 DOI: 10.1002/jpln.201000415 *J. Plant Nutr. Soil Sci.* 2012, *175,* 68–77

Effects of vegetation type on mercury concentrations and pools in two adjacent coniferous and deciduous forests

Daniel Obrist[1]*, Dale W. Johnson[2], and **Robert L. Edmonds[3]**

[1] Desert Research Institute, Division of Atmospheric Sciences, Reno, Nevada, USA
[2] Department of Natural Resources and Environmental Science, University of Nevada, Reno, Nevada, USA
[3] School of Forest Resources, University of Washington; Seattle, WA, USA

Abstract

Vegetation type and ecosystem structure affect major aspects of the mercury (Hg) cycle in terrestrial ecosystems which serve as important storage pools for a long-term legacy of natural and anthropogenic Hg release to the environment. The goal of this study was to evaluate the integrated effects of 80 y of different vegetative type on Hg accumulation and partitioning in terrestrial ecosystems by comparing Hg concentrations and pools of two adjacent forests: a coniferous Douglas fir (*Pseudotsuga menziesii*) and a deciduous red alder (*Alnus rubra*) stand. These stands grew for > 80 y in close proximity (200 m) with identical site histories, soil parent materials, and atmospheric exposure. Results showed that the Douglas fir stand was characterized by significantly higher Hg concentrations and Hg : C ratios in aboveground biomass compared to the deciduous red alder forest. For foliage, higher Hg concentrations (*plus* 43 $\mu g\,kg^{-1}$) were expected due to foliage age, but Hg concentrations also were higher in woody tissues (by 2 to 18 $\mu g\,kg^{-1}$) indicating increased uptake of atmospheric Hg by coniferous tissues. These differences were reflected—and further increased—in litter horizons where Hg-concentration differences increased in highly decomposed litter to > 200 $\mu g\,kg^{-1}$. In soils, no difference in concentrations of Hg was observed, but Hg : C ratios were consistently higher in the coniferous Douglas fir. Estimation of pool sizes of C and Hg in soils and at the whole ecosystem level showed that considerably smaller C pools in the coniferous stand as a result of faster C turnover and lower productivity did not lead to corresponding declines in Hg-pool sizes. The partitioning of Hg among ecosystem components—including distribution between aboveground and belowground components and distribution through the soil profile—was largely unaffected by forest type. Methyl-Hg concentrations observed in litter layers were also significantly higher in litter of Douglas fir, along with a higher proportion of methylated Hg of total Hg. In soils, methyl-Hg concentrations were similar in both stands. Comparison of these adjacent forest stands highlights that vegetation type affects concentrations of total Hg in otherwise equivalent sites and that differences also exist in respect to methylated Hg.

Key words: mercury sequestration / mercury deposition / retention / carbon cycling / nutrient dynamics

Accepted August 23, 2011

1 Introduction

Vegetation is known to exert significant influence on the biogeochemical cycling of mercury (Hg) in terrestrial ecosystems. For example, plants are modulating the exchange of Hg between the atmosphere and surfaces as aboveground tissues sorb atmospheric mercury (*Beauford* et al., 1977; *Lindberg* et al., 1979; *Godbold* and *Hüttermann*, 1988; *Bishop* et al., 1998; *Frescholtz* et al., 2003; *Millhollen* et al., 2006a, b; *Fritsche* et al., 2008a, b). When plant tissues senescence, their detritus lead to significant plant-derived Hg inputs to ecosystems (*Iverfeldt*, 1991; *Munthe* et al., 1995; *Lindberg*, 1996; *Rea* et al., 1996). In addition, plant canopies are known to lead to significant through-fall deposition fluxes whereby Hg is washed-off from plant canopies leading to enhanced Hg deposition under canopies as compared to nonvegetated sites (*Iverfeldt*, 1991; *Lindberg*, 1996; *Grigal* et al., 2000; *St Louis* et al., 2001; *Hall* and *Louis*, 2004). Once Hg is present in terrestrial ecosystems, Hg closely associates with litter and soil organic matter (SOM): Hg concentration and stocks are generally linked to the presence of organic C (*Aastrup* et al., 1991; *Meili*, 1991; *Grigal*, 2003; *Obrist* et al., 2011). Mobility of Hg within and from watersheds also is closely linked to that of organic C, *e.g.*, as evident in links between Hg in runoff and dissolved organic matter (DOM) (*e.g.,* to DOC: *Driscoll* et al., 1995; *Babiarz* et al., 1998; *Dittman* et al., 2010). Hence, the presence of plants, canopies, plant detritus, and organic matter exert profound influence on the presence and biogeochemistry of Hg in terrestrial ecosystems.

Mercury concentrations differ significantly among different plant tissues and species, tissue age, and vegetation type. For example, Hg concentration differences are observed

* Correspondence: Dr. D. Obrist; e-mail: daniel.obrist@dri.edu

© 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

among different plant groups (*i.e.*, angiosperms *vs.* gymnosperms; *Rasmussen* et al., 1991), among functional groups (*e.g.*, trees *vs.* shrubs *vs.* herbaceous species; *Moore* et al., 1995; *Hall* and *Louis*, 2004), among plant tissues (*e.g.,* leaves *vs.* branches or bole wood; *Obrist* et al., 2009, 2011), across different locations in canopies (*Bushey* et al., 2008; *Siwik* et al., 2009), and even within tissues in individual leaves (*Siwik* et al., 2009). Vegetation types also affect retention and loss of Hg from watersheds, as evidenced by reported differences in Hg concentrations in leachate of coniferous and deciduous forests (*Demers* et al., 2007), differences in lake-sediment Hg concentrations from inputs of coniferous-dominated *vs.* deciduous-dominated forests or open landscapes (*Teisserenc* et al., 2009), or differences in Hg runoff in streams between coniferous and softwood watersheds (*Nelson* et al., 2007).

The goal of this study was to assess Hg concentrations and pools in all major ecosystem compartments (*i.e.*, leaves, bole, bark, wood, understorey, litter, and soils) of two closely adjacent (200 m apart) forest stands, a deciduous red alder (*Alnus rubra* Bong.) and a coniferous Douglas fir (*Pseudotsuga menziesii* [Mirb.] Franco) forest in the NW United States. Both stands were established in the 1930s after logging and slash fires removed an original old-growth Douglas fir/western hemlock (*Tsuga heterophylla* [Raf.] Sarg.) forest. A Douglas fir plantation was established in one area, while adjacent areas were left to naturally re-establish and red alder stands naturally grew. Hence, soil parent material, microclimate, stand age, prior site history (such as logging), precipitation, temperature, and atmospheric Hg exposure are excluded as significant sources of variability between these two different forest stands, and observed differences between the two sites can be attributed to almost 80 y of different vegetation types. This study did not measure individual input and output fluxes of Hg in the respective stands, but rather assessed the integrated (*i.e.*, over 80 y) effects of different vegetation types on Hg concentrations and pools, under otherwise equal site history and exposure. This study addressed the following specific questions: (1) How do Hg concentrations and pools in aboveground biomass differ between the two stands? (2) Are concentration and pool differences consistent among ecosystem components, *e.g.*, from aboveground tissues to surface litter and to soil horizons? (3) How are differences in ecosystem Hg concentrations and pools related to biomass and C contents and pools sizes?

