ATMOSPHERIC INPUTS OF MERCURY AND ORGANIC CARBON INTO A FORESTED UPLAND/BOG WATERSHED

R. K. KOLKA[1,*], E. A. NATER[2], D. F. GRIGAL[2] and E. S. VERRY[3]
[1] *Department of Forestry, University of Kentucky, Lexington, KY 40546, U.S.A.:*
[2] *Department of Soil, Water; and Climate, University of Minnesota, St. Paul, MN 55108, U.S.A.;*
[3] *USDA Forest Service, N.C. Forest Experiment Station, Grand Rapids, MN 55744, U.S.A.*
(author for correspondence, e-mail: rkolk2@pop.uky.edu)*

(Received 30 July 1997; accepted 26 August 1998)

Abstract. Inputs of mercury (Hg) and dissolved organic carbon (DOC) in throughfall and stemflow waters were measured for an upland/bog watershed in northern Minnesota, and were compared to the deposition in a nearby opening to determine the influence of tree canopies on Hg and DOC deposition. Twice as much Hg and seven times as much DOC was deposited in the forested watershed compared to the opening. Mass balance studies that are based on wet-only deposition in openings severely underestimate atmospheric deposition of Hg in forests. Conifer canopies are more efficient filters of airborne particulates than are deciduous canopies as indicated by much higher Hg concentrations and total deposition in throughfall and stemflow waters under conifers. Significant positive relationships existed between Hg and DOC in both throughfall (36-57% of the variation) and stemflow waters (55588% of the variation). Hg complexation by DOC appears to be related to the contact time between precipitation and carbon sources.

Keywords: atmospheric deposition, dissolved organic carbon, mercury, stemflow, throughfall

1. Introduction

Mercury (Hg) contamination in fish is widespread in the Great Lake States, as well as in the northeastern U.S., Canada, and northern Europe, even in remote wilderness areas. The source of Hg to aquatic systems is both by direct atmospheric deposition and by transport from terrestrial systems. Studies in Minnesota and adjacent areas indicate that between 4 and 25% of atmospheric Hg deposited on upland terrestrial basins reaches the associated lakes (Krabbenhoft *et al.,* 1995; Krabbenhoft and Babiarz 1992; Swain *et* al., 1992), or between 6 and 75% of the total Hg loading of these lakes (the exact proportion depends on the terrestrial to lake surface area ratio and on the presence of peatlands in the watershed) (Krabbenhoft *et al.*, 1995; Lindqvist 1991; Henning *et al.*, 1989). If effective land management strategies are to be developed to minimize the transport of Hg into aquatic environments, knowledge of inputs at the landscape or watershed scale are necessary.

Atmospheric deposition is the main source of Hg to most terrestrial systems. Hg from geologic materials contributes very little to the local or regional inventory

Water; Ail; and Soil Pollution **113: 273-294, 1999.**

except in areas of elevated concentration (Barghigiani and Ristori 1994). Fitzgerald (1995) estimates that human activities contribute about 70–80% of the total annual Hg input to the atmosphere. Elemental mercury (Hg^0) comprises approximately 99% of the total gaseous Hg in the atmosphere (Fitzgerald *et* al., 1991). Particulate Hg exists in the atmosphere mainly as complexes with the divalent form of Hg (Hg^{2+}) although recent analytical techniques indicate that 0–5% exists as methyl mercury (MeHg) (Lindqvist 1991). Hg^0 is nearly insoluble in water, hence, the major input of Hg to the earth's surface is via wet and dry deposition of Hg compounds, most notably as rain-scavenged particulates and as soluble complexes with Cl-, OH-, and SO_3^{2-} (Pleijel and Munthe 1995). Atmospheric particulates can also be deposited by dry deposition, a process involving not only the settling of particles by gravity but also their adsorption by surfaces, notably leaves. Particulate Hg deposition is associated with both regional-scale variability due to precipitation scavenging and local variability resulting from differences in roughness and adsorption characteristics of vegetation. In forests, throughfall and stemflow are the avenues by which adsorbed particulates and leached constituents from vegetation reach the soil. Throughfall is precipitation that passes through the forest canopy and understory, reaching the forest floor. The size and shape of the forest canopy, total leaf area, the number of layers of vegetation, and rainfall intensity determine the amount, intensity and spatial distribution of throughfall (Brooks *et al.*, 1991). Stemflow, the flow of water down branches and the tree stem, is affected by branch attitude, shape of tree crowns, and roughness of bark (Brooks *et al.*, 1991). Although stemflow is not a large hydrologic flux over an entire watershed (usually <2% of gross annual precipitation), it can have a significant impact on the flux of organic and inorganic ions (Parker 1990; Verry and Timmons 1977). If Hg deposition follows similar patterns, a significant fraction of the total hydrologic flux of Hg has been neglected in watershed mass balance studies.

Organic carbon (OC) has gained attention because it forms complexes that control the transport and solubility of heavy metals in natural waters (Rueter and Perdue, 1977). Hg is no exception, as it exhibits a strong affinity for organic matter in soils, surface waters, peats and sediments (Hurley *et* al., 1995; Benoit *et* al., 1994; Johansson and Iverfeldt 1994; Lee *et al.*, 1994; Meili, 1994; Lee and Iverfeldt, 1991; Meili *et al.*, 1991; Mierle and Ingram, 1991; Schuster, 199). The mobile aqueous phase of OC is either referred to as dissolved organic carbon (DOC), operationally defined as organic particles less than a certain diameter (commonly <0.45 or 0.70 μm), or total organic carbon (TOC), the total unfiltered OC in aqueous samples, Open precipitation is characterized by very low DOC. Leaching of the forest canopy by throughfall increases DOC concentrations. Stemflow waters are generally characterized by greater DOC concentrations than throughfall waters because of longer contact time between water and carbon sources. If contact time between Hg and carbon sources is a determining factor in the complexation of inorganically bound Hg by OC, stemflow relationships would be hypothesized to

