A PRELIMINARY ASSESSMENT OF WET DEPOSITION AND EPISODIC TRANSPORT OF TOTAL AND METHYL METCURY FROM LOW ORDER BLUE RIDGE WATERSHEDS, S.E. U.S.A.

C. J. ALLAN
Dept. of Geography and Earth Sciences, Unievrsity of North Carolina at Charlotte, Charlotte, North Carolina, 28223, U.S.A.

A. HEYES
Dept. of Geography, McGill University, Montreal, Quebec, Canada

(Received 13 August, 1996; accepted 7 April, 1997)

Abstract. Results from a preliminary sampling program designed to investigate total (THg) and methyl Hg (MeHg) deposition, cycling and transport at the Coweeta Hydrologic Laboratory western North Carolina are presented. Wet deposition samples were collected in June and July 1994 and throughfall, seep and streamwaters were intensively collected during and after a rainfall event in June 1994. All water samples were collected using ultra clean trace sampling protocol. Low elevation Watershed 18 streamwater THg concentrations peaked with discharge, increasing 6 fold to 9 ng L^{-1}. High elevation Watershed 27 which received less than one half the precipitation Watershed 18 received during the event, exhibited THg concentrations only 1.3 times over base flow conditions. Methyl Hg concentrations remained near detection limits ($\leq$ 0.025 ng L^{-1}) in both streams. Dissolved MeHg concentrations were higher in shallow seep (0.097 ng L^{-1}), throughfall (0.135 ng L^{-1}) and precipitation (0.16 0.035 ng L^{-1}) than streamwaters. Initial estimates of annual THg and MeHg deposition and transport indicate >90% retention of THg and a >80% retention or demethylation of wet deposition MeHg is occurring in these low order watersheds,

Key words: episodic transport, methyl mercury, total mercury, wet deposition

1. Introduction

Concern over high methyl mercury (HeHg) contents in sport fish in remote forested lakes in Scandinavia and N. America has spurred recent investigations detailing the cycling and transport of Hg within natural terrestrial and aquatic ecosystems (Driscoll et *al.,* 1995; Hultberg et *al.,* 1995). The coupling of ultra-clean trace element sampling protocol with recent analytic developments for the detection of total mercury (THg) and methyl mercury (MeHg) at sub-ng L^{-1} concentrations has allowed researchers to begin to investigate the magnitude of the fluxes and pools of Hg within natural systems (e.g., Bloom, 1989; Bloom and Fitsgerald, 1998; Horvat *et al.,* 1993). Several recent studies have indicated that significant water transport of astmospherically deposited Hg can occur from terrestrial to aquatic systems through both surface and sub surface flow (Mierle, 1990; Aastrup *et al.,* 1991; Krabbenhoft and Babiarz, 1992; Swain *et al.,* 1992). Owing to the high analytic cost and the strict ultracelan sampling protocol necessary to ensure sample integrity in the field and lobaratory, the majority of Hg sampling programs have relied on regular weekly to monthly sampling schedules rather than intensive short

Water, Air; and Soil Pollution **105: 573-592, 1998.**

Table I

Summary of some physiographic features and mean hydrologic characteristics of Watershed 18 and Watershed 27

	Watershed 18	Watershed 27
Drainage area (ha)	13	39
Slope %	52	55
Elevation at weir (m)	726	1061
Maximum elevation (m)	993	1454
Annual runoff coefficient%[a]	53.6	70.9
Storm runoff ratio %[b]	9.4	29.8

[a] Mean annual runoff (cm)/mean annual precipitation (cm) x 100.

[b] $\frac{(\mathit{Quickflow} + \mathit{quickflow\ after\ peak\ (cm)})}{\text{Mean annual runoff (cm)}} \times 100.$

term sampling. Intensive sampling over rapidly changing hydrologic conditions is necessary to asses the temporal variability of Hg transport during episodic storm runoff or snowmelt events. Here we report the results of a pilot sampling program designed to investigate the short term temporal dynamics of THg and MeHg in S. E. Blue Ridge Watersheds. In addition, initial estimates of Hg wet deposition and streamwater export for this site are presented.

2. Study Area

The Coweeta Hydrologic Laboratory is located in the Nantahala Mountain Range of the Blue Ridge Physiographic Province in western North Carolina, (35” 3′N, 83” 25′W). The study areas physiography, climate, hydrology and vegetative cover has previously been described in detail by Swank and Crossley (1988) and we briefly summarize this work in the following description. The two streams monitored during this study were Grady Branch in Watershed 18 (WS 18) and Hard Luck Creek in Watershed 27 (WS27). Selected physiographic features and hydrologic characteristics of both watersheds are presented in Table I.

Watershed 18 is primarily underlain by the Tullulah Falls bedrock formation while Watershed 27 is underlain by the Coweeta group (Velbel, 1985). The Tallulah falls formation consists of metagraywackes, leptic schists, and metavolcanic rocks. The Coweeta group consists of biotite gneiss, metaarkoses, metasandstones, quartzites, and peltic and biotite schists. Similar assemblages of rock-forming minerals characterize both bedrock types. Major minerals include quartz, muscovite, biotite, plagioclase and almandine garnet; subsidiary minerals include chlorite, kyanite, epidote, clinozoisite, magnetite, staurolitem sillimanite, with local occurrences of microcline, hornblende, zircon, apatite, sphene and tourmaline (Hatcher, 1976 and 1979). Soils at Coweeta fall within two orders: immature Inceptisols and older developed Ultisols, the later having the largest area1 coverage.

Low elevation watersheds at Coweeta such as WS 18 are characterised by gentler slopes and deeper soils than higher elevation watersheds such as WS27. Typically annual hydrologic yields average 50% of precipitation inputs with 9% of this total occurring as quickflow. High elevation watersheds average 75% annual hydrologic yields with 30% of this occurring as quickflow (Swank and Crossley, 1988). Watersheds 18 and 27 both serve as long term reference catchments at Coweeta and are covered with mixed hardwood stands dominated by *Quercus* and *Carya* species and *Acer rubrun L* which have remained unlogged and unburnt since 1924. The tree species comprising the canopy overlying the throughfall collector installed on WS 18 included *Acer rubrum, Tsuga canadesis, Magnoliafraseri, Carya tomentosu* and *Fagus grandiflor.*

In addition to the sampling of the main channelized runoff from Watersheds 18 and 27 during the June 11 storm event, seep waters which supply hillslope runoff to each stream channel were also sampled. The WS 18 seep supplied drainage from a several hectare subwatershed. This seep is characterized by a dynamic seepage face which expands rapidly upslope, during precipitation events under wet antecedent moisture conditions. A significant percentage of the total Watershed 18 runoff is supplied by this seep via saturation overland flow, return flow, and subsurface stormflow. The WS18 seep flows during most of the year but surface runoff does cease during prolonged dry periods (W. Swank personal communication). The ground surface of the WS18 seep is covered by several centimetres of forest liter. The WS27 seep consisted of a thin veneer of vascular and non-vascular plants overlying a major bedrock outcrop. The thickness of the organic material overlying the bedrock ranged from 0 to 25 cm and runoff only occurs during, and immediately after precipitation events. The major species of the vegetation overlying the bedrock at this site included mosses: *Thudium delicatulum, Fissidens cristatus. Altrichum undulatum, Hypnum imponens, Hookeria acutifolia;* Liverworts: *Trichocolea tomentella, Scapania nemorosa;* Lichens: *Cladonia subtenuis;* and the vascular plant *Houstonia serpyllifolia.*

Monthly precipitation at Coweeta ranges from 11.2 cm in October to 20.3 cm in March. Two to ten per cent of the annual precipitation occurs as snow. Average annual rainfall for Watersheds 18 and 27 is 194 and 245 cm, respectively. Monthly temperature averages range from 3.3 °C in Jabuary to 21.6 °C in July.

3. Methods

Ultraclean trace element sampling protocol was practised throughout this study. All water samples were collected in Teflon@ bottles, which were prewashed in hot nitric acid and deionized water. Sample bottles were double-bagged and remained full of acidified (1% HCI), deionized water until sample collection to reduce contamination. Fields samplers wore clean room grade polyethylene gloves when handling the sample bottle. New gloves were utilised for each sample collected.