2 Material and methods

2.1 Site description

The two forest stands are located at the Thompson Research Center in the Cedar River watershed 56 km SE of Seattle, Washington. The watershed has been closed to the public since 1911 and used by the University of Washington for education and field research since 1961—including studies on plant productivity, acid rain, mineral cycling, tree physiology, and micrometeorology. The elevation of the site is 220 m asl. and mature Douglas fir and red alder stands are located ≈ 200 m apart. After a series of slash fires followed by logging of the original, old-growth Douglas fir/western hemlock forest in the early 1900s, a Douglas fir plantation was established in 1931. Understory vegetation consists of salal (*Gaultheria shallon*), Oregon grape (*Berberis nervosa*), and bracken fern (*Pteridium aquilinum*). Areas adjacent to this plantation were not planted with Douglas fir and naturally re-established with a red alder, developing into mature red alder forests with an average tree age of ≈ 70 y. Understory species include a dense growth of sword fern (*Polystichum munitum*) and bracken fern intermixed with Oregon grape. The underlying soil of both stands belongs to the Alderwood series (Dystric Entic Durochrept) of glacial origin, developed from ablation till overlying compacted basal till with a gravelly, sandy-loam texture. The climate is maritime with cool, dry summers and moderate, wet winters. Mean annual precipitation of the sites is 130 cm, with 75% falling as rain between October and March. Mean annual temperature is 9.8°C, with average monthly temperatures of 2.8°C and 16.8°C in January and July, respectively (*Cole* and *Gessel*, 1968).

2.2 Sample collection and analysis

We collected field samples at the end of July 2008 in four randomly assigned replicate plots (radius of ≈ 10 m) in each stand. Samples were collected in triplicate locations within each plot, resulting in 12 sampling locations and 4 pooled analyses for each component and stand. Aboveground ecosystem compartments sampled included green leaves/needles, dry leaves/needles, branches, bark, bole wood, understory vegetation, and litter horizons (Oi: undecomposed surface litter; Oe: partially decomposed litter; Oa: fully decomposed humus layer; and coarse woody debris). Mineral soil was sampled at depths of 0–7, 7–15, 15–30, and 30–45 cm, and roots were collected throughout the soil depth (*i.e.*, 0–45 cm). All sampling was conducted using clean latex gloves and sampling equipment made of stainless steel. All sampling equipment was washed prior to use in the field using deionized water. All samples were immediately double-bagged in plastic freezer bags and stored on ice until transport to the laboratory and transfer to a –25°C freezer. Green and dry leaves and branches were directly picked and clipped from lower tree branches and trees fallen by a chain saw; bark was cut with a clipper; and bole wood was cored after removal of the surrounding bark using a 40 cm long, 5.15 mm core-diameter tree borer. Understory vegetation was randomly clipped using clippers. Forest litter (Oi, Oe, Oa, and coarse woody debris) was picked directly from the forest floor using clean gloves and a spade. Using stainless-steel hand shovels, we sampled soil at different depths from the walls of larger soil pits excavated with shovels. All samples were freeze-dried in acid-cleaned (5% HNO_3) 25 mL glass test tubes using a freeze dryer with an 8-port column flask (1 L volume) manifold and a –50°C stainless-steel ice condenser (Model MicroModulyo-115, Thermo Scientific, Waltham, MA, USA).

After freeze drying, samples were milled and homogenized using stainless-steel coffee mills. Samples were analyzed for total Hg concentration using a Nippon Model MA-2000 total Hg analyzer in accordance with U.S. EPA method 7473. The analyzer was calibrated using 0.1 ppm and 0.01 ppm Hg

© 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

stock made of a 1000 ppm $HgCl_2$ standard (FGS chemicals) in 0.001% L-cysteine solution according to the manufacturer's manual. National Institute of Standards and Technology (NIST) solid standard reference materials (pine needles; [39.9 ± 0.4] μg Hg kg^{-1}) were run after every eight samples. When NIST standards deviated > 5% from expected values, the analyzer was recalibrated immediately and all samples since the last acceptable NIST standard were rerun. The 25 performed NIST standards showed excellent data quality with an average concentration value of (39.8 ± 1.05) μg kg^{-1} (mean ± standard deviation) and a coefficient of variation (CV) of 2.6%. Samples were analyzed in duplicate, and analyses were repeated when the CV of two samples exceeded 10%, with the exception of concentration values < 10 ng g^{-1} where a sample CV of 20% was allowed. We determined total C and N concentrations using a Leco Truspec CN Analyzer (LECO, St. Joseph, Michigan, USA) at the Soil Forage and Water Analysis Laboratory at Oklahoma State University. Soil texture was analyzed at the same laboratory using the hydrometer method which determines percent sand, silt, and clay settling rates measured by an ASTM 152-Type hydrometer. We calculated total Hg litter pools in both stands and for each ecosystem component by multiplying litter C : Hg ratios by C-pool estimates (*Cole* et al., 1995). Due to the difference in sampling protocols and use of previous C inventories, no consistent estimation of errors or variability for pool estimates were possible; hence, comparison of pool sizes should be viewed mainly as qualitative measures.

Methyl-Hg analyses were performed by an external laboratory (Brooks Rand Labs in Seattle, Washington, accredited by the National Environmental Laboratory Accreditation Program [NELAP]). Methyl-Hg (monomethyl-Hg) concentrations were determined by aqueous-phase ethylation, preconcentration, isothermal gas-chromatograph separation, and CVAFS detection according to EPA methods 1630. Preparation of samples included alkaline digestion using KOH methanol solution, and prepared samples were buffered, ethylated, and volatile organic species collected with Tenax. Upon thermal desorption, a gas-chromatograph column was used to separate Hg species chromatographically, and pyrolized Hg(0) was quantified by cold vapor atomic fluorescence. Method detection limits were between 0.013 and 0.044 ng g^{-1}, and method reporting limits were between 0.039 and 0.138 ng g^{-1} depending on dilution of samples. Due to cost limitations, only two replicate plots were used for analysis of methyl-Hg in each site.