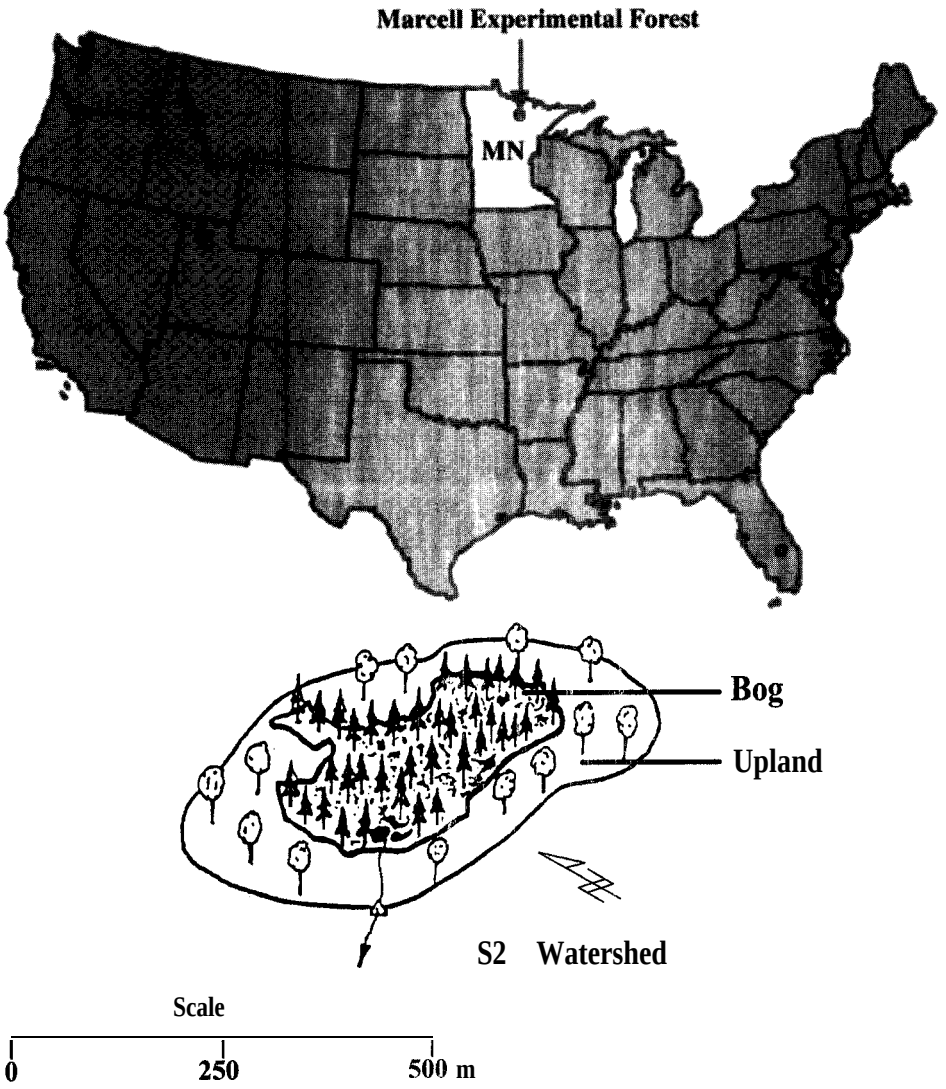


Figure 1. Location of the MEF and a schematic of the S2 watershed. Note: Lagg area is approximately equivalent to solid line separating bog from upland.

have the strongest correlation of those two constituents among open, throughfall and stemflow waters.

This study was designed to investigate the hydrologic inputs of Hg and OC to an upland/peatland watershed and the role that OC plays in Hg deposition.

2. Methods

2.1. STUDY SITE

The S2 watershed is located on the USDA Forest Service Marcel1 Experime tal Forest (MEF), located 40 km north of Grand Rapids, Minnesota (47°32′ I, 93°28′W) (Figure 1). The watershed contains a 3.2 ha black spruce (Picea ma ana) Sphagnum bog (pH at the watershed outlet = 3.9 ± 0.2) and a 6.5 ha uplai dominated by mature trembling aspen (*Populus tremuloides*) and paper birch (*B tula papyrifera*). The S2 watershed has been instrumented and studied in deta including hydrology (Nichols and Brown, 1980; Boelter and Verry, 1977), nutrie t cycling and behavior (Grigal, 1991; Verry and Timmons, 1982), and release f organic carbon and acidity (Verry, 198 1; Urban *et al.*, 1989).

2.2. CLIMATE

The climate of the MEF is subhumid continental, with wide and rapid diurn I and seasonal temperature fluctuations (Verry *et* al., 1988). The mean annual a r temperature is 2 °C, with extremes of -46 °C and 40 "C. Average January a l July temperatures are -14 °C and 19 °C, respectively (Verry 1984). Mean annu l precipitation at the MEF is 78 cm with 75% occurring in the snow-free peri I (mid-April to early November). An average of 65 rainstorms occur each year b t normally only 3 to 4 exceed 2.5 cm (Verry *et al.*, 1988).

2.3. SAMPLINGANDPRETREATMENTMETHODS

The design of the precipitation and throughfall collectors was similar to the Swedi IVL (Institute1 for Vatten-Och Luftvårdsforskining) bulk collectors (Iverfeldt, 199). Collectors consisted of a glass funnel that was connected to a glass collection vess l with Teflon tubing. An inverted watch glass placed in the funnel and a loop in t tubing minimized contamination. The 1.5 m high collectors were housed in 15 c diameter PVC tubes. Throughfall collector placement was based on a survey f canopy and understory cover from multiple transects in the upland, lagg, and b areas (66 points surveyed; Kolka, 1996) of S2. The lagg is a hydrologically acti area around the perimeter of the bog where nutrient-rich upland and nutrient-pot . bog waters meet, resulting in different vegetation than found in either the upla I or bog. Cover and spatial extent of the upland, bog, and lagg were used to repr . sentatively place ten collectors (five in the upland, four in the bog and one in t lagg). An eleventh collector was rotated as a duplicate to the established collector A twelfth collector was placed in an opening where the National Atmospher Deposition Program (NADP) is monitoring Hg in wet deposition. The NADP si is approximately 1.5 km from the S2 watershed.

The IVL bulk collectors were maintained for the snow-free period in 199 Throughfall and precipitation volumes for this period were measured directly fro

the bulk collectors. Snow water volume was measured with a standard rain gauge in the opening. Relationships developed in S2 between canopy type and open snow water volume were used to predict snow water volume for the upland and bog areas (Verry, 1976). Snow water deposition in the lagg was estimated as the mean of that deposited in the upland and bog.

Stemflow collectors were designed to capture a representative sample of stemflow via a spiral of slotted Teflon tubing wrapped around the tree and connected to a collection bottle. Fourteen collectors were installed, based on a survey of canopy species and diameter distributions (Kolka, 1996). Stemflow Hg and OC concentrations were converted to fluxes by estimating the volume of stemflow from previously determined rainfall volume-stemflow volume relationships for individual species. Stemflow volumes for trembling aspen and black spruce were estimated from equations developed in S2 (Verry, 1976). Stemflow volumes for red maple-paper birch (Freedman and Prager, 1986) and balsam fir (*Abies balsamea*) (Plamondon et *al.*, 1984) were estimated with relationships developed in Canada. Paper birch and red maple (*Acer rubrum*) had similar Hg concentrations in stemflow and the literature indicated they had similar stemflow volumes and thus they were grouped together for further analysis.