Precipitation samplers were collected at the main Coweeta meteorological station (685 m) in acid-washed glass funnels which drained into prewashed Teflon@ bottles. The funnels were supported by a Teflon@ coated wooden frame 1 m above the ground surface. Sample bottles were set out immediately prior to the onset of precipitation and removed immediately after the event. Throughfall was manually collected from WS18 in Teflon@ bottles from a acid-washed Teflon® lined eavestrough style collector during the rain event on June 11, 1994.

Samples to be analyzed for THg were acidified with HCl, assayed to contain little Hg, and shipped to Flett Research Ltd., Winnipeg, Manitoba, Canada. Total Hg concentrations were determined using the method of Bloom and Fitzgerald (1988). Water samples in the Teflon® bottles were oxidized with 1% BrCl, and subsamples placed in glass bubblers with 0.5% SnCl. Hg was purged from solution using ultra high purity nitrogen and collected on a gold trap which was flash heated in a stream of He and the resulting Hg° gas determined by atomic fluorescence.

Samples to be analyzed for MeHg were immediately frozen upon collection and express mailed on dry ice to the trace metal laboratory at the Experimental Lakes Area (ELA), north western Ontario, Canada. Methyl Hg was determined using the method of Bloom (1989) and later modified by Horvat *et al* (1993). Water samples were digested with H_2SO_4 and distilled to remove interferences. The Hg species were ethylated, and purged from the distillate onto Tenax® traps. All Hg species were released from the Tenax® by flash heating the trap in a stream of ultra high purity He. The Hg species were separated chromatographically, converted to Hg° gas at high temperature and detected by atomic fluorescence. The limit of detection and analytic error, based on two standard deviations around the mean, for THg is 0.16 ng L^{-1} and for MeHg is 0.013 ng L^{-1}. Streamwater and seep samples were filtered with 0.45 μm cellulose nitrate filters in Nalgene® disposable polycarbonate filter packs.

Samples to be analyzed for DOC and TOC analysis were immediately frozen after collection and express mailed with dry ice to McGill University. Dissolved organic carbon and TOC concentrations were determined by high temperature combustion (Shimadzu TOC 5000). The detection limit for the carbon analyses were 0.1 mg L^{-1} with an analytical error of <0.1 mg L^{-1} at concentrations >5 mg L^{-1}. Specific conductance was measured with a Yellow Springs Instruments combination temperature/conductivity/salinity meter corrected to 25 “C. pH was determined with a Cole-Palmer glass electrode pH meter standardised to buffers of pH 4 and pH 7. Total suspended solids and total dissolve solids were measured through filtration and evaporation as outlined in APHA (1985).

4. Results and Discussion

4.1. WETDEPOSITIONATCOWEETA

The rainfall concentrations for THg (5.75 to 25 ng L^{-1}) fall between those reported for low deposition areas such as the Experimental Lakes Area (ELA), N. W. Ont. (0.95 to 9.31 ng L^{-1}, St. Louis et al., 1995) and high deposition areas such as S. Sweden (11 to 90 ng L^{-1}, Iverfeldt 1991; Johanessen *et al.*, 1991; Lee and Iverfeldt, 1991; Hultberg *et* al., 1994 and Munthe and Iverfeldt 1994). Concentrations of MeHg in precipitation recorded during June and July (~0.025 to 0.16 ng L^{-1}) are lower or fall within the range of values recorded at ELA (0.01 to 0.179 ng L^{-1}, St. Louis *et* al., 1995), Little Rock Lake, WI (0.0 to 0.224 ng L^{-1}, Fitzgerald *et al.*, 1991) and Washington State (0.015 to 0.35 ng L^{-1}, Bloom and Watras, 1989).

By multiplying the average Hg concentrations recorded during our study period, 13.2 ng L^{-1} THg and 0.062 ng L^{-1} MeHg by the average annual precipitation at Coweeta we estimate THg deposition total of approximately 256 mg ha-' yr^{-1} for low elevation sites and 323 mg ha-' yr^{-1} for upper elevation sites. The same calculation for MeHg yields deposition totals of 1.20 and 1.52 mg ha^{-1} yr^{-1} for low and high elevation sites, respectively. Our sampling regime represents approximately 8% of the average annual low elevation precipitation totals for Coweeta, and therefore our estimation for annual wet deposition represents a preliminary estimate of wet deposition. These estimates may be sowewhat high, as several North American studies: e.g., St Louis *et al.,* 1995; Burke *et al.*, 1995 and Guentzel *et al.*, 1995 have reported seasonal differences in wet precipitation Hg concentrations, with higher concentrations generally been recorded during the growing season. However, owing to Coweeta's relatively even precipitation distribution, if our chosen mean concentration is double the actual value for the winter period, this would only reduce our annual estimate by ~25%. In addition, some of the seasonal decrease in wet deposition Hg concentrations observed at other North American sites is attributed to the cessation of washout of suspended dust by rainfall, where ground snowpacks become established (St. Louis *et al., 1995).* The seasonal washout of resuspended terrestrial material at Coweeta should be more evenly distributed, given it's southern location.

The relatively high estimated wet deposition of THg at Coweeta is of similar magnitude to other areas such as Florida (150-300 mg $ha^{-1}yr^{-1}$, Guentzel *et al.*, 1995) and S. Sweden (100-350 mg ha^{-1} yr^{-1}, Iverfeldt, 1991; Johanessen *et al.,* 1991; Lee and Iverfeld 1991; Hultberg *et al.,* 1994 and Munthe and Iverfeldt, 1994). The high wet deposition of THg at Coweeta results from moderate Hg concentrations in precipitation and a high precipitation total. Wet deposition of MeHg at Coweeta is estimated to fall between that reported for low deposition sites such as ELA (0.35 mg ha^{-1} yr^{-1} St. Louis *et al.*, 1995), Little Rock Lake, Wi (0.88 mg ha^{-1} yr^{-1}, Fitzgerald *et al.*, 1991) and N. Sweden (0.7 mg ha-' yr^{-1}, Munthe and Iverfeldt 1994) and high wet deposition areas such as S. and W. Scandinavia

Table II

Summary of Total and MeHg concentrations recorded in rainfall at the Coweeta meteorologic station for the period June 11-July 14, 1994. Average annual precipitation is 194 and 245 cm for WS 18 and WS27 respectively

Data	Depth (mm)	Total Hg (ng L^{-1})	MeHg (ng L^{-1})
June 11	33.0	8.09	0.160
June 28	27.9	13.68	0.057
July 4	12.7	24.80	0.035
July 7	6.9	5.75	0.044
July 12	20.8	16.82	<0.025
July 13	38.4	10.03	0.067

Table III

Hydrologic and Hg inputs and yields to WS 18 and WS27, June 11-12

	Water (m^3)			THg (mg)			MeHg (mg)		
	Precip. Inputs	Runoff	Yield	Inputs	Outputs	Yields	Inputs	Outputs	Yield
WS18	1,898	306	16.1%	15.35	0.74	4.8%	0.30	0.002	0.7%
WS27	2,535	641	25.3%	20.58	1.11	5.4%	0.41	0.016	3.9%

(1.94.1 mg ha^{-1} yr^{-1}, Iverfeldt 1991; Johanessen et al., 1991; Lee and Iverfeldt, 1991; Hultberg *et* al., 1994 and Munthe and Iverfeldt, 1994).

4.2. TEMPORAL TRENDS IN STREAM AND SEEP WATER CHEMISTRY

The precipitation distribution at Coweeta was spatially variable during the June 11 sampling event with WS27 receiving 44% of the precipitation WS18 experienced (Table III). Runoff for WS18 and WS27 during this event was 16.1 and 25.3% of precipitation, respectively. Quickflow comprised 6.0 and 2.1% of the precipitation total during the June 11-12 period. Peak discharge from WS27 occurred 0.75 hr after peak discharge from WS 18.