2.3 Statistical analysis

We performed two sets of analysis of variance (ANOVA) to test for differences in means of Hg, C, and N concentrations and Hg : C ratios. The first set of analyses was performed for aboveground ecosystem components *plus* roots and included independent variables *Forest Type* ($n = 2$; red alder and Douglas fir), *Tissue Type* ($n = 9$; leaves, branches, bole wood, understory, litter: Oi, Oe, Oa; and coarse woody debris, and roots), and interactions of the two. The second set of analyses was performed for soil samples using the variables *Forest Type* and *Soil Depth* ($n = 4$; soils 0–7 cm, 7–15 cm, 15–30 cm, and 30–45 cm), and interactions. We also performed individual Student t-tests to test when individual ecosystem components were statistically different, and marked these results in Figs. 1 and 3 with letter labels. The same tests were also performed for methyl-Hg concentrations. Due to low replication (four replicate plots for total Hg and two replicate plots for methyl-Hg), we show results to a significance level of 10% (a: $p < 0.01$; b: $p < 0.05$; c: $p < 0.10$; n.s.: not significant). Linear regressions were performed to quantify relationships between soil Hg and soil C contents using data from both stands and all four soil depths (*i.e.*, 32 data points). All analyses were performed using the statistical package Stata 9.1 (StataCorp., College Station, Texas, USA).

3 Results and discussion

3.1 Total Hg in aboveground biomass tissues

Figure 1A shows Hg concentrations of aboveground biomass and litter components of the two stands (top panel) and concentrations of woody tissues (middle panel: aboveground components plus roots). Overall, Hg concentrations in roots and aboveground ecosystem components of the Douglas fir stand were significantly higher in the Douglas fir stand compared to those in the red alder stand (Tab. 1A: significant effect of *Forest Type* in ANOVA). Different plant tissues showed highly variable Hg concentrations (Tab. 1A: significant effect of *Tissue Type)*, and a significant interaction of *Tissue Type* × *Forest Type* showed that different tissues were not equally affected by *Forest Type*. Using individual t-tests, Hg differences were statistically significant—in spite of the small replication of four plots—in foliage, branches, roots, and litter Oe and Oa layers, but not in understory vegetation, surface Oi litter, nor woody debris (Fig. 1A).

Species-specific differences in foliar Hg concentration have been reported in many forests (*e.g., Rasmussen*, 1995; *Melieres* et al., 2003; *Hall* and *Louis*, 2004; *Siwik* et al., 2009) and laboratory studies (*Du* and *Fang*, 1982; *Schwesig* and *Krebs*, 2003; *Millhollen* et al., 2006b). In our study, the perennial Douglas fir showed higher foliar Hg concentrations compared to the deciduous red alder, in agreement with similar observations made by others (*e.g., Rasmussen* et al., 1991; *Hall* and *Louis*, 2004). A likely reason for such differences includes greater foliage age of perennial trees (*Rasmussen*, 1995); Douglas fir needles at our site reach ages of up to 6 y (*Cole*, 1981). While differences in Hg concentrations were pronounced in foliage, other aboveground components showed higher Hg concentrations in Douglas fir as well (including branches, roots, and bole wood at the 10% level), indicating that factors other than age—possibly tree morphology, geometry, or physiology—also may affect Hg uptake and sorption by aboveground tissues. It has been shown that location within tree canopies can greatly influence Hg concentrations (*Barghigiani* et al., 1991; *Rasmussen*, 1995; *Rea* et al., 2002; *Siwik* et al., 2009).

Cole et al. (1995) estimated higher aboveground C pools in Douglas fir forest, exceeding those in red alder by 77% for standing foliar biomass and by 20% for woody aboveground tissues (*Cole* et al., 1995; Fig. 2; Tab. 2). Using their C-pool