Throughfall and stemflow samples were collected biweekly throughout the snow-free period in 1995 (April 19th – November 14th) except at the NADP site where sampling was weekly. Triplicate snow samples were collected from the open, upland and bog in 1995 (March 14) and adjacent to each throughfall collector in 1996 (March 12) when snow was at or near its maximum seasonal water content. Snow was collected by digging a pit to expose a face of the snowpack, cleaning the face with gloved hands (cleanroom gloves), and collecting an integrated sample from the entire depth of the snowpack.

Ten mL of tested, high purity HCl was added as a preservative to empty collection bottles prior to field placement. Sample volume was measured by weighing the collection bottles and subtracting their dry weight. Collection bottles were subsampled for Hg into rigorously cleaned Teflon bottles within 72 hr after collection. A second subsample was collected in polyethylene bottles for the analysis of DOC and TOC. Field blanks for stemflow and throughfall consisted of milli-Q water poured through the collectors in the field and sampled and stored using the same protocol as above.

A weighted mean, based on the area1 proportion of cover types represented by each collector, was used to calculate the deposition of Hg and DOC in throughfall to the S2 watershed. The areal deposition of Hg and DOC in stemflow to the upland, lagg and bog was based on the tree distributions in each land type. The total deposition to the watershed was based on the area1 proportions of each land type.

2.4. Hg ANALYSIS

Rigorously tested cleaning and analytical procedures were used throughout sa n-
ple handling and analysis. Hg was measured by double amalgamation cold va or
atomic fluorescence spectrometry (CVAFS) (Fitzgerald and Gill, 1979; Bloom a d
Crecelius, 1983). Most samples for total-Hg determination had bromine mo o-
chloride (BrCl) added during subsampling and were analyzed within the follow' g
few days. Samples not immediately oxidized with BrCl were frozen; BrCl w as
added directly to frozen samples and digestion occurred while thawing. After B Cl
addition, samples were placed into their original ziploc bags and allowed to dig st
overnight on a heated sand bath at 70 "C. Prior to analysis, excess BrCl was redu d
by the addition of hydroxylamine hydrochloride (NH_2OH-HCl). Sample aliqu ts
(OS-100 mL, depending on expected Hg concentration) were added to bubbl rs
and Hg^{+2} was reduced to Hg" by 5 mL of $SnCl_2$. The bubblers were purged or
20 min with Hg-free N_2 gas and Hg" was collected on the sample gold trap. Sam le
traps were heated for 4 min at . 500 °C, and Hg" was collected on the analyti al
trap which was then heated for 3 min. Hg" peak area was recorded by an integral r.

2.5. Hg QUALITY CONTROL/QUALITY ASSURANCE

All open container operations were conducted under a HEPA filter in a cleanroc n.
Field collection and laboratory analyses were conducted in full cleanroom garb 1-
cluding lint-free coats and hats. Cleanroom quality, polyvinyl chloride gloves w re
worn at all times during handling of samples and sampling equipment. All ga es
were precleaned by gold traps prior to contact with the sample. Reagents were r 1-
tinely analyzed and cleaned of Hg to the extent possible and sets of standards a d
blanks were analyzed several times each day. A minimum of 20% duplicates w re
included within each sample train. Duplicate analysis of 193 open precipitati n,
throughfall and stemflow samples had a mean concentration for all samples of 3 .0
ng L^{-1}, and a pooled standard error (SE) of 3.35%. To assess the impact of freez g
on Hg concentration, a set of 17 samples were immediately analyzed and compa d
to a duplicate set that was frozen for two months prior to analysis. There were IO
significant differences among paired samples (paired t-test = 1.55, p = 0.14).

2.6. OC ANALYSIS AND QUALITY CONTROL/QUALITY ASSURANCE

Samples measured for DOC were filtered through 0.7 μm glass fiber filters a d
analyzed by a standard low temperature Dohrman DC-80 total organic C analy: r.
Unfiltered (TOC) throughfall and stemflow samples were measured using the sa ne
procedure. A minimum of 10% duplicates was included within each sample tra n.
The mean concentration for all samples was 41.4 mg L^{-1}, with a SE of 3.27% (=
58).

3. Results

3.1. VOLUME OF OPEN PRECIPITATION, THROUGHFALL AND STEMFLOW

The IVL bulk sampler in the opening at the NADP site collected volumes similar to the standard rain gauge located nearby. In 1995, the rain gauge collected 869 mm compared with 882 mm by the IVL sampler. Similar collection efficiency between the two types of samplers agrees with that recently reported in Wisconsin (Morrison *et al.*, 1995) and lends confidence to the volumes measured in throughfall. The duplicate sampler was rotated to all collection locations once (including the NADP site) and was located at a few of them twice. Although this was considered a field duplicate, 'true' field duplication is impossible because of spatial variability in cover. In spite of these shortcomings, no significant differences existed in volume collected between the pairs of collectors (paired t-test = 1.20, p = 0.256, n = 12).

Throughfall volume in the upland in 1995, a wetter year than normal (890 mm vs. 775 mm), ranged from 83 to 89% (mean = 85%) of that in the open. A previous study in the S2 upland found throughfall to be 74% of open precipitation in an average year (Verry and Timmons, 1977). The greater number of large storms in 1995 led to greater throughfall because the canopy interception capacity was frequently exceeded. Throughfall volume in aspen forests in eastern Canada averaged 80% of that in the open, with a range of 70–128% (Mahendrappa, 1990). Throughfall volumes in the bog ranged from 79 to 93% (mean = 85%) of that in the open, compared to 77% in a normal year (Verry and Timmons, 1977). The throughfall collector in the lagg had the lowest volume collected (65% of open volume). A fairly large proportion of balsam fir in the lagg likely led to the higher interception and less throughfall. Throughfall volume in balsam fir forests in eastern Canada average 75% of that collected in the open with a range of 57-92% (Mahendrappa 1990).

The y-intercept of the relationship between throughfall volume and open volume is indicative of the canopy interception capacity, although it would be more precise if the data were event-based instead of over biweekly sampling intervals. The canopy interception capacity calculated for each collector was proportional to the canopy cover, independent of canopy type (Figure 2). The strength of this relationship lends confidence to both the estimates of canopy coverage and the reliability of the IVL samplers in collecting throughfall volumes.

Estimated stemflow volumes were greatest for aspen, somewhat less for red maple-paper birch and balsam fir, and very low for black spruce (Table I). Stemflow from black spruce is especially low because of its rough, flaky bark and canopy geometry (Verry and Timmons, 1977; Mahendrappa and Ogden, 1972).