Peak concentrations of THg, DOC, TDS, TSS, specific conductance and H^+ (WS18 only), coincided with or near peak discharges in WS18 and WS27 and WS 18 seep waters and then declined during the June 11 storm event (Figures 1-7). Hydrogen ion concentrations peaked approximately four hours after peak discharge in WS27 (Figure 7b). The difference in peak and recession flow chemistry for the above chemical constituents was most pronounced for WS18 where concentration declines ranged from approximately 28% for H^+ to 98% for TSS. The temporal changes in water chemistry were generally less pronounced in runoff from the WS18 seep and WS27.

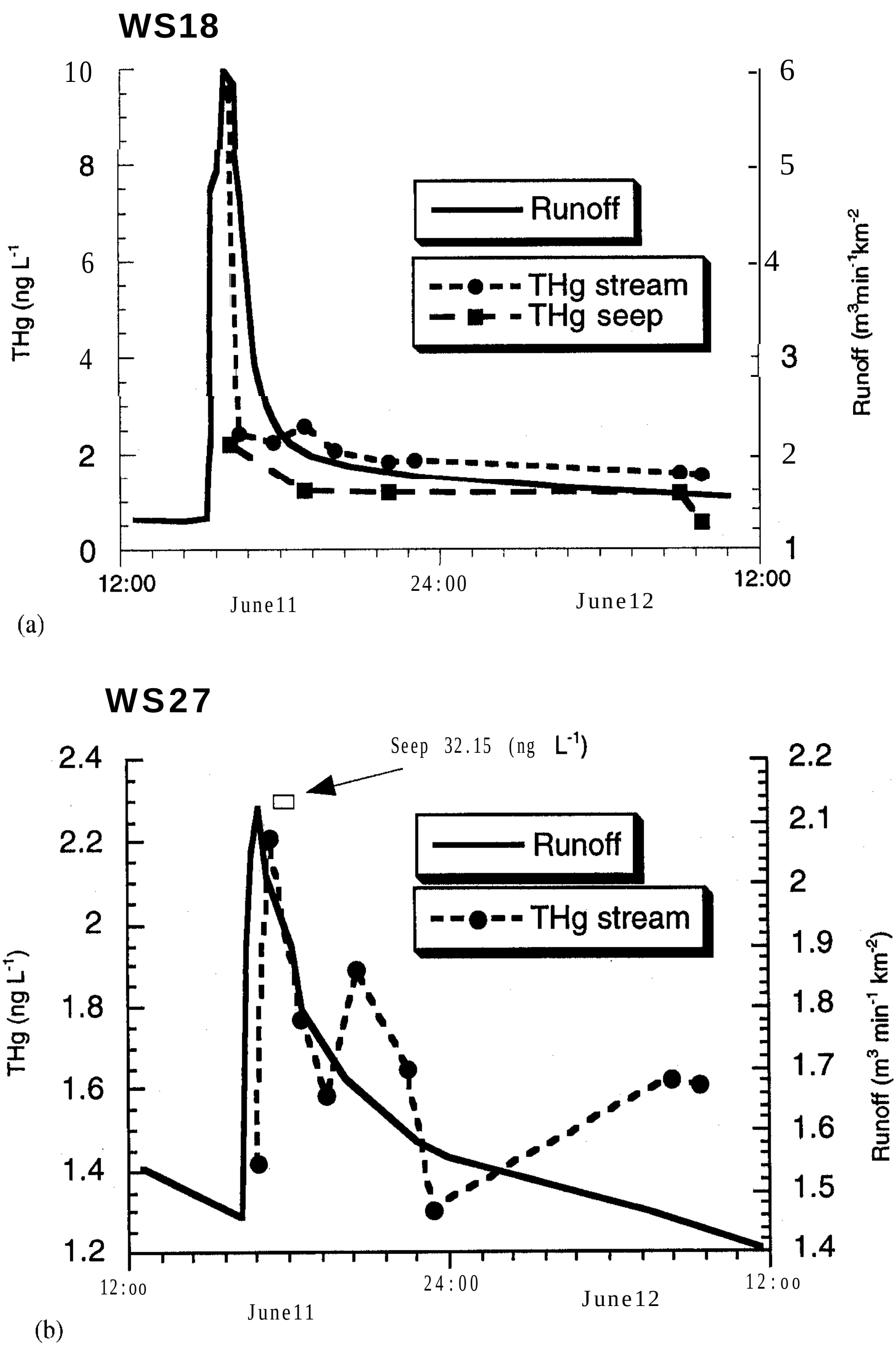
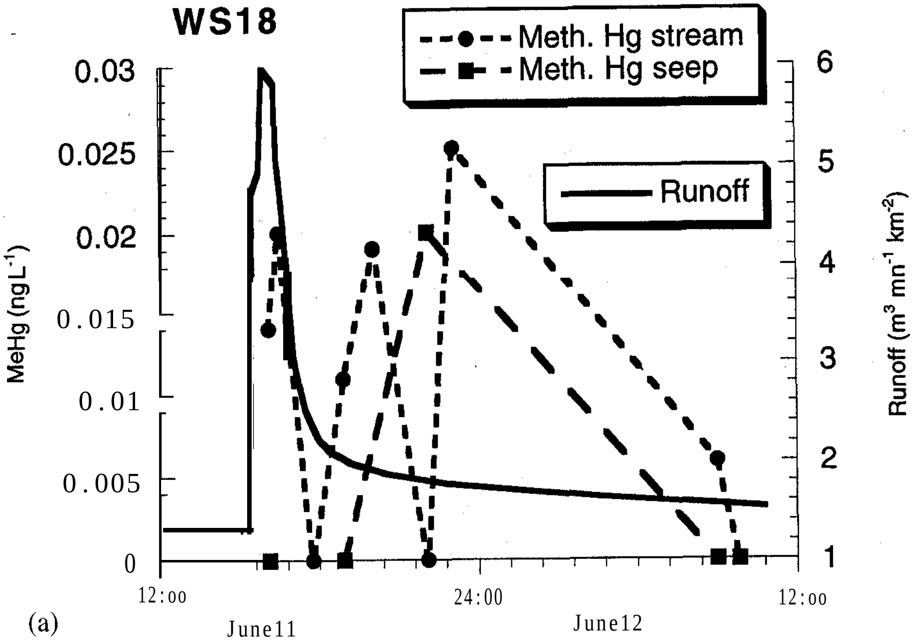
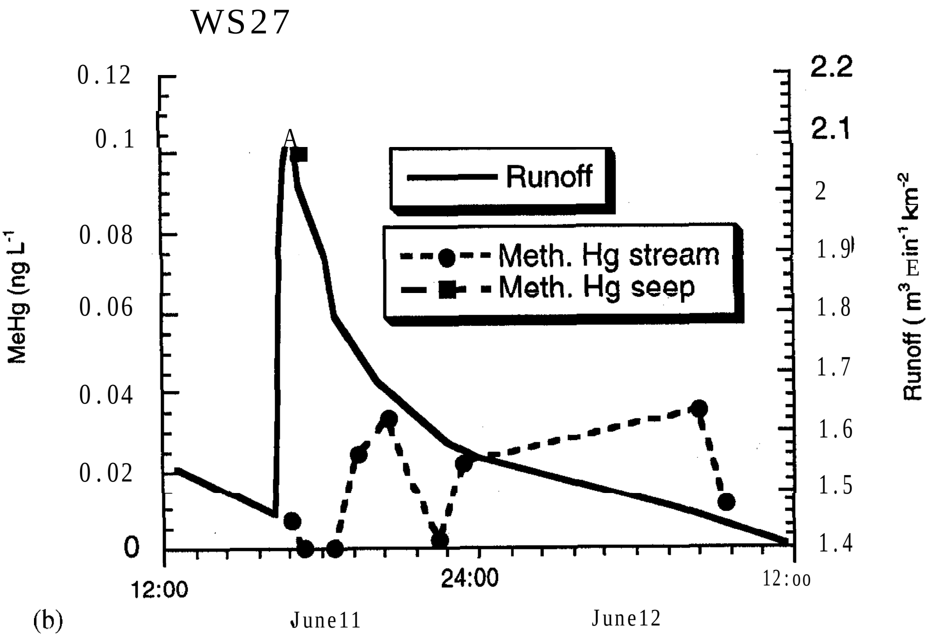


Figure 1. Temporal changes in runoff and THg, for WS 18 and WS27, June 11-l 2, 1994.