© 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

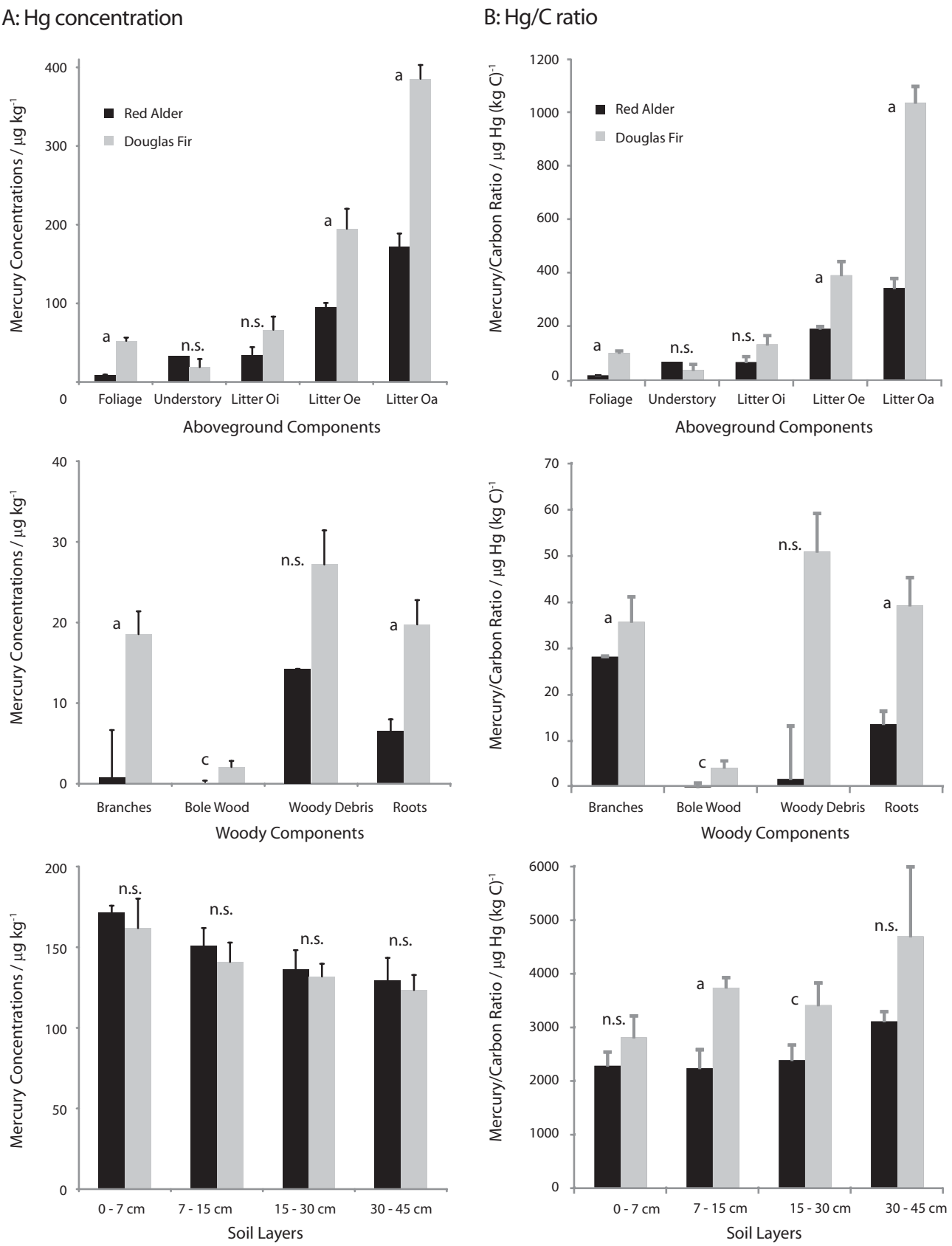

Figure 1: A: Mercury concentrations (in µg [kg d.m.]$^{-1}$) of 13 main ecosystem components in adjacent red alder (black bars) and Douglas fir (gray bars) forests. Values are mean concentrations of four plots per stand (with three pooled samples per plot), and bars represent standard errors. Letter labels indicate significance level based on individual unpaired, Student t-tests (a: $p < 0.01$; b: $p < 0.05$; c: $p < 0.10$; n.s.: not significant); B: Hg : C ratios (in µg [kg C]$^{-1}$) of the same samples.

© 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

Table 1: A: Results of statistical analysis of variance (ANOVA) of plant tissue and litter samples to test for differences between *Forest Type* ($n = 2$: red alder and Douglas fir), *Tissue Type* ($n = 9$: leaves, branches, bole wood, understorey, litter: Oi, Oe, and Oa; coarse woody debris, and roots), and their interactions. Dependent variables tested include Hg concentrations, Hg : C ratios, and methyl-Hg concentrations.
B: Results of statistical analysis of variance (ANOVA) of soil samples to test for differences between *Forest Type* ($n = 2$: red alder and Douglas-fir), *Soil Depth* ($n = 4$: 0–7 cm, 7–15 cm, 15–30 cm, and 30–45cm), and their interactions. Dependent variables tested include Hg concentrations, Hg ; C ratios, and methyl-Hg concentrations.

A) Aboveground		
Dependent variable: Hg concentration	**Dependent variable: Hg : C ratio**	**Dependent variable: methyl-Hg conc.***
ANOVA results	ANOVA results	ANOVA results
Forest Type: DF = 1, $\boldsymbol{p < 0.01}$	*Forest Type:* DF = 1, $\boldsymbol{p < 0.01}$	*Forest Type:* DF = 1, $\boldsymbol{p < 0.01}$
Tissue Type: DF = 8, $\boldsymbol{p < 0.01}$	*Tissue Type:* DF = 8, $\boldsymbol{p < 0.01}$	*Tissue Type:* DF = 3, $\boldsymbol{p < 0.03}$
interaction: DF = 8, $\boldsymbol{p < 0.01}$	interaction: DF = 8, $\boldsymbol{p < 0.01}$	interaction: DF = 8, $\boldsymbol{p < 0.01}$
B) Soils		
Dependent variable: Hg concentration	**Dependent variable: Hg : C ratio**	**Dependent variable: Methyl-Hg conc.**
ANOVA results	ANOVA results	ANOVA results
Forest Type: DF = 1, $p < 0.37$	*Forest Type:* DF = 1, $\boldsymbol{p < 0.06}$§	*Forest Type:* DF = 1, $p < 0.30$
Soil Depth: DF = 3, $\boldsymbol{p < 0.01}$	*Soil Depth:* DF = 8, $\boldsymbol{p < 0.10}$	*Soil Depth:* DF = 3, $\boldsymbol{p < 0.09}$§
interaction: DF = 8, $p < 0.99$	interaction: DF = 8, $p < 0.75$	interaction: DF = 8, $\boldsymbol{p < 0.01}$

* For methyl-Hg: tissue types only included litter Oi, Oe, and Oa; § significant only at the 10% level

Table 2: A: Calculated pools of Hg at the ecosystem level based on C inventories by *Cole* et al. (1995) and measured Hg : C ratios. Numbers in parentheses represent coefficients of variation (CV).
B: Calculated plant-derived Hg inputs based on C fluxes published by *Cole* et al. (1995) and measured Hg : C ratios. Numbers in parentheses represent coefficients of variation (CV).

A)	**Douglas fir**			**Red Alder**		
	C pools / kg C ha^{-1}	Hg : C ratio / μg kg^{-1}	Hg pools / g ha^{-1}	C pools / kg C ha^{-1}	Hg : C ratio / μg kg^{-1}	Hg pools / g ha^{-1}
Tree foliage	3 100	102 (16%)	0.3	1 750	18 (11%)	0.0
Tree woody*	136 000	4 (75%)	0.5	113 000	< d.l.	0.0
Understorey	1 550 (32%)	39 (105%)	0.1	3 000 (35%)	69	0.2
Litter Oi**	947 (3%)	134 (47%)	0.1	3 030 (2%)	68 (60%)	0.2
Litter Oe**	1 894 (3%)	393 (26%)	0.7	6 060 (2%)	193 (9%)	1.2
Litter Oa**	6 629 (3%)	1 038 (12%)	6.9	21 210 (2%)	345 (21%)	7.3
Coarse woody debris	6 020 (19%)	51 (33%)	0.3	9 300 (13%)	28 (82%)	0.3
Soil 0–15 cm	37 700	3 265 (23%)	123.1	50 200	2 250 (25%)	113.0
Soil 15—30 cm	21 900	3 402 (24%)	74.5	32 700	2 378 (24%)	77.8
Soil 30–45 cm	20 100	4 686 (55%)	94.2	21 600	3 101 (12%)	67.0
Total ecosystem-level	**235 840**		**300.7**	**261 850**		**267.0**
B)	**Douglas fir**			**Red Alder**		
	C inputs / kg C ha^{-1} y^{-1}	Hg : C ratio / μg kg^{-1}	Hg inputs / μg m^{-2} y^{-1}	C inputs / kg C ha^{-1} y^{-1}	Hg : C ratio / μg kg^{-1}	Hg inputs / μg m^{-2} y^{-1}
Woody tissue mortality	1 880	4 (75%)	0.8	1 570	(< D.L.)	0
Tree leaf litterfall§	525 (8%)	102 (16%)	5.4	1 560 (6%)	29 (10%)	4.5
Tree nonleaf litter§§	365 (34%)	36 (31%)	1.3	680 (14%)	2	0.1
Understory litterfall	233	36 (114%)	0.9	630	69	4.4
Total plant-derived inputs	**3 003**		**8.4**	**4 440**		**9.0**