All measurements and calculations of throughfall and stemflow volumes and of Hg and DOC deposition were based on separate calculations for the snow and snow-free seasons. Throughfall+stemflow volumes are similar for the upland and bog during the snow-free period, but snow deposition is greater in the upland,

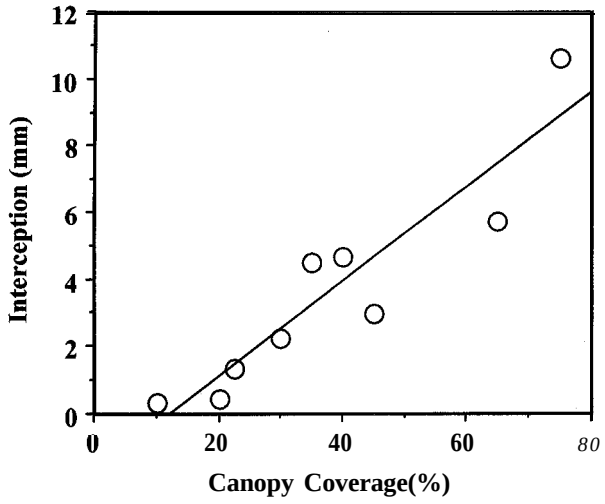


Figure 2. Relationship between mean growing season interception capacity and canopy coverage f individual throughfall collectors in the S2 watershed (Interception = - 1.73 + 0.14 (Cover%), R^2 0.86, p = 0. 0003).

TABLE I

Estimated stemflow volumes sampled in S2 for 1995. Volumes assume a complete canopy of those species

Species	Volume (mm)	% of Open Precipitation	#Events
Aspen	25.1	3.7	64
Red Maple-Paper Birch	16.9	2.5	61
Balsam Fir	15.0	2.2	60
Black Spruce	0.4	0.1	8

leading to slightly higher annual volumes (Table II). Snow-free volumes in the lag were considerably less than those in either the upland or bog because of the den canopy. For 1995 in the S2 watershed, 87% of the incident precipitation reache the forest floor, but < 2% was attributed to stemflow.

Uncertainty for throughfall was considered to be the SE among the annual vo umes for individual collectors. Uncertainty in stemflow volumes were estimate from the literature (Verry, 1976). Based on the calculated uncertainty, stemflow insignificant in terms of total water flux (Table II), volumes are highly variable, b because they are small, they scarcely affect total uncertainty. For the S2 watershe in 1995, volume fluxes via throughfall+stemflow were 769 ± 16 mm; this compar

TABLE II

S2 open precipitation, throughfall and stemflow volume fluxes for 1995

	Snow-free season			Snow season			Annual total			Uncertainty	
	mm	% of Open		mm	% of Open		mm	% of Open		(mm)	%
Aspen Upland											
Throughfall	572	84		189	92		760	86		12	2
Stemflow	24	4					24	3		3	13
Total	596	88		189	92		784	89		12	2
Black Spruce Bog											
Throughfall	604	89		157	77		761	86		25	3
Stemflow	0	0					0	0		0	36
Total	604	89		157	77		762	86		25	3
Aspen, Balsam Fir, Black Spruce Lagg											
Throughfall	434	64		168	82		602	68		16	3
Stemflow	14	2					14	2		3	23
Total	448	66		168	82		616	70		17	3
Entire S2 Watershed											
Throughfall	575	85		178	87		753	85		16	2
Stemflow	16	2					16	2		2	14
Total	591	87		178	87		769	87		16	2
Open – IVL Collector											
Gross Precipitation	677			205			882			30	3
Open NADP Collector											
Gross Precipitation	664			205			869				

to 882 ± 30 mm for open precipitation (Table 11). Canopy interception therefore accounted for 113 mm of precipitation.

3.2. Deposition of Hg in open precipitation, throughfall and stemflow

The IVL collector in the open had significantly lower Hg concentrations (by about 2.5 ng L^{-1}, paired t-test = 3.05, p = 0.007, n = 18), than the site monitored by the NADP. Although dry deposition in an opening is likely to be small when surrounded by forest, concentrations from a bulk collector would be expected to

be similar (Guentzel et al., 1995) or higher than those from a wet-only collector (Morrison ***et al.,*** 1995). Spatial variability in Hg deposition could be a possible explanation for the differences, but the two collectors were located < 5 m apart. Volatilization losses from the IVL collectors could also explain the difference, but these losses should be minimal because we precharged the sample bottles with concentrated HCl prior to sampling. Also, if volatilization was the cause of the differences, we would expect to see seasonal variation in the differences between the two collector types because volatilization is related to temperature (Lindberg ***et al.,*** 1995). No seasonal trend in the differences in concentration between collector types was apparent. We suspect a small persistent contamination or methodology bias. Sample collection was performed by the same individuals for both collectors, so the problem is either contamination by surfaces in contact with the sample or in handling of samples after collection. Although the NADP samples had significantly higher concentrations, total Hg deposition was similar (paired t-test = 1.13, 1: = 0.275, n = 18). The NADP uses the nearby rain gauge in the opening to calculi; te deposition. The rain gauge in the opening reported 869 mm of rainfall for 1995 (vs. 882 for the IVL collector) leading to nearly identical Hg deposition for the two collectors (see Table II).

There were no significant differences either in concentration (paired t-test = 1.45, p = 0.176, n = 12) or in deposition (paired t-test = 0.40, p = 0.694, r = 12) between the rotating duplicate collector and the established collector, although concentrations were more variable than deposition. No significant relationship was found between mean annual volume weighted Hg concentration and volume collected for individual collectors (r^2 = 0.26, p = 0.110, n = 11).

Hg concentrations in upland throughfall were approximately 1.6 times those in the open, while bog and lagg concentrations were 2.1 and 3.1 times higher (data not shown). Hg deposition by throughfall was greater than in the open even though volumes were smaller, presumably caused by Hg-containing particulates (dry deposition) being washed from the forest canopy during precipitation events. Deposition of Hg by upland, bog and lagg throughfall was approximately 1.3, 1.0 and 3.1 times higher than in the open, respectively (see Table III). Conifer species apparently capture more dry deposition than deciduous species. Bog deposition was always greater than that in the upland, illustrating the importance of coniferous species in capturing dry deposition. When upland, bog and lagg collectors are considered separately by cover type, obvious relationships exist between Hg deposition and canopy coverage (Figure 3). No relationship exists when all collectors are considered together. The slope of the relationships indicate that black spruce has approximately 5.5 times more capture efficiency for dry deposition than the upland species (mainly aspen, paper birch, red maple). Although only one collector was placed in the lagg, its efficiency fell between those in the black spruce bog and deciduous upland; its canopy is dominated by both conifers and deciduous species. There appears to be a canopy cover threshold of approximately 35% in the black