(a)



(b)

Figure 2. Temporal changes in runoff and MeHg, for WS 18 and WS27, June 11-12, 1994.

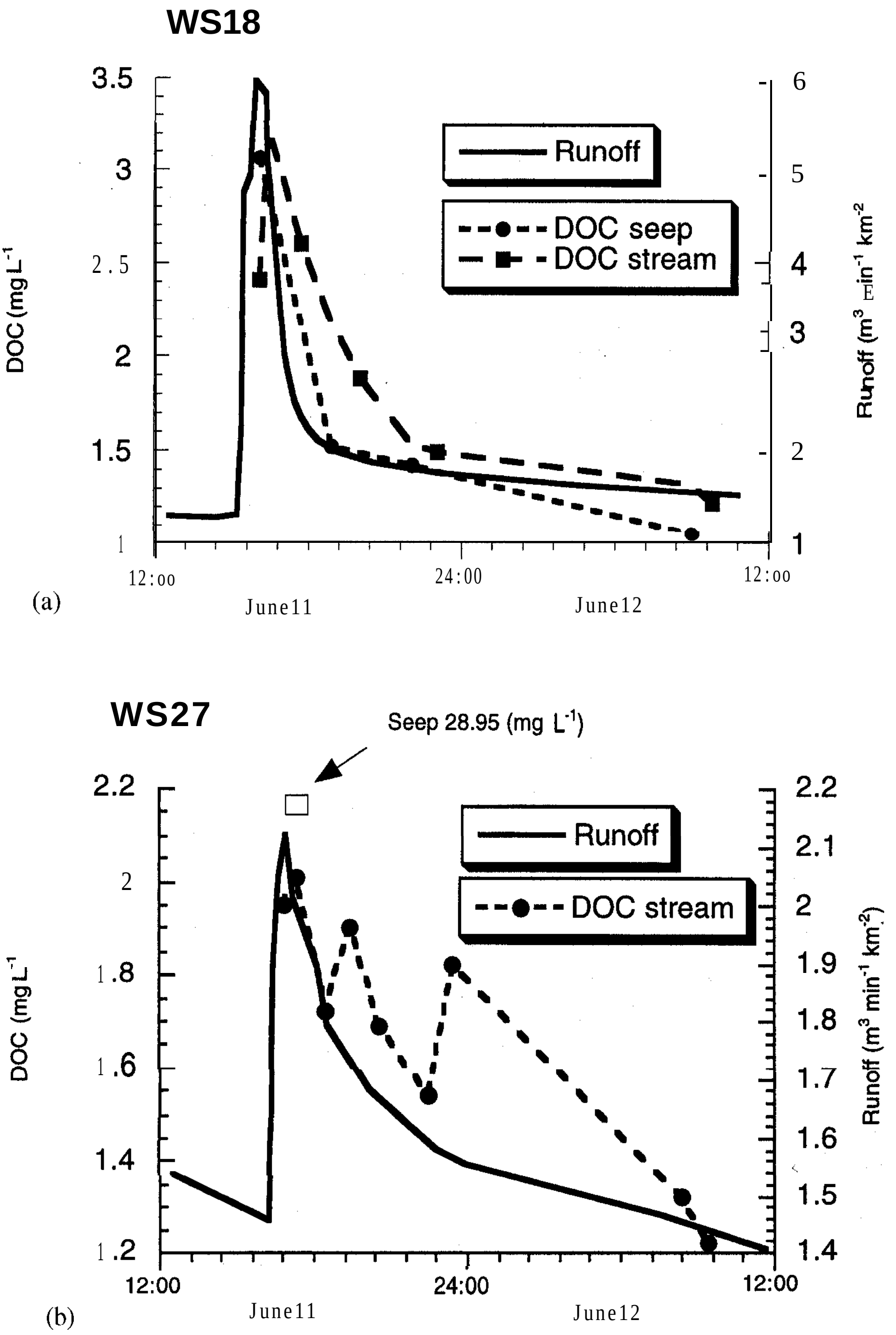


Figure 3. Temporal changes in runoff and DOC, for WS18 and WS27, June 11-12, 1994.

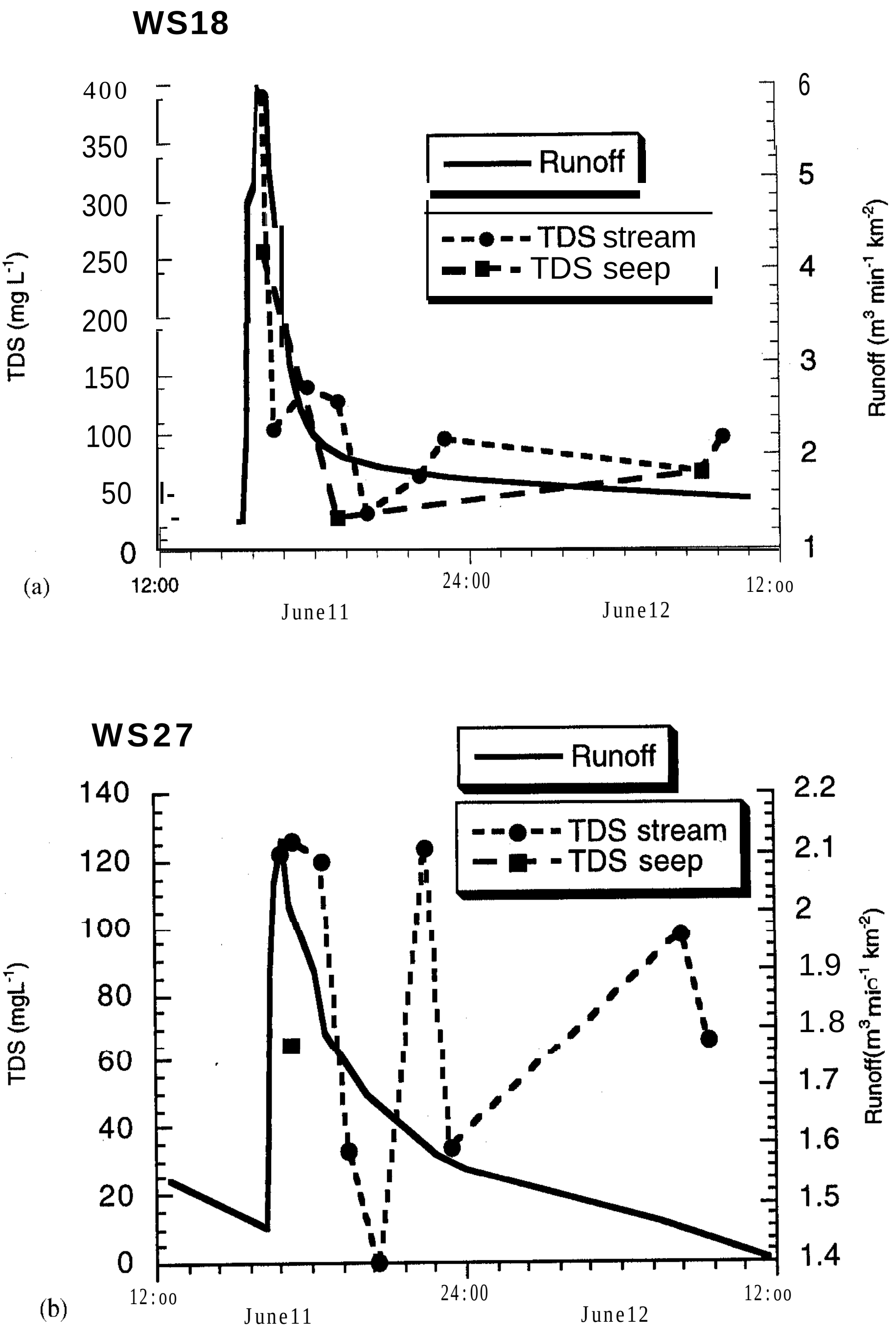


Figure 4. Temporal changes in runoff and TDS, for WS 18 and WS27, June 11–12, 1994.