* Bole wood Hg : C ratios used for calculations of aboveground woody pools; ** C mass of O horizon separated into Oi (10%), Oe (20%), and Oa (70%); § used Hg : C ratios of senesced foliage; §§ used Hg : C ratios of branches

© 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

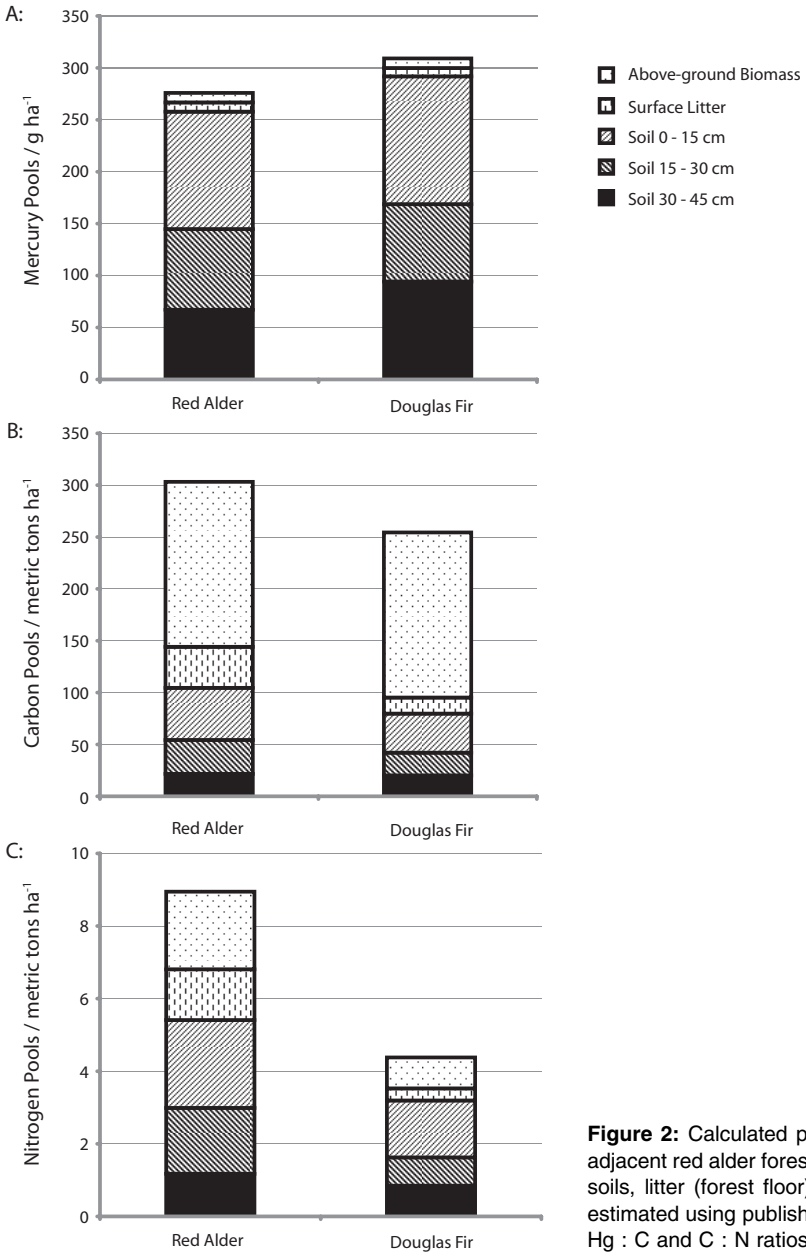

Figure 2: Calculated pools of Hg (panel A), C (panel B), and N (panel C) of adjacent red alder forest and Douglas fir stands with respective pools of mineral soils, litter (forest floor), and aboveground biomass components. Pools were estimated using published C-pool inventories (*Cole* et al., 1995) and measured Hg : C and C : N ratios.

estimates, we estimated Hg pools in aboveground biomass of 0.9 g ha^{-1} in Douglas fir and only 0.2 g ha^{-1} in red alder. This difference was mainly due to lower tissue Hg concentrations in red alder (*e.g.*, lack of Hg in bole wood) combined with its lower standing biomass. Estimated aboveground biomass Hg pools, however, are negligibly small compared to other ecosystem pools of Hg (Tab. 2A). Still, Hg in aboveground biomass is important in regard to atmospheric deposition *via* plant detritus (*Iverfeldt*, 1991; *Munthe* et al., 1995; *Lindberg*, 1996; *Rea* et al., 1996), and we estimated annual deposition related to plant detritus in Tab. 2B. *Cole* et al. (1995) reported that the red alder forest is characterized by markedly greater net biomass productivity compared to the Douglas fir stand, including three times higher leaf-litter mass fluxes and 50% higher overall plant-derived detritus C inputs (including tree mortality, leaf and nonleaf litter inputs, and understory biomass inputs; Tab. 2B). These patterns are consistent with generally higher foliar litter and plant detritus production in deciduous trees compared to coniferous species (*Cole* and *Rapp*, 1980) and with high productivities of forests with symbiotic N_2-fixing species such as red alder (*e.g, Cole* et al., 1995). We estimated that Hg deposition fluxes were similar in both stands, accounting for 8.4 and 9.0 μg m^{-2} y^{-1}, which is very small difference in regards to the uncertainties associated with C estimates and Hg : C ratios used to calculate these fluxes (Tab. 2B). Higher Hg concentrations of aboveground tissues in Douglas fir were almost fully compensated by lower productivity of that stand, showing that the higher tissue Hg levels did not lead to correspondingly higher deposition loads. An interesting fact was that leaf litterfall only accounted for between 50% and 64% of total Hg deposition associated with plant detritus in both stands. Hence, accounting for leaf litterfall alone does not well represent overall plant-derived detritus Hg inputs in forests.