TABLE III

Hg precipitation fluxes for the S2 watershed in 1995

	Snow-free season		Snow season		Annual total		Uncertainty	
	$\mu g\ m^{-2}$	% of Open	$\mu g\ m^{-2}$	%of Open	$\mu g\ m^{-2}$	% of Open	$\mu g\ m^{-2}$	%
Aspen Upland								
Throughfall	7.63	134	0.93	116	8.56	132	0.32	4
Stemflow	0.76	13			0.76	12	0.10	13
Total	8.39	147	0.93	116	9.32	143	0.33	4
Black Spruce Bog								
Throughfall	17.96	315	1.50	188	19.46	299	0.91	5
Stemflow	0.05	1			0.05	1	0.02	37
Total	18.01	316	1.50	188	19.51	300	0.91	5
Aspen, Balsam Fir, Black Spruce Lagg								
Throughfall	17.57	308	2.37	296	19.94	307	0.86	4
Stemflow	0.62	11			0.62	10	0.14	23
Total	18.19	319	2.37	296	20.56	316	0.87	4
Entire S2 Watershed								
Throughfall	11.32	199	1.18	147	12.50	192	0.53	4
Stemflow	0.53	9			0.53	8	0.08	15
Total	11.85	208	1.18	147	13.03	200	0.53	4
Open IVL Collector								
Gross Precipitation	5.70		0.80		6.50		0.22	3
Open – NADP Collector								
Gross Precipitation	5.89		0.63		6.52			

spruce bog after which all dry deposition is scavenged (collectors with 35 and 65% canopy cover had equal deposition).

Stemflow Hg concentrations were grouped by species for each biweekly sampling interval. Concentrations for balsam fir and black spruce were . 2 and 3.5 times higher, respectively, than those of aspen and red maple-paper birch (Table IV). Like the canopy, the bark of conifers apparently has greater capture efficiency for dry deposition when compared to deciduous species. In addition, the interval between flow events is longer for the conifers, allowing more time for Hg capture

TABLE IV

Stemflow mean Hg concentrations (ng L^{-1}) and annual fluxes ($\mu g\ m^{-2}$) for species sampled in S2 for 1995, assuming entire canopy of sampled species

Species	Concentration	SE	# of Biweekly Intervals	Hg Flux
Aspen	32.0	3.4	8	0.83
Red Maple-Paper Birch	29.8	4.4	12	0.41
Balsam Fir	66.0	9.3	6	0.98
Black Spruce	112.9	22.5	5	0.05

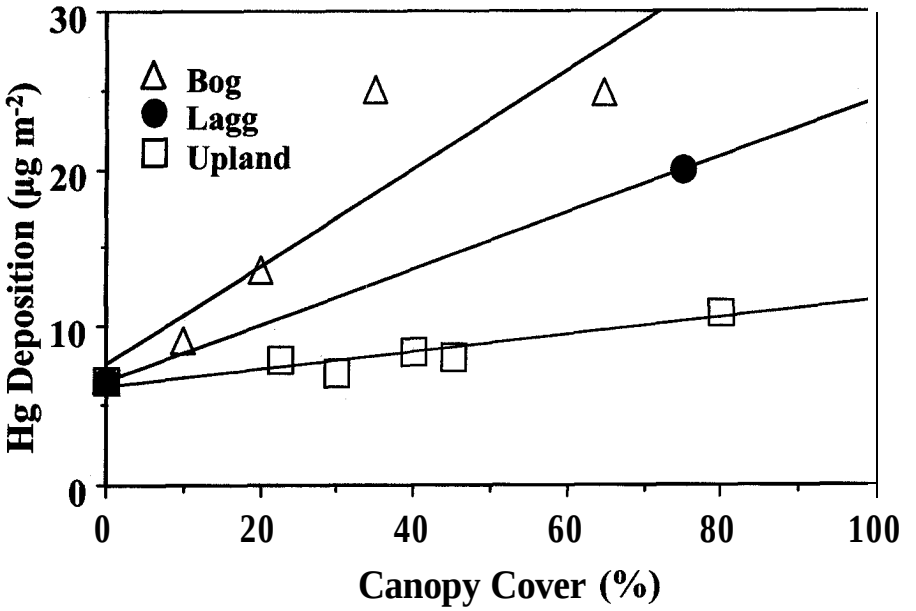


Figure 3. Relationship between canopy cover and annual Hg deposition for groups of collectors based on land type in the watershed (slope = 0.31 for bog, $r^2 = 0.82$; slope = 0.06 for upland, $r^2 = 0.8$; slope = 0.18 for lagg).

prior to wash-off. This explanation is illustrated by the inverse relationship between the number of intervals in which stemflow occurred and mean concentration (Table IV). Stemflow Hg concentrations were multiplied by the volume for each biweekly interval and summed to estimate annual stemflow fluxes for each species (Table IV). Although black spruce stemflow had some of the highest Hg concentrations ever reported in natural waters (up to 201 ng L^{-1}), the small volume led to little deposition. Results for the other species shows that stemflow is an important

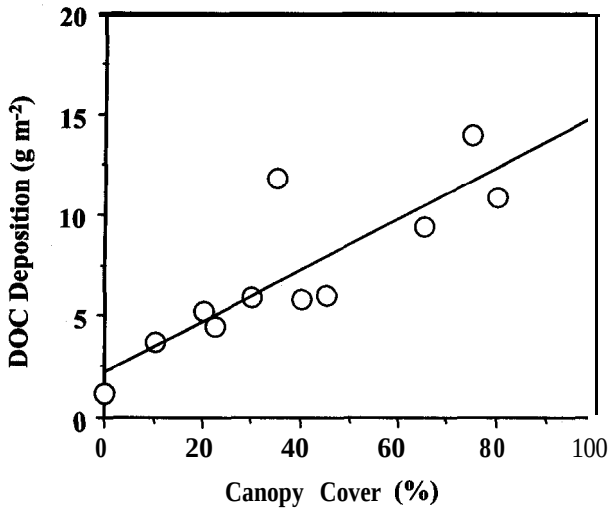


Figure 4. Relationship between canopy coverage and annual DOC deposition in throughfall for all collectors (DOC = 2.3 + 0.13(Canopy%), R^2 = 0.72).

source of Hg to the watershed, especially when compared to the deposition in the open (Table III).

Annual open Hg deposition at Marcel1 (Table III) is at the lower end of the range of that reported for other sites across the world. Open Hg deposition ranges from 18–42 $\mu g\ m^{-2}$ in Great Britain (Jensen and Iverfeldt, 1994) to 2.5-3.4 $\mu g\ m^{-2}$ in Ontario, Canada (St. Louis et al., 1995). Deposition at Marcel1 is similar to that in Michigan, USA, (5.8-9.1 $\mu g\ m^{-2}$), Finland (6-l 1 $\mu g\ m^{-2}$), Wisconsin, U.S.A. (6.8-10.3 $\mu g\ m^{-2}$) and other sites in Minnesota, U.S.A. (6.5-41.8 $\mu g\ m^{-2}$) (Hoyer et *al.*, 1995; Mukherjee *et* al., 1995; Fitzgerald *et al.*, 1991; Glass *et al.*, 1991).