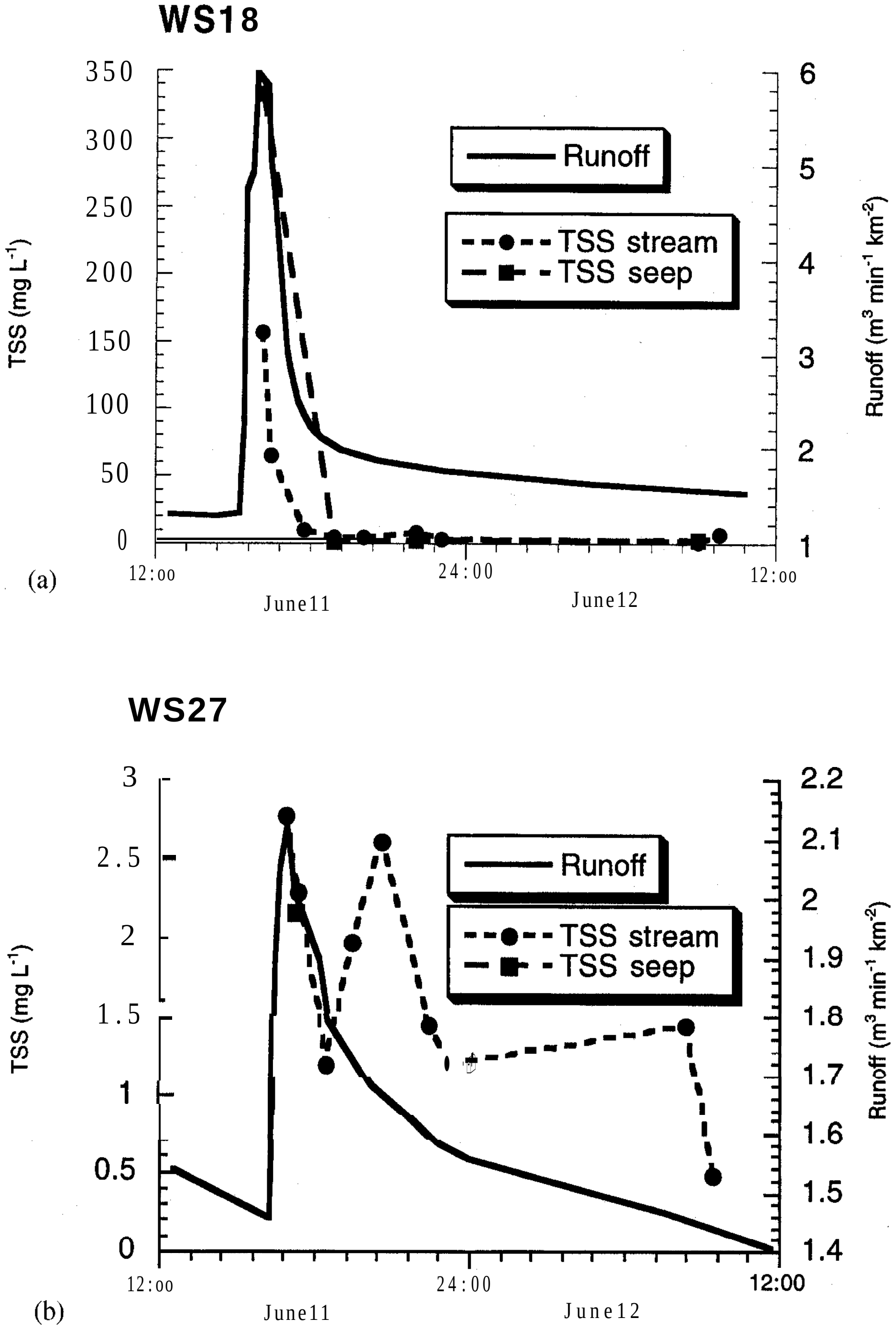
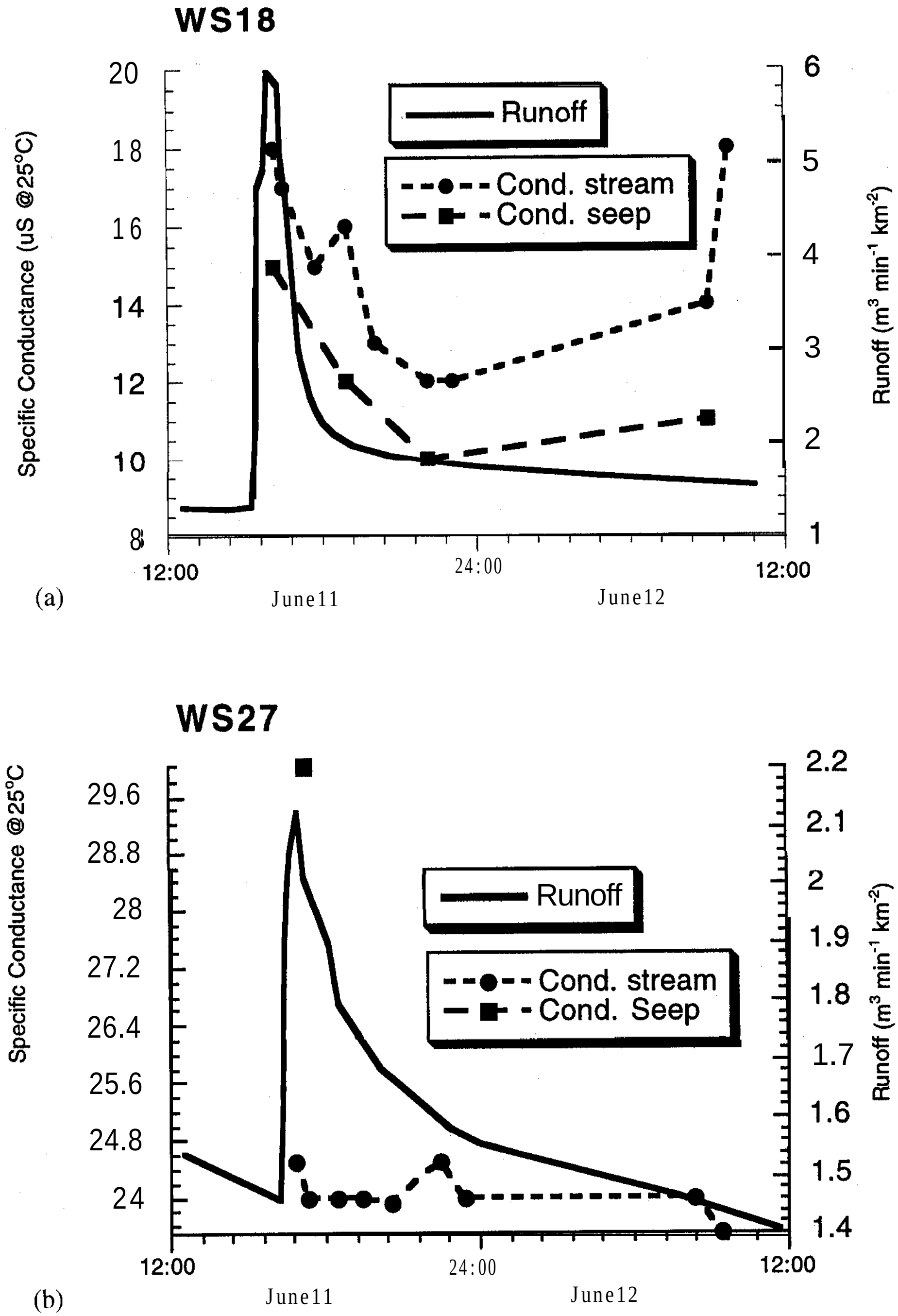
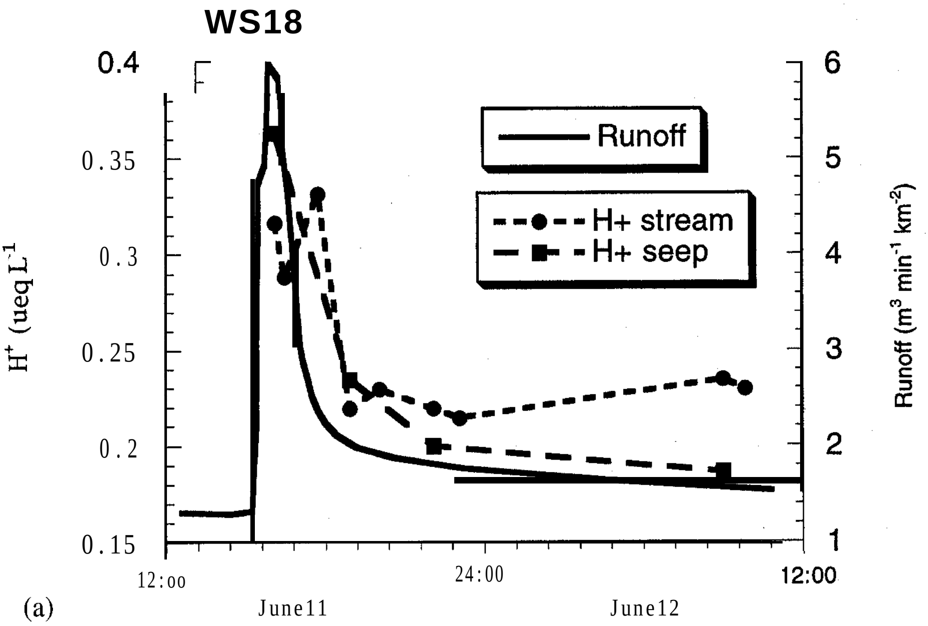