© 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

3.2 Total Hg in litter horizons

We expected that higher Hg concentrations in Douglas fir in key aboveground tissues would lead to higher Hg concentrations in litter. But in contrast to leaves or branches, initial Oi litter layers in Douglas fir were not statistically higher (based on individual t-tests; Fig. 1), possibly because Oi litter included significant understory tissues that were similar in Hg concentrations in both stands. However, Hg concentrations in Oe litter (partially decomposed litter horizon) and Oa litter (well-decomposed organic humus layer) were more than double in Douglas fir compared to red alder litter, and Oa litter in Douglas fir exceeded Hg concentrations observed in red alder by > 200 μg kg^{-1}. This difference far exceeded any original difference in leaf litter or other tissues that formed these litter layers. Increasing Hg concentrations through decomposing litter are in agreement with other studies: in litter-decomposition studies, *Hall* and *St. Louis* (2004) and *Demers* et al. (2007) observed pronounced Hg-concentration increases in forest litter decomposing in the field. *Pokharel* and *Obrist* (2011) observed similar Hg-concentration increases during litter decomposition in the field and attributed Hg-concentration increases in the field mainly to sorption of additional atmospheric deposition. Three possible reasons may explain more pronounced Hg-concentration increases in Douglas fir litter compared to red alder. First, atmospheric deposition, particularly throughfall deposition, may be higher under coniferous stands compared to deciduous stands, as shown by others (*Demers* et al., 2007; *Nelson* et al., 2007; *Poulain* et al., 2007; *Witt* et al., 2009), leading to higher sorption of Hg. A second possible reason includes the presence of deeper litter horizons and higher litter pools and in red alder compared to Douglas fir: C-pool sizes in litter were estimated at 30 300 kg C ha^{-1} in red alder and 9470 kg C ha^{-1} in Douglas fir (Tab. 2A; *Cole* et al., 1995). This may cause atmospheric Hg deposition to sorb to higher litter mass, basically leading to a dilution effect. Based on C-pool estimates, we estimated total litter Hg pools of 8.9 g ha^{-1} in red alder and 7.8 g ha^{-1} in Douglas fir (Tab. 2A). Hence, in spite of very large litter Hg concentration and Hg : C ratio differences in litter between the two sites, actual pool sizes of Hg stored in litter were quite similar. A third possibility is that higher C-turnover rates in Douglas fir (*Cole* et al., 1995) may lead to higher litter Hg concentrations; such "internal accumulation" of Hg would occur when Hg is efficiently retained in OM during mineralization while C (and dry mass) is lost at a faster rate than Hg. *Pokharel* and *Obrist* (2011) indicated internal accumulation of Hg in litter during controlled laboratory decomposition studies, although they also observed significant atmospheric re-emissions of Hg. It is currently highly uncertain, however, to what degree "internal" accumulation of Hg leads to Hg-concentration increases in litter and soil OM pools in the field.

3.3 Total Hg in soils

Figure 1A also shows soil Hg concentrations for various depth horizons at the two sites (lower panel). Highest soil Hg concentrations were observed in the top soil layers (0–7 cm), and concentrations decreased significantly with increasing soil depth (Tab. 1B). Similar depth patterns have been reported from other soils (*Aastrup* et al., 1991; *Grigal* et al., 1994; *Schwesig* and *Matzner*, 2000; *Obrist* et al., 2011) and are attributed to links between soil Hg and OM or C content (*Meili*, 1991; *Schuster*, 1991; *Yin* et al., 1996) which generally also are highest in upper soils. The link between soil Hg and C was supported in our study by a statistically significant linear correlation of soil Hg to respective C content—as well as to N content—in both stands (not shown). We observed no systematic differences in soil Hg concentrations between the two stands ($p = 0.37$; Tab. 1B), but observed significant differences in C content in the two forest types, with ≈ 50% higher soil C content in red alder across the soil profile. The similar Hg concentrations but enhanced levels of C in red alder lead to significant differences in Hg : C ratios between the two stands (Tab. 1B). Hg : C ratios were consistently higher in soils of Douglas fir and hence were consistent with patterns in aboveground and litter components (Fig. 1B). We characterized soil texture at both sites as sandy loam to loamy sand and found no difference in percentage of sand, silt, or clay between the two sites. A previous study reported similar mineralogies at both stands (*April* and *Newton*, 1992). Therefore, it is unlikely that differences in Hg : C ratios were due to differences in geology or soil texture between sites.

We calculated total soil pools of Hg in both stands (Fig. 2, Tab. 2) using C-pool estimates by *Cole* et al. (1995) and measured Hg : C ratios, and estimated soil Hg pools of 292 g ha^{-1} in Douglas fir and 258 g ha^{-1} in red alder. Although pool estimates were based on older C inventories, C distribution showed strong similarities between Cole et al.'s results and our study; for example, both studies showed 50% higher soil C concentrations in red alder compared to Douglas fir, and data of the two studies showed a strong linear regression between C concentrations of all soil depths at both sites ($r^2 = 0.70$; slope of 1.1). Hence, while absolute C content may have changed since the study by *Cole* et al. (1995), relative differences between the two sites still are similar. Considerably higher soil C pools in red alder were not associated with correspondingly higher Hg stocks; in contrast, we observed ≈ 12% higher soil Hg pools in Douglas fir compared to red alder. This difference is not likely statistically significant given the variability in Hg : C ratios (coefficients of variability between 23% and 55%; Tab. 2A; note that missing error estimates in C-pool calculations by *Cole* et al. (1995) preclude consistent error propagations for Hg-pool-size estimates). Our results, however, indicate that pool sizes of Hg were not directly related to C stocks or C-turnover rates at these two sites. This observation contradicts a hypothesis we stated in earlier manuscripts (*Obrist*, 2007; *Obrist* et al., 2009) that losses of C due to mineralization may translate into corresponding losses of soil Hg to the atmosphere contributing to lower soil Hg pools. The results also are not in agreement with the strong links between C and Hg concentrations we observed in litter and soils across 14 forest sites (*Obrist* et al., 2011) where soil C alone explained up to 46% of the variability in soil Hg and we proposed that C may shape the distribution of Hg in forests at continental scales. It is possible that site-specific differences, including differences in species composition (*e.g.*, N-fixing plants) or soil properties disrupt relationships between Hg and C commonly observed: for example, Hg pools at these sites were likely influenced by an 11% to 17% (depending on soil depth) lower soil bulk den-

© 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

sity at the red alder site (*Brozek*, 1990), which is consistent with commonly observed lower bulk densities observed in soils with high OM content (*Federer* et al., 1993).

Mercury concentration and pool partitioning across soil and ecosystem components were similar at the two sites. Uppermost soil horizons showed highest Hg concentrations at both sites, and deeper soils showed consecutively lower Hg concentrations, with a 24% concentration decline from top to bottom at both sites (Fig. 1). Top 15 cm soil profiles accounted for 42% and 43% of the total soil Hg pools in Douglas fir and red alder, respectively. Finally, soil pools accounted for 97% of total ecosystem-level Hg pools at both sites; as a result, total ecosystem pools of Hg resembled patterns observed in soil pools (*i.e.*., higher in Douglas fir compared to red alder: 301 g ha^{-1} *vs.* 267 g ha^{-1}).

