lead to an estimated flux of the order of  $10 \text{ ng m}^{-2} \text{ h}^{-1}$  for soil gas displacement which would be only a few percent of the mean Hg emission measured over the area for the 2.5-hour period following the rain event ( $260 \pm 190 \text{ ng m}^{-2} \text{ h}^{-1}$ ,  $n = 27$ ). Although only a crude estimate, this calculation suggests that gas displacement alone could not account for a significant fraction of the emitted Hg.

It is more likely that the second process listed above has a major contribution. The soil analyses [Gustin, et al., 1996, this issue (a)] show that most of the soil plots contained a large proportion of total Hg as Hg $^0$ ,  $\sim 30\text{--}50\%$ . Since the soil mercury flux over prerain dry soils was relatively low ( $\sim 40 \text{ ng m}^{-2} \text{ h}^{-1}$ ), we propose that before the rain, most of the Hg $^0$  in the soils was adsorbed to dry soil particle surfaces and not directly available for emission. Various kinds of oxygen surface functional groups on soil mineral particle surfaces have a higher affinity for water molecules than for Hg $^0$  atoms (as a class B soft acid, Hg $^0$  favors S and N groups [Schuster, 1991]), and the adsorption of Hg $^0$  on dry soil particles has been reported [Fang, 1978; Klusman and Matoske, 1983]. It follows that percolation of rainwater into the soil pores led to exchange of the water molecules with the Hg $^0$  adsorbed on the previously dry soil particles. As a result, the Hg $^0$  was desorbed into soil gas (and/or overlying air) creating a pool of "available" Hg $^0$ , which was emitted during the broad postrain peak of elevated Hg flux (Figure 2). A similar phenomenon is known to influence volatile pesticides, which are also more strongly bound to dry than wet soils [e.g., Spencer and Cliath, 1974]. In a study of competitive sorption between VOCs and water in Nevada soils, small additions of water drastically decreased VOC sorption, leading to increased volatilization [Steinberg and Kreamer, 1993].

In laboratory studies, adsorption of Hg $^0$  on soil particle surfaces was found to depend on soil mineralogical composition and surface area [Fang, 1978; Klusman and Matoske, 1983]. The observation that measured Hg concentrations in the clay and silt fractions of the soil samples from most sites were higher than those of all other fractions (P. Rasmussen, Geological Survey, Canada, personal communication, 1998) provides further evidence that desorption of Hg $^0$  could have been a major contributing process to account for the sustained increase in Hg flux. Upon drying, more soil particle surfaces became available for Hg $^0$  adsorption. Consequently, the Hg $^0$

readily available for diffusion and emission would be read-sorbed, resulting in decreased flux upon soil drying, which agrees well with our observations (Figure 3). Manual irrigation 2 days after the rain again liberated the adsorbed Hg $^0$ , leading to another emission pulse. Recent laboratory studies have confirmed our hypothesis: manual addition of water to dry Steamboat Springs soils (as well as background soils from Tennessee) liberated significant Hg $^0$ , while a similar addition of less polar methanol to the Steamboat Springs soils elicited no emission response (M. S. Gustin and H. Zhang, unpublished data, 1998).

Aqueous reactions involving Hg(II) in soil solution are also a possible explanation. If there were sufficient Hg(II) present in a form readily reduced by either biotic or abiotic processes, then the addition of water to soils could enhance the production of Hg $^0$ . Such reactions would have been suppressed in the prerain dry soils. The role of possible biotic activities stimulated by rainwater still remains debatable, but the extreme aridity of the prerain soil combined with the rapid flux response seems to rule out a significant role of microbial processes. However, there are several possible abiotic pathways, and desorption of soil-bound Hg(II) and subsequent reduction to Hg $^0$  in soil solution must also be considered as contributing processes. Once rainwater was added to the dry soils, desorption of Hg(II) could readily occur into the initially low-Hg solution. In the presence of soil organic acids, dissolved dioxygen, and photoactive Fe(III), Hg(II) could be reduced via various pathways by reactions enhanced to different degrees in sunlight (discussed by Zhang and Lindberg [this issue]). However, we suspect that these contributions should be smaller than the desorption of Hg $^0$  by the percolating water molecules because the water-soluble Hg(II) fractions for all the sites were shown to be quite small [Gustin et al., this issue (a, b)]. However, another candidate process could involve photosolubilization of the cinnabar (HgS) present in these soils [Gustin et al., this issue (b)]. While this reaction directly generates Hg(II), it has also been reported to result in reduction of Hg(II) and subsequent volatilization of Hg $^0$  in the laboratory during UV photoirradiation [Okouchi and Sasaki, 1983]. Because of the role of irradiation, this process would seem to be limited to the surface most soil layer, but without further information this process could not be ruled out as having contributed some Hg $^0$ .

Clearly, further research is required to reveal the mechanisms by which soil moisture affects mercury emission. These observations illustrate the gaps in our current understanding of Hg soil emission mechanisms, Hg $^0$  desorption rates, and Hg(II) reduction processes in soils. It will be difficult to reasonably estimate the contribution of these various processes to the rainfall response measured at Steamboat Springs without much better data on soil Hg speciation and its role in soil emissions. Even with such data, quantitative attribution of the elevated flux to any single process or species would be tenuous since the overall postrain Hg flux (although clearly elevated) represented  $\ll 0.1\%$  (flux/total Hg equal  $1.4 \times 10^{-2}$  to  $4 \times 10^{-6}$ ) of the total Hg pool available in the upper 2 cm of the soils. This study and the other recent observations cited above have clarified the importance of soil moisture in influencing Hg emissions from both background and geologically enriched soils. The dramatic increase in emissions of Hg following irrigation of these desert soils has interesting implications for the role of changing climate regimes on regional biogeochemical cycles of Hg. This is especially true if the response is generally as reproducible as we demonstrated with our irrigation studies

after 2 days of soil drying, and considering the large pool of apparently available mercury in these soils.

**Acknowledgments.** Research is sponsored by the Electric Power Research Institute under contract with Oak Ridge National Laboratory (ORNL). ORNL is managed by Lockheed-Martin Energy Research, Inc. for the U.S. Department of Energy. This paper was prepared in part while the author was a visiting scientist at the Institute for Physical and Chemical Analysis at the GKSS Research Center, Geestacht, Germany. Authors affiliations during this study: S. L., H. Z., J. O. (ORNL); M. G. (University of Nevada, Reno); F. M., A. V. (University of Michigan); A. C., L. P., M. P. (Atmospheric Environment Service, Toronto); R. E., H. K. (GKSS, Germany); C. F., J. K., G. E. (University of Guelph, Canada); P. R. (Geological Survey Canada); M. M. (USGS, California); F. S., D. S. (Tekran Inc., Toronto); J. S., Z. X. (Goteborg University, Sweden); J. L., R. T., D. W. (Frontier Geosciences, Seattle). The authors would like to thank the Electric Power Research Institute for the support for development and testing of Hg flux methodologies which made this study possible. We would also like to thank the UNR students and staff for significant field assistance during Nevada STORMS, and G. Southworth for helpful comments on the manuscript. This is publication 4870 Environmental Sciences Division, ORNL.

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(Received September 29, 1998; revised March 17, 1999; accepted March 22, 1999.)