Total atmospheric Hg fluxes in the upland, including both throughfall and stemflow, are 1.4 times those in the open, while fluxes in the bog and lagg are 3.0 and 3.2 times those in the open (Table III). Total deposition in the bog (19.51 $\mu g\ m^{-2}$) is within the range of that estimated by Pb-210 dating techniques (1980-1991 deposition = 16.8-29.2 $\mu g\ m^{-2}$) for a bog approximately 100 km from our site (Benoit et *al.*, 1994). In 1995, twice as much Hg was deposited in the forested S2 watershed than in the open (S2 watershed = 13.03 $\pm$ 0.53 $\mu g\ m^{-2}$ vs. open = 6.50 $\pm$ 0.22 $\mu g\ m^{-2}$). This is a considerably greater difference (100%) than that found for coniferous forests in Sweden (50%, Munthe et *al.*, 1995) and deciduous forests in Tennessee, U.S.A. (43%, Lindberg *et al.*, 1994). Although stemflow volumes were a small fraction of the annual hydrologic inputs into the watershed (<2%), they contributed 4% of Hg deposition in the watershed or the equivalent of 8% of the flux in the opening.

TABLE V

Stemflow mean DOC concentrations (mg L^{-1}) and annual fluxes (g m^{-2}) for species sampled in S2 for 1995, assuming entire canopy of sampled species

Species	DOC Concentration	SE	#Events	DOC Flux
Aspen	28.4	6.3	7	0.91
Red Maple-Paper Birch	34.5	9.6	11	0.41
Balsam Fir	38.8	3.0	6	0.58
Black Spruce	174.4	43.8	5	0.08

3.3. DEPOSITION OF DOC IN OPENPRECIPITATION, THROUGHFALLAND STEMFLOW

DOC concentrations were not measured by the NADP. Like Hg, DOC deposition was related to canopy cover, but unlike Hg, the relationship was independent of species (Figure 4). Throughfall DOC fluxes appear to be a function of the leaching of the vegetative material and dry deposition apparently exerts little influence on DOC concentrations. This is not surprising considering dry deposition is mainly inorganic (Ragsdale and Berish, 1987).

There were no significant differences between duplicate collectors in either DOC concentration (paired t-test = 0.95, p = 0.364) or deposition (paired t-test = 2.01, p = 0.070), although both measures were more variable than for Hg. A significant relationship was found between mean annual volume weighted DOC concentration and volume collected for individual collectors (r^2 = 0.63, p = 0.0041 n = 11). DOC appears to be more sensitive than Hg to collector placement under the canopy. Hg in dry deposition is likely washed from the canopy in a relatively short period after a precipitation event begins, while DOC is continually leached from the canopy during the event. Because DOC continually accumulates over the duration of the storm, even small differences in cover affect concentration as the duration of an event increases.

Stemflow DOC concentrations were grouped by species for each biweekly sampling interval. Concentrations for black spruce were 5 times higher than those for aspen, red maple-paper birch and balsam fir (Table V). As with throughfall, concentrations in stemflow appear to be related to the water-vegetation contact time during which soluble organics are leached. Black spruce, with coarse flaky bark slows stemflow and increases the contact time, yielding high DOC concentration!'; Although balsam fir had considerably higher Hg concentrations in stemflow than did the deciduous species, it had a similar DOC concentration. Balsam fir, much like the deciduous species, has fairly smooth bark which reduces the residence time

TABLE VI
DOC precipitation fluxes for the S2 watershed in 1995

	Snow-free season		Snow season		Annual total		Uncertainty	
	$g\ m^{-2}$	%of Open	$g\ m^{-2}$	%of Open	$g\ m^{-2}$	%of Open	$g\ m^{-2}$	%
Aspen Upland								
Throughfall	6.51	834.6	0.30	69.8	6.81	562.8	0.25	3.7
Stemflow	0.81	103.3			0.81	66.6	0.11	13.5
Total	1.32	937.9	0.30	69.8	7.62	629.4	0.27	3.6
Black Spruce Bog								
Throughfall	7.79	998.7	0.60	139.5	8.39	693.4	0.39	4.7
Stemflow	0.08	9.8			0.08	6.3	0.03	36.5
Total	7.87	1008.6	0.60	139.5	8.47	699.7	0.39	4.7
Aspen, Balsam Fir, Black Spruce Lagg								
Throughfall	13.35	1711.5	0.66	153.5	14.01	1157.9	0.60	4.3
Stemflow	0.53	67.6			0.53	43.6	0.12	23.1
Total	13.88	1779.1	0.66	153.5	14.54	1201.4	0.62	4.2
Entire S2 Watershed								
Throughfall	7.25	929.5	0.41	95.5	7.66	633.1	0.31	4.1
Stemflow	0.57	72.6			0.57	46.8	0.08	14.9
Total	7.82	1002.1	0.41	95.5	8.23	679.9	0.32	3.9
Open								
Gross Precipitation	0.78		0.43		1.21		0.04	3.4

of water on the stem and leads to lower DOC levels. Black spruce stemflow had some of the highest DOC concentrations ever measured in natural waters (up to 341 mg L^{-1}), but the small stemflow volume led to little deposition (Table V).

Total DOC fluxes in the upland were 6.3 times those in the open while fluxes in the bog and lagg were 7.0 and 12 times those in the open (Table VI). During 1995, 6.8 times as much DOC was deposited in the S2 watershed than in the open. Although stemflow was a small fraction of the annual volume inputs to the watershed (<2%), it contributed 7% of the DOC deposition in the watershed or the equivalent of 47% of the flux in the open. DOC deposition associated with stemflow is highly variable, but because of its small quantity, it scarcely affects the total uncertainty of DOC deposition. For the S2 watershed in 1995, fluxes of DOC

via throughfall and stemflow were 8.23 ± 0.32 g m^{-2}, compared to 1.21 ± 0.04 g m^{-2} for open precipitation (Table VI). Deposition of DOC at Marcel1 is similar to that found for a coastal plain swamp in North Carolina, U.S.A., where deposition in open precipitation was 2.0 g m^{-2} with throughfall+stemflow deposition of 9.2 g m^{-2} (Brinson *et al.*, 1980).