3.4 Methyl-Hg concentrations

We analyzed methyl-Hg concentrations for a subset of litter and soil samples. Despite limited sample replication (n = 2 per component and site), we found statistically higher methyl-Hg concentrations in aboveground litter horizons in Douglas fir compared to red alder (Fig. 3, Tab. 1). ANOVA analysis also showed significant differences in methyl-Hg concentrations between various litter layers, with concentrations increasing in the order Oi < Oe < Oa litter horizons. In soils, we observed no statistically significant differences of methyl-Hg concentration between the two stands (Fig. 3, Tab. 1). Soil methyl-Hg concentrations were much lower compared to litter that showed the highest concentration of all ecosystem compartments. These patterns indicate that methyl-Hg concentrations followed patterns of total Hg at both sites and that higher total Hg concentrations in litter of Douglas fir were accompanied by higher methyl-Hg concentrations. In addition, Douglas fir litter layers also showed a higher proportion of methyl-Hg to total Hg (1.4% compared to 0.6%). Although this difference was only statistically significant at the 10% level (p = 0.07), our results indicate that the proportion of methyl-Hg of total Hg is affected by forest type. In soils, where methyl-Hg only accounted for ≈ 0.1% of total Hg, no differences between the proportion of methyl-Hg to total Hg was observed between sites. Observed litter methyl-Hg concentrations were similar to studies that have reported methyl-Hg in leaf litter between 0.5% and 2.2% of total Hg (*St Louis* et al., 2001; *Hall* and *Louis*, 2004). Our patterns showing highest methyl-Hg concentrations in Oa layers, however, contrast with those of *Schwesig* and *Matzner* (2000) in two forest catchments reporting highest methyl-Hg concentrations in the top Oi layers. In one of the two sites, the authors also reported highest methyl-Hg concentrations in a mineral soil horizon, in contrast to highest methyl-Hg concentrations in litter in our study. A litter-decomposition study by *Hall* and *Louis* (2004) reported that methyl-Hg concentrations increased during decomposition in upland forest, which is in agreement with the highest methyl-Hg concentrations observed in highly decomposed organic forest-floor horizons in our study.

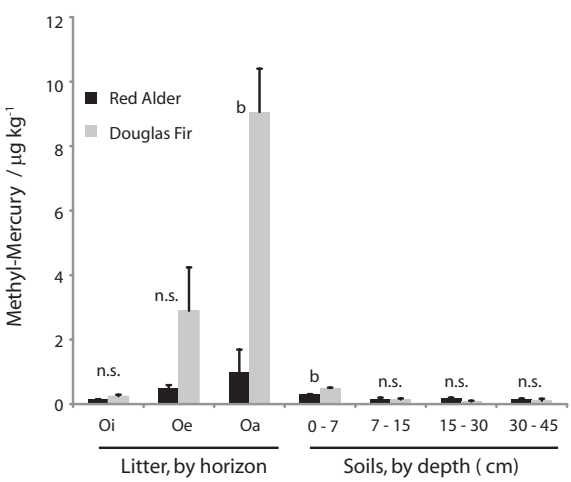

Figure 3: Concentrations of methyl-Hg in litter (forest floor) and mineral soil horizons at the two sites. Values are mean concentrations of a subset of plots (n = 2) in both stands and standard errors. Letter labels indicate levels of significance based on unpaired Student t-tests.

4 Conclusions

Comparison of Hg concentrations, Hg : C ratios, and methyl-Hg concentrations in two adjoining forest stands in the NW United States showed pronounced differences in biomass, litter, and soils between coniferous and deciduous stands. The coniferous Douglas fir stand was characterized by higher Hg concentrations of aboveground biomass compared to the deciduous red alder forest, an effect which also showed in litter horizons but not in mineral soils—possibly due to differences in soil C and soil bulk densities. Hg : C ratios, however, were consistently higher in Douglas fir, including in soils, and greatly increased from aboveground to litter and soil horizons. Previous studies at the two stands showed lower productivity, faster C-turnover rates, and lower C pools in the Douglas fir stand. Estimated total ecosystem and soil Hg pools, calculated using previously developed biomass and soil C inventories, showed that pool sizes of Hg were not directly related to C stocks or to C-turnover rates, and imply that accumulation rates of Hg were not directly linked to those of C at these two sites.

Given the similar site exposure and site histories, we attribute observed differences in Hg levels to almost 80 y of difference in vegetative types, which highlights a strong effect of vegetation and ecosystem structure on Hg accumulation in terrestrial ecosystems. Site differences also were evident in methyl-Hg concentrations, with the Douglas fir litter layers showing significantly higher methyl-Hg concentrations in litter horizons and a higher proportion of methyl-Hg to total Hg.

Acknowledgments

We thank *Bob Gonyea* and *Bert Hasselberg* for assistance during field sampling; *Carsen Berger, Johnny Dagget, Rebecca Higgins, Gabriel Marty,* and *So Lee* for sample collection, processing, laboratory analyses, and manuscript preparation; *Steve Lindberg* for guidance and advice, and *Roger Kreidberg* for editorial assistance. This study was sup-

© 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

ported by the *U.S. Environmental Protection Agency* through a *Science To Achieve Results (STAR) grant (RD833378010)* to study the consequences of global change for air quality, and also received support from the *Desert Research Institute's Internal Project Assignment program.*

References

Aastrup, M., Johnson, J., Bringmark, E., Bringmark, L., Iverfeldt, A. (1991): Occurrence and transport of mercury within a small catchment-area. *Water Air Soil Pollut.* 56, 155–167.

April, R., Newton, R. (1992): Mineralogy Mineral Weathering, in: D. W. Johnson, S. E. Lindberg (eds): Atmospheric Deposition and Forest Nutrient Cycling. A Synthesis of the Integrated Forest Study. Springer-Verlag, New York, pp. 378–425.

Babiarz, C. L., Hurley, J. P., Benoit, J. M., Shafer, M. M., Andren, A. W., Webb, D. A. (1998): Seasonal influences on partitioning and transport of total and methylmercury in rivers from contrasting watersheds. *Biogeochemistry* 41, 237–257.

Barghigiani, C., Ristori, T., Bauleo, R. (1991): Pinus as an atmospheric Hg biomonitor. *Environ. Technol.* 12, 1175–1181.

Beauford, W., Barber, J., Barringer, A. R. (1977): Uptake and distribution of mercury within higher plants. *Physiol. Plant.* 39, 261–265.

Bishop, K., Lee, Y., Munthe, J., Dambrine, E. (1998): Xylem sap as a pathway for total mercury and methylmercury transport from soils to tree canopy in the boreal forest. *Biogeochemistry* 40, 101–113.

Brozek, S. (1990): Effect of soil changes caused by red alder (*Alnus rubra*) on biomass and nutrient status of Douglas-fir (*Pseudotsuga menziesii*) seedlings. *Can. J. Forest Res.* 20, 1320–1325.