Figure 5. Temporal changes in runoff and TSS, for WS 18 and WS27, June 1 I-12, 1994.



6. Temporal changes in runoff and Specific Conductance, for WS18 and WS27, June 1 I-12, ***1994.***



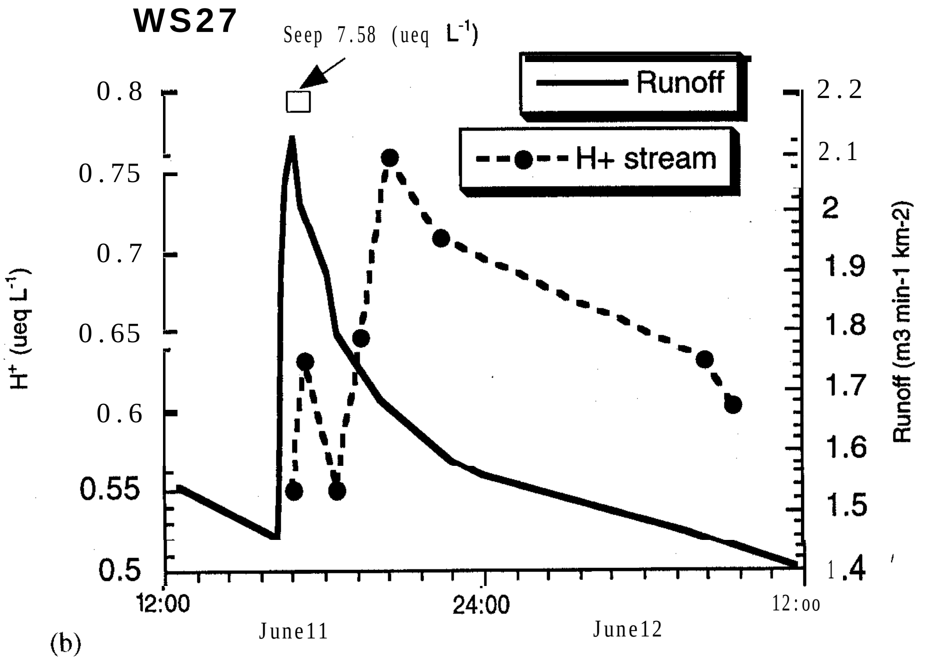


Figure 7. Temporal changes in runoff and pH, for WS18 and WS27, June 1 l-12, 1994.

The differences in the hydrochemical response between WS18 and WS27 is attributed to the different precipitation amounts each watershed received. WS18 exhibited a 5 x increase in discharge as compared to a 1.5 x increase for WS27 during the June 11 rain event. Substantial saturation overland flow was generated from rapidly expanding variable source areas in the lower WS18 watershed. This surface flow mobilized substantial quantities of both particulate and dissolved material from soil and litter surfaces. In addition, large amounts of Hg from direct precipitation and throughfall, falling onto saturated areas would have been quickly transported to stream channels with minimal soil litter contact. The lower rainfall totals received by WS27 probably did not generate the same degree of saturation overland flow.

The magnitude of the temporal concentration changes in THg (5 x) observed in WS18 streamwater was similar to that observed for TDS (5.6×). Because stream and seep water samples were filtered during this study, and Hg transported as particulate material >0.45 μm is not accounted for by our sampling. Given the high absorptive affinity of Hg for organic and some inorganic particulates, (Mucci, 1995; Parks, 1986) and the high TSS concentrations at peak flow during this event (Figure 5a), particulate Hg transport may have been significant but short lived. Streamwater THg concentrations at peak flow increased toward those concentrations observed for precipitation and throughfall during the June 11 rain event and declined rapidly after precipitation ceased. Thus, the elevated concentrations of THg observed in streamwater may simply reflect precipitation and throughfall inputs to the near stream zone. It is estimated that direct input of approximately 2% of the precipitation from this event onto stream and neat-steam areas could account for the THg increases observed in streamwater. However, the exceedingly high THg concentrations (32.15 ng L^{-1}) measured in WS27 seep runoff indicates that significant pools of Hg may be present in porewaters of shallow organic soils at Coweeta.

Unlike the other chemical constituents examined there appeared to be no recognizable temporal trends in MeHg concentrations in stream and seep waters during the June 11 rain event (Figure 2). Methyl Hg concentrations were near or below detection levels for all but the Watershed 27 seep (Figure 2b). The low MeHg concentrations in stream and WS 18 seep waters is indicative of the absence of significant in *situ* methylation sites such as riparian wetlands and that atmospherically derived MeHg is rapidly retained or demethylated. The deeply incised stream channels at Coweeta preclude the formation of significant riparian wetlands which have been identified as methylation sites and sources of MeHg in forested watersheds (Bishop *et al.,* 1995a; Branfireun *et* al., 1996; Krabbenhoft *et al.,* 1995; St. Louis *et al.,* 1994). Similar retention or demethylation in low order upland watersheds has been reported in other studies (St. Louis *et al.,* 1994). The MeHg concentrations observed in WS27 seep waters were in the same range as precipitation and throughfall MeHg concentrations and therefore may simply reflect event derived

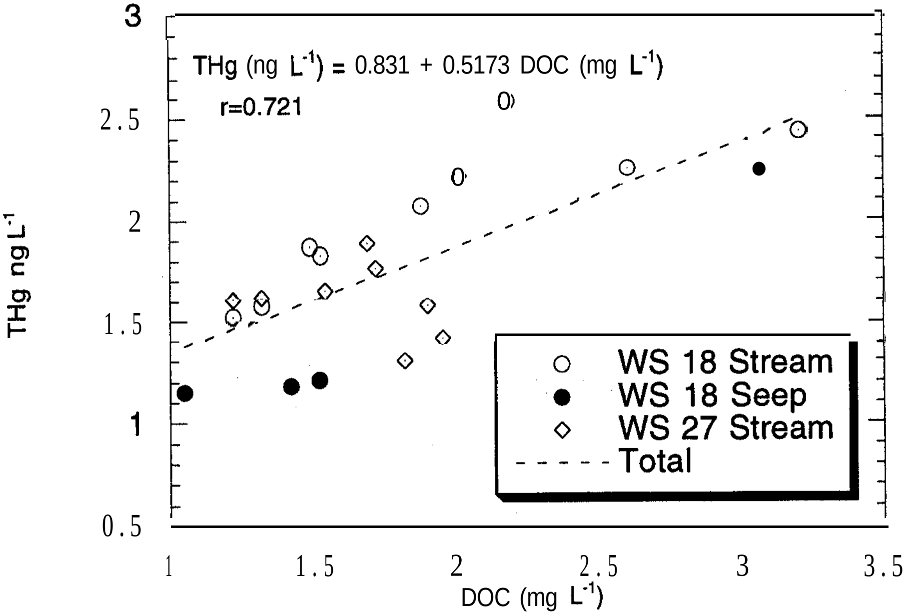


Figure 8. Relationship between THg and DOC for Coweeta stream and seep waters, June 1 1-12, 1994. The dashed line represents the linear best fit line for the data.