3.4. RELATIONSHIPS BETWEEN Hg AND OC IN OPEN, THROUGHFALL AND STEMFLOWWATERS

While DOC was measured on all samples, TOC was measured on a subset of 42 open (n = 4), throughfall (n = 15) and stemflow samples (n = 23) to investigate the influence of particulate organic carbon (POC) on Hg deposition. The difference in concentration between TOC and DOC was operationally defined as POC concentration. Only 16 of the 42 samples (12 stemflow, 4 throughfall and 0 open) had POC concentrations above the operational detection limit of the OC analyzer (<1.0 mg L^{-1}). Those samples with POC concentrations above the detection limit of the analyzer, showed a moderate relationship with Hg concentration (mean POC = 5.3 ± 1.2 mg L^{-1}, r^2 = 0.62, p = 0.0002, n = 16). From these results we can infer that POC can be an important pathway of Hg deposition, especially for stemflow, and it is likely that the influence of POC on Hg deposition is dependent on the intensity and duration of individual events.

Significant positive relationships existed between Hg and DOC concentration:, for open precipitation and for upland and bog throughfall for each biweekly collection period, although only 36-57% of the variation in Hg concentration could be explained by DOC concentration (Figure 5). DOC concentrations appear to have a moderate influence on Hg concentrations in precipitation and throughfall waters, Considering the short time inorganically-bound forms of Hg are in contact with carbon sources prior to collection, the lack of a strong relationship with DOC is not surprising.

Significant positive relationships also existed between Hg and DOC concentrations in stemflow with 83% of the variability in Hg concentration explained by DOC concentration when all species are grouped (Figure 6). When we examine the Hg-DOC relationship for only the deciduous species the correlation decreases to 55%, however, the correlation is 88% for conifer species (Figure 7). Conifers have a higher Hg-DOC correlation than do the deciduous species, presumably caused by bark and canopy differences between species types, leading to longer contact time The slope of the Hg-DOC stemflow relationship is fairly uniform among forest types, but the intercepts are very different (Figure 7). The intercepts are related to the fraction of Hg likely bound by inorganics, either in the dissolved inorganic fraction or complexed with inorganic particulates. The intercept for conifers is 2.5 times greater than that for deciduous species. Generally it takes large, less periodic storms for stemflow to occur on conifers, often leading to long duration between stemflow occurrences. Longer duration between storms allows for longer

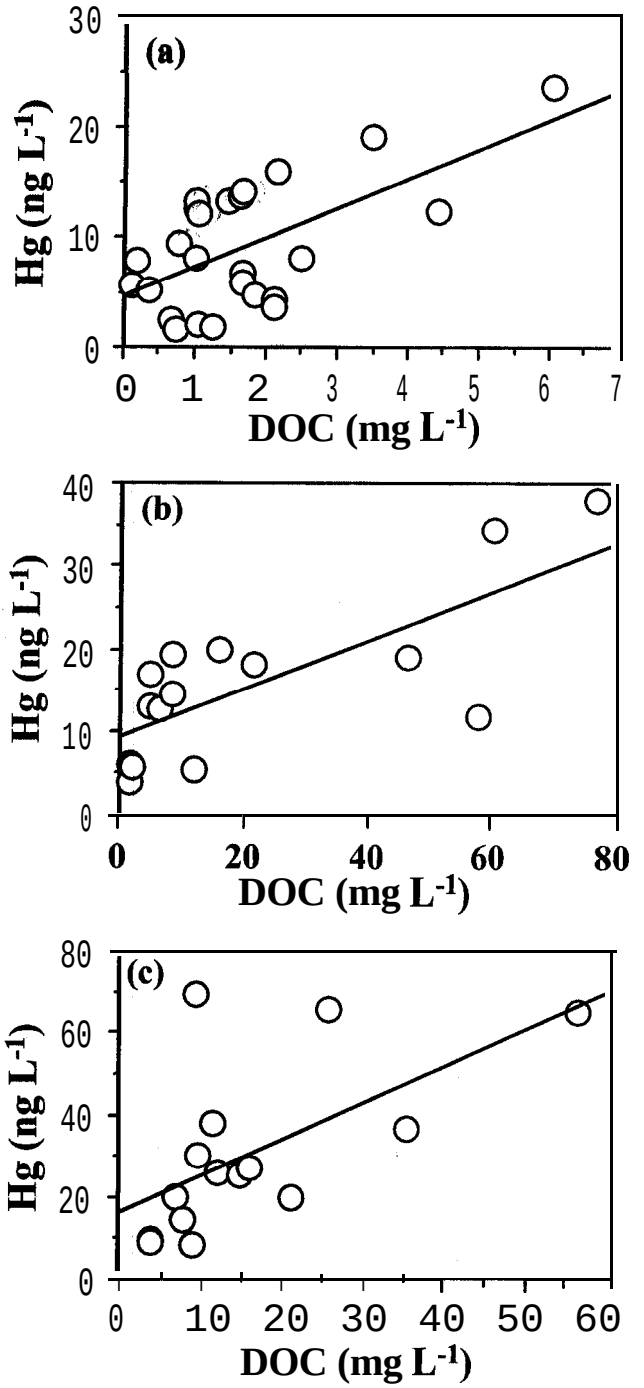
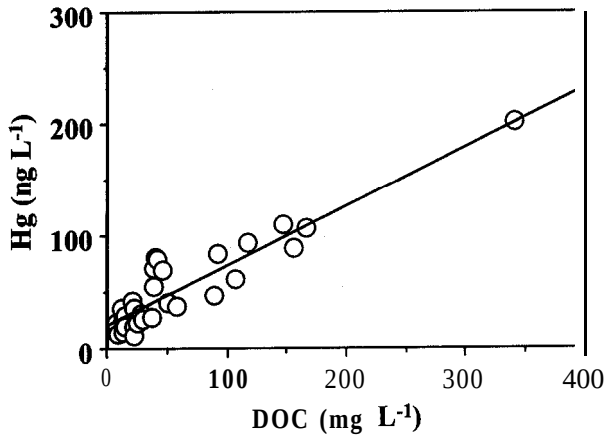


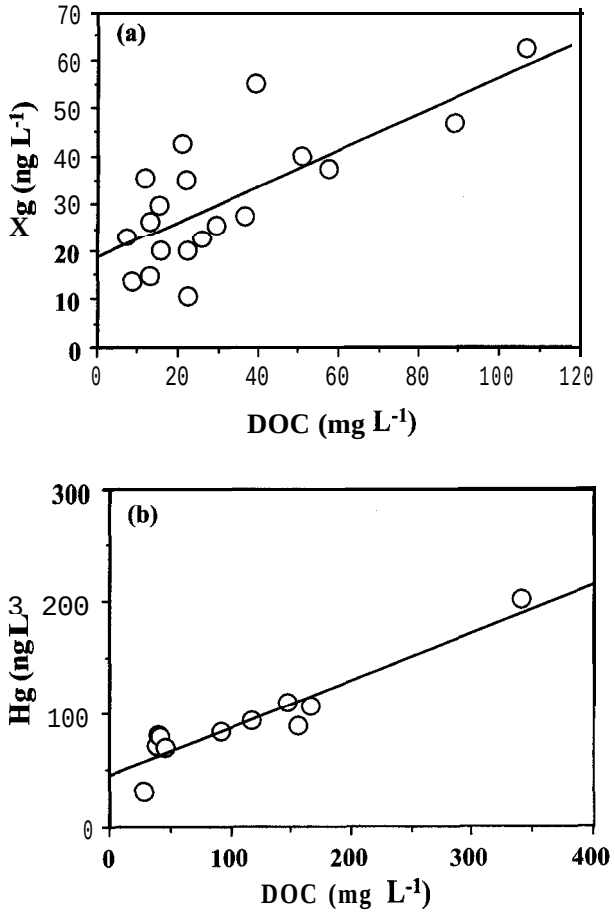
Figure 5. Relationship between weekly Hg and DOC concentrations in (a) open precipitation (Hg = 4.6 + 2.7(DOC), R^2 = 0.38), (b) upland throughfall (Hg = 9.5 + 0.29(DOC), R^2 = 0.57), and (c) bog throughfall (Hg = 16.5 t 0.89(DOC), R^2 = 0.36).