MeHg. However, shallow organic soils containing moss species similar to those found at the WS27 seep, may represent active methylation sites.

Results from intensive short term sampling of Hg during episodic runoff events are rare in the literature. Daily sampling of runoff in forested catchments in N. Sweden, Bishop *et al.* (1995b) and (1995c) showed increases of THg in runoff of similar magnitude to those observed at Coweeta. Methyl Hg concentrations from these same studies exhibited slight declines of approximately 0.1 ng L^{-1} that was attributed to the depletion of labile MeHg from riparian wetlands during prolonged runoff events. Branfireun *et al.* (1996) at ELA observed MeHg concentrations to be sustained by in *situ* wetland sources of MeHg through entire rain runoff events, indicating some wetland areas contain substantial pools of labile MeHg or very high production rates.

As has been reported for several other studies, no correlation was evident between THg and MeHg concentrations in seep or streamwaters during this sampling event, indicating the methylation process is to some degree uncoupled from the absolute abundance of Hg in forested systems (Bishop *et al.*, 1995b; Kelly *et al.*, 1995). A significant positive correlation (r=0.721) was found between DOC and THg in WS 18 and WS27 stream and WS 18 seep waters during this event (Figure 8). The initial high THg concentration sample from WS 18 (Figure la) and the WS27 seep sample (Figure lb), are not included in this relationship as both exhibited greater THg/DOC ratios than other stream and seep samples. These samples may contain significant inputs of rain derived Hg which had minimal soil contact. Similar positive relationships between Hg and dissolved and particulate organic material have been found in other studies (e.g. Mierle, 1990) but the exact form of these relationships has been found to change as the physicochemical character of DOC changed seasonally (Mierle, 1990; Lee et al., 1995b; Petterson et *al.*, 1995).

4.2.1. Annual Estimates of Hg Export and Accumulation at Coweeta

To date, few annual watershed mass balances for Hg have been published. The reasons for this include the relatively high cost for THg and MeHg analyses, limited availability of analytic facilities capable of analysing ambient freshwater Hg concentrations and the logistic requirements of the ultra clean sampling protocol. As a result, the long term mass balances for Hg that have so far appeared in the literature are at best, based on regular weekly to monthly sampling, supplemented with some daily sampling. The temporal trends we observed in Hg concentration during the June 11 rain event indicate that significant temporal changes in Hg concentration may occur during episodic runoff events. Such short term concentration variations are likely significant to long term mass balances, particularly for areas like Coweeta where quickflow may comprise up to 30% of the annual runoff and may be underrepresented in a more rigid sampling program. Branfireun *et al.* (1996) reported that approximately 50% of the MeHg exported from a small Precambrian Shield wetland occurred during the 16% of the time storm runoff was occurring during a 112 day sampling period. As an initial estimate of THg and MeHg export from low order watersheds at Coweeta based on the limited data available, we multiplied the volume weighted average of the stormflow Hg concentration measured in WS18 and WS27 streamwater during the June 11 event by the average quickflow yield for high and low elevation watersheds at Coweeta and added this to the average delayed flow yield. The THg value assigned to annual quickflow volumes for both watersheds was 2.07 ng L^{-1} which was the average of the volume weighted stormflow concentration for WS27 and WS 18 during this event. A THg concentration of 1.6 ng L^{-1} taken from the average of the four lowest recession flow samples was assigned to the delayed flow volume for each watershed. Because MeHg concentrations did not vary systematically during the June 11 event the volume weighted averages from each watershed, 0.01 ng L^{-1}, WS 18 and 0.026 ng L^{-1} , WS27 were multiplied by the annual runoff yield to estimate annual MeHg export. This results in an estimated annual THg export of 16.8 and 34.7 mg ha^{-1} yr^{-1} and an annual MeHg export of 0.10 and 0.5 1 mg ha-' yr^{-1} for low and high elevation watersheds, respectively (Table IV).

The estimated yields of THg for low elevation WS 18 is similar to those reported for other forested and wetland catchments in North America and Europe. The calculated THg yield for WS27 is 1.6 times to 4 times that reported for any other forested watershed in the literature. The high THg yield for WS27 results from a combination of the high annual hydrologic yield (70.9% as compared to 54% for WS 18) and the high proportion of annual runoff comprised by quickflow (30% as

Table IV

Annual export and retention estimates of THg and MeHg from Coweeta and other forested watersheds

Site	THg (mg ha^{-1} yr^{-1})	% Retention[a]	MeHg (mg ha^{-1} yr^{-1})	% Retention
Coweeta WS 18, W.N. Carolina	16.8	93	0.10	92
Coweeta WS27, W.N. Carolina	34.7	89	0.51	66
[1] ELA Upland, N. W. Ontario	20.4	34	0.07	53
[1] ELA Upland/Wetland 1, N. W. Ontario	22.8	26	0.32	0
[1] ELA Upland/Wetland 2, N. W. Ontario	19.3	37	0.35	0
[1] ELA Wetland, N. W. Ontario	12.3	60	0.96	0
[1] ELA Lake. N. W. Ontario	3.1	90	0.06	60
[2] L Gärdsjon F1, S. Sweden	22.0	84	1.25	66
[3] Allequash Creek, N. Wisconsin	23.0	92		
[4] Svartberget M, N. Sweden	15.0		1.70	
[4] Svartberget MK, N. Sweden	12.0		1.10	
[4] Svartberget V, N. Sweden	18.0		0.80	
[5] Harp 3A, S. Ontario	8.0	92		
[5] Harp 4, S. Ontario	8.8	91		
[5] Harp 5A, S. Ontario	16.3	84		

[a] Retention calculated as (Annual Wet Deposition Hg Annual Hg Export)/Annual Wet Deposition Hg.

[1] After St. Louis *et al., 1994.*

[2] After Hultberg *et al.*, 1995.

[3] After Krabbenhoft *et al., 1995.*

[4] After Lee *et al.*, 1995.

[5] After Mierle et al., 1990.

compared to 9% for WS 18). Approximately 22% and 43% of the annual THg export is estimated to occur during quickflow periods for low and high elevation watershed, respectively. THg retention at Coweeta is similar to that reported for most other forested catchments except ELA where greater propertions of atmospherically derived Hg appear to be exported (Table III). The estimated accumulation of Hg from wet deposition for Coweeta watersheds is approximately 265 mg ha-' yr^{-1}, which is over double the accumulation from wet deposition reported for the L. Gardsjon catchment in south-west Sweden (Hultberg *et* al., 1995).

The estimated MeHg export for WS 18 and WS27 fall within the range reported for other watersheds in the literature (Table IV). Significant differences in the annual MeHg exports between the two Coweeta watersheds is attributed to differences in streamwater concentration as well as differences in runoff totals. WS27 volume weighted concentrations of MeHg in runoff were 1.5X higher than for WS18 during the June 11 event. The significantly higher streamwater concentrations of MeHg in WS27 may reflect the thinner soils and shorter water residence times characteristic of high elevation catchments at Coweeta. These characteristics may result in reduced total MeHg detention and/or less opportunity for demethylation of atmospherically deposited MeHg within catchment soils. Alternatively, significant MeHg production may occur in WS27. The proportion of MeHg export attributed to quickflow is 9 and 29% of the annual MeHg export for low and high elevation watersheds, respectively. Branfireun *et al.,* 1996 report that 53% of the annual MeHg transport from a forested wetland at ELA occurred during stormflow. The estimated MeHg accumulation and/or demethylation rate from wet deposition is approximately 1 .1 mg ha-' yr^{-1} which is <1/2 the accumulation/demethylation rates reported for the L. Gardsjon catchment in south-west Sweden (Hultberg *et al.*, 1995).