6. Relationship between biweekly Hg and DOC concentration in all stemflow (Hg = 20.9 0.53(DOC), R^2 = 0.83).

time for inorganic to organic transformation leading to a higher correlation fo conifer stemflow. The longer time between storms also results in greater inorgani dry deposition which leads to a greater intercept for conifers when compared t deciduous species.

If organic carbon contact time is the determining factor in the inorganic t organic Hg transformation, we would expect a positive relationship between Hg DOC correlations and DOC concentration, a surrogate measure of contact time This is indeed the case, as DOC concentration increases so does the certainty o the Hg-DOC relationship (Figure 8). The correlation for deciduous stemflow (55% is nearly identical to that from deciduous (upland) throughfall (57%), with mea DOC concentrations also similar. Stemflow generated by deciduous species appea to have a contact time similar to that of deciduous throughfall. This result is nc surprising considering that the deciduous species in this study tend to have smoot bark, leading to quick flow down the branches and stem. Conversely, the correlatio (88%) and mean DOC concentration for conifer stemflow is much greater than tha for conifer (bog) throughfall (36%). The rough, flaky bark present on the conifer in this study slows flow, allowing a greater opportunity for the inorganic to organi Hg transformation to occur. Conifer throughfall appears to have to shortest contac time with organic carbon based on it's relatively low mean DOC concentratio which leads to a low correlation among Hg and DOC. Again, this result is not su prising considering that the conifer (bog) canopy is less dense (mean = 33% cove than the deciduous (upland) canopy (mean = 44% cover). The denser cover of th deciduous canopy leads to greater throughfall contact time with leaves, leading t a higher Hg-DOC correlation when compared to the conifer canopy.



Relationship between biweekly Hg and DOC concentrations in (a) deciduous (Hg = 18.9 + 0.37(DOC), R^2 = 0.55) and (b) conifer stemflow (Hg = 45.4 + 0.42(DOC), R^2 = 0.88).

4. Conclusion

Significantly more Hg (two times) and OC (seven times) deposition occurs under a forest canopy than in a nearby opening. The elevated Hg deposition in forest systems is caused by the capture of particulates by the forest canopy (dry deposition). Stemflow, although a minor hydrologic flux, is equivalent to 8% of the Hg deposition in the open. Terrestrial Hg budgets based solely on wet deposition measured in an opening significantly underestimate atmospheric inputs to a forested watershed system. Studies investigating litterfall deposition at the MEF have been initiated to more fully characterize Hg inputs to forested systems.

Deposition associated with precipitation is related to both canopy cover and canopy type for Hg but only to canopy cover for DOC. Because of greater leaf and branch surface area, the conifer canopy collected greater dry deposition than did the

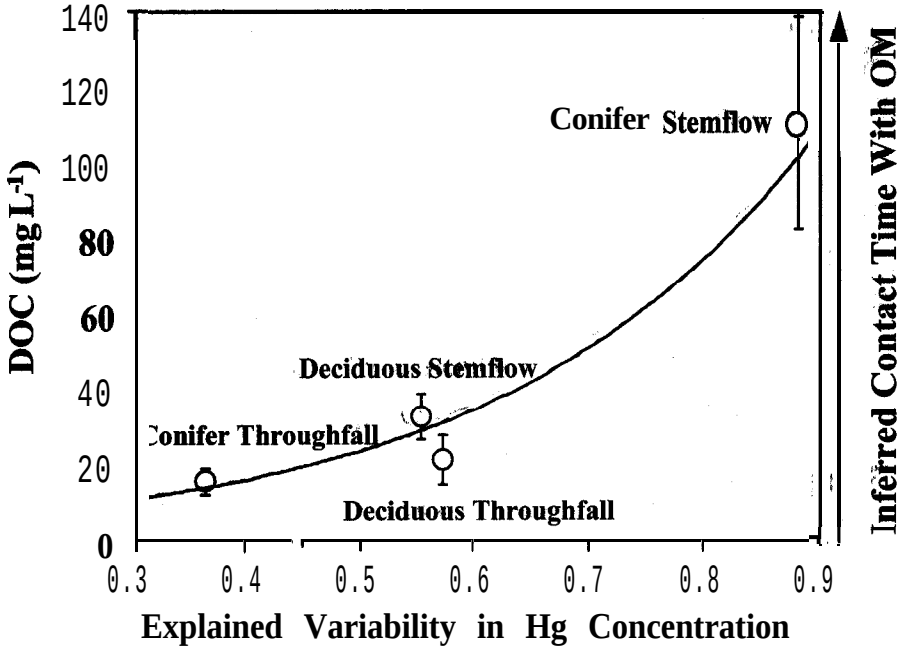


Figure 8. Influence of DOC concentration on the relationship between Hg and DOC concentration for throughfall and stemflow waters.

deciduous canopy, leading to greater Hg deposition. Conifer stemflow water had higher Hg-DOC correlation than did that for deciduous species. Based on these results, we hypothesize that the extent of Hg complexation with organic carbon is related to the residence time that Hg-bearing waters are in contact with carbon sources. As contact time increases, atmospherically-derived inorganic Hg become, complexed with organically-bound functional groups in DOC.

Acknowledgments

Thank you to Art Elling and Deacon Kylander of the USDA Forest Service and Jacob Fleck, Roger Wijnands, Steve Claas, Linda Kernik, Carissa Pang, William Zanner and James Thompson of the University of Minnesota for their help in sampling and analyses. Partial funding for this project was acquired through grant from the USDA Forest Service entitled 'Assessment of Methodology for Collection and Analysis of Environmental Samples for Mercury". This project was also partially funded by a grant from the Water Resources Research Center and the Minnesota Agricultural Experiment Station on research conducted under project 25-054 and 25-032 of the station.

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