Results from this pilot sampling program indicate substantial wet deposition of Hg is occurring in S.E. Blue Ridge watersheds. Data from the Lake Gkdsjon catchment in S. W. Sweden indicate that wet deposition estimates of Hg may actually be 3X lower than those obtained from throughfall + litterfall estimates (Hultberg *et al.,* 1995). If this is the case, atmospheric THg deposition at Coweeta may be on the order of 800 mg ha-' yr^{-1} with THg retention >95%. Methyl Hg wet deposition appears to fall between that of high deposition sites such as S. W. Sweden and more pristine sites such as ELA in N. W. Ontario. Presently, over 80% of the wet deposited THg impacting Coweeta appears to be accumulating in catchment soils and vegetation. The high runoff totals at Coweeta result in high THg export fluxes in high elevation watersheds. The low MeHg yields at Coweeta are likely the result of retention/demethylation of atmospherically derived MeHg and the lack of in *situ* MeHg sources such as riparian wetlands. Substantial changes in THg concentrations occur during episodic runoff events as a result of direct precipitation onto saturated areas and the occurrence of saturation overland flow. The proportion of the annual Hg occurring during stormflow can be substantial and the temporal variability is dissolved Hg concentrations in response to changing conditions should be taken into account and event based sampling carried out when developing Hg sampling programs at this and other sites.

Acknowledgements

The authors wish to thank E. Waksmunski for his assistance in the field and laboratory. Vegetation identification were performed by L. Reynolds U.S.F.S. and R.E. Wyatt, University of Georgia Botany Dept. Two anonymous reviewers and W. Swank provided comments which greatly improved earlier drafts of this report. This research was supported by a faculty research grant from the University of North Carolina at Charlotte. Logistics support, hydrologic and meteorologic data was provided by U.S.F.S. personnel at the Coweeta Hydrologic Laboratory. Analytic support was provided by T. Moore and L. Matos, McGill University Geography Dept. and the Experimental Lakes Area Reservoir Project (ELARP).

References

Aastrup, M., Johnson, J., Bringmark, E., Bringmark, I. and Iverfeldt, A.: 1991, *Water, Ail; and Soil Pollut. 56, 155.*

American Public Health Association: 1985, Standard Methods for the Examination of Water and Waste Water, 16th ed., Wash., D.C.

Bishop, K., Lee, Y. H., Pettersson, C. and Allard, B.: 1995a, *Water, Ail; and Soil Pollut. 80,* 221.

Bishop, K., Lee, Y.-H., Pettersson, C. and Allard, B.: 1995b, *Water, Ail; and Soil Pollut. 80,435.*

Bishop, K., Lee, Y.-H, Pettersson, C. and Allard, B.: 1995c, *Water; Air,* and *Soil Pollut. 80,445.*

Bloom, N. S.: 1989, Can. *J. Fish. Aquat. Sci. 46,* 1131.

Bloom, N. S. and Fitzgerald: 1988, *Annal. Chimica Acta 208,* 151.

Bloom, N. S. and Watras, *C.* J.: *1989, Sci. Total Environ.* **87/88,** *199.*

Branfireum, B. A., Heyes, A. and Roulet, N. T.: 1996, 'The Hydrology and Methylmercury Dynamics of a Precambrian Shield Headwater Peatland', *Water Resour. Res.* (in press).

Burke, J., Hoyer, M., Keeler, G. and Scherbatskoy, T.: 1995, *Water, Ail; and Soil Pollut.* **80**, *353.*

Driscoll, C. T., Blette, V., Yan, C., Schofield, C. L., Munson, R. and Holsapple, J.: 1995, *Water, Air; and Soil Pollut. 80,499.*

Fitzgerald, W. F., Mason, R. P. and Vandal, *G.* M.: 1991, *Water, Air; and Soil Pollut. 56,745.*

Guentzel, J. L., Landing, W. M., Gill, G. A. and Pollman, C. D.: 1995, 'Atmospheric Deposition of Mercury in Florida': The FAMS project (1992-1994).

Hatcher, R. D. Jr.: 1976, *Introduction to the Geology of the Eastern Blue Ridge of the Carolinas and Nearby Georgia, Carolina Geol. Soc.* Field Trip Guidebook, 53 p.

Hatcher, R. D. Jr.: 1979, The Coweeta Group and Coweeta Syncline: Major Features of the North Carolina-Georgia Blue Ridge, Southeastern Geol, (21): 17-29.

Horvat, M., Bloom, N. S. and Liang, L.: 1993, *Analytica Chimica* 281, 135.

Hultberg, H., Iverfeldt, A. and Lee, Y.-H: 1994, in C. Watras and J. W. Huckabee (eds.), Mercury as a Global Pollutant - Toward Integration and Synthesis, Lewis Publ.

Hultberg, H., Munthe, J. and Iverfelft, A.: *1995, Water, Air; and Soil Pollut. 80,415.*

Iverfeldt, A.: *199 1, Water, Air, and Soil Pollut.* **56**, 25 1.

Johanssen, K., Aastrup, M., Anderson, A., Bringmark, L. and Iverfeldt, A.: 1991, *Water, Ail; and Soil Pollut. 56,267.*

Kelly, C. A., Rudd, J. W. M., St. Louis, V. and Heyes, A.: 1995, *Water Air; and Soil Pollut. 80, 715.*

Krabbenhoft, D. P. and Babiarz, *C.* L.: *1992, Wat. Resour. Res.* **28**(12), 3119.

Kabbenhoft, D. P., Benoit, J. M., Babiarz, C. L., Hurley, J. P. and Andren, A. WW.: 1995, *Water; Ail; and Soil Pollut. 80,425.*

lee, Y.-H, and Iverfeldt, A.: 1991, *Water; Air; and Soil Pollut. 56, 309.*

Lee, Y.-H, Bishop, K., Pettersson, C., Iverfeldt, A. and Allard, B.: 1995, *Water, Air; and Soil Pollut. 80,455.*

Mierle, G.: 1990, *Environ. Tox. And Chem. 9, 843.*

Moore, T. R., Bubier, J. L., Heyes, A. and Flett, R. J.: 1995, *J. of Environ. Qual. 24, 845.*

Mucci, A., Luucotte, M., Montgomery, S., Ploude, Y., Pichot, P. and Tra, H. V.: 1995, Can. *J. Fish. Aquat. Sci.* **52**, 2507.

Munthe, J. and Iverfeldt, A.: *1994, Mercury as a Global Pollutant - Toward Integration and Synthesis,* Watras and Huckabee Eds. Lewis Publ.

Parks, J. W., Sutton, J. A. and Lutz, A.: *1986, Can. J. Fish. Aquat. Sci. 43,* 1246.

Petterson, C., Bishop, K., Lee, Y.-H, and Allard, B.: 1995, *Water, Ail; and Soil Pollut. 80, 971.*

St. Louis, V. L., Rudd, J. W. M., Kelly, C. A., Beaty, K. G., Bloom, N. S. and Flett, R. J.: 1994, *Can. J. Fish Aquat. Sci.* 51, 1065.

St. Louis, V. L., Rudd, J. W. M., Kelly, C. A. and Barrie, L. A.: 1995, *Water, Air, and Soil Pollut. 80,* 405.

Swank, W. T. and Crossley, D. A.: *1988, Forest Hydrology and Ecology at Coweeta,* Springer-Verlag, New York 469 p.

Velbel, M. A.: 1985, *Amer. J. Science, 285, 904.*