Bushey, J. T., Nallana, A. G., Montesdeoca, M. R., Driscoll, C. T. (2008): Mercury dynamics of a northern hardwood canopy. *Atmos. Environ.* 42, 6905–6914.

Cole, D. W. (1981): Nitrogen Uptake and Translocation by Forest Ecosystems, in FE, C., Rosswall, T. (eds.): Terrestrial Nitrogen Cycles. Ecological Bulletin, Stockholm, pp. 219–232.

Cole, D. W., Gessel, S. P. (1968): Cedar River research: A means for studying the nutrient cycling in forest ecosystems. Forest Resources Monograms, University of Washington, College of Forest Resources, Seattle, WA.

Cole, D. W., Rapp, M. R. (1980): Elemental Cycling in Forest Ecosystems, in Reichle, D. (ed.): Dynamic Properties of Forest Ecossystems – IBP Synthesis. Cambridge University Press, Cambridge, England, pp. 341–409.

Cole, D. W., Compton, J. E., Edmonds, R. L. (1995): Comparison of Carbon Accumulation in Douglas Fir and Red Alder Forests, in McFee, W. W., Kelly, L. M. (eds.): Carbon Forms and Function in Forest Soils. Soil Science Society of America, Inc., Madison, Wisconsin, USA, pp. 527–546.

Demers, J. D., Driscoll, C. T., Fahey, T. J., Yavitt, J. B. (2007): Mercury cycling in litter and soil in different forest types in the Adirondack region, New York, USA. *Ecol. Appl.* 17, 1341–1351.

Dittman, J. A., Shanley, J. B., Driscoll, C. T., Aiken, G. R., Chalmers, A. T., Towse, J. E., Selvendiran, P. (2010): Mercury dynamics in relation to dissolved organic carbon concentration and quality during high flow events in three northeastern US streams. *Water Resour. Res.* 46, W07522, DOI: 10.1029/2009WR008351.

Driscoll, C. T., Blette, V., Yan, C., Schofield, C. L., Munson, R., Holsapple, J. (1995): The role of dissolved organic-carbon in the chemistry and bioavailability of mercury in remote Adirondack lakes. *Water Air Soil Pollut.* 80, 499–508.

Du, S., Fang, S. (1982): Uptake of elemental mercury-vapor by C3-species and C4-species. *Environ. Ex. Bot.* 22, 437–443.

Federer, C. A., Turcotte, D. E., Smith, C. T. (1993): The organic fraction bulk-density relationship and the expression of nutrient content in forest soils. *Can. J. Forest Res.* 23, 1026–1032.

Frescholtz, T. F., Gustin, M. S., Schorran, D. E., Fernandez, G. C. J. (2003): Assessing the source of mercury in foliar tissue of quaking aspen. *Environ. Toxicol. Chem.* 22, 2114–2119.

Fritsche, J., Obrist, D., Zeeman, M. J., Conen, F., Eugster, W., Alewell, C. (2008a): Elemental mercury fluxes over a sub-alpine grassland determined with two micrometeorological methods. *Atmos. Environ.* 42, 2922–2933.

Fritsche, J., Wohlfahrt, G., Ammann, C., Zeeman, M., Hammerle, A., Obrist, D., Alewell, C. (2008b): Summertime elemental mercury exchange of temperate grasslands on an ecosystem-scale. *Atmos. Chem. Phys.* 8, 7709–7722.

Godbold, D., Hüttermann, A. (1988): Inhibition of photosynthesis and transpiration in relation to mercury-induced root damage in spruce seedlings. *Physiol. Plant.* 74, 270–275.

Grigal, D. F. (2003): Mercury sequestration in forests and peatlands: A review. *J. Environ. Qual.* 32, 393–405.

Grigal, D. F., Nater, E. A., Homann, P. S. (1994): Spatial Distribution Patterns of Mercury in an East-Central Minnesota Landscape, in Watras, C. F., Huckabee, J. W. (eds.): Mercury Pollution: Integration and Synthesis. CRC Press Inc, Monterey, California, USA, pp. 305–312.

Grigal, D. F., Kolka, R. K., Fleck, J. A., Nater, E. A. (2000): Mercury budget of an upland-peatland watershed. *Biogeochemistry* 50, 95–109.

Hall, B., Louis, V. (2004): Methylmercury and total mercury in plant litter decomposing in upland forests and flooded landscapes. *Environ. Sci. Technol.* 38, 5010–5021.

Iverfeldt, A. (1991): Mercury in forest canopy throughfall water and its relation to atmospheric deposition. *Water Air Soil Pollut.* 56, 553–564.

Lindberg, S. E. (1996): Forest and the Global Biogeochemical Cycle of Mercury: The importance of Understanding Air/vegetation Exchange Processes, in Aeyens, W., Ebinghaus, R., Vasiliev, O. (eds.): Global and Regional Mercury Cycles: Sources, Fluxes and Mass Balances. NATO ASI Series 21, Kluwer Academic Publishers, Dordreacht, The Netherlands, pp. 359–380.

Lindberg, S. E., Jackson, D. R., Huckabee, J. W., Janzen, S. A., Levin, M. J., Lund, J. R. (1979): Atmospheric emissions and plant uptake of mercury from agricultural soils near the Almaden mercury mine. *J. Environ. Qual.* 8, 572–578.

Meili, M. (1991): The coupling of mercury and organic matter in the biogeochemical cycle – towards a mechanistic model for the boreal forest zone. *Water Air Soil Pollut.* 56, 333–347.

Melieres, M. A., Pourchet, M., Charles-Dominique, P., Gaucher, P. (2003): Mercury in canopy leaves of French Guiana in remote areas. *Sci. Total Environ.* 311, 261–267.

Millhollen, A., Obrist, D., Gustin, M. (2006a): Mercury accumulation in grass and forb species as a function of atmospheric carbon dioxide concentrations and mercury exposures in air and soil. *Chemosphere* 65, 889–897.

Millhollen, A. G., Gustin, M. S., Obrist, D. (2006b): Foliar mercury accumulation and exchange for three tree species. *Environ. Sci. Technol.* 40, 6001–6006.

Moore, T. R., Bubier, J. L., Heyes, A., Flett, R. J. (1995): Methyl and total mercury in boreal wetland plants, Experimental Lakes Area, Northwestern Ontario. *J. Environ. Qual.* 24, 845–850.

Munthe, J., Hultberg, H., Iverfeldt, A. (1995): Mechanisms of deposition of methylmercury and mercury to coniferous forests. *Water Air Soil Pollut.* 80, 363–371.

© 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

Nelson, S. J., Johnson, K. B., Kahl, J. S., Haines, T. A., Fernandez, I. J. (2007): Mass balances of mercury and nitrogen in burned and unburned forested watersheds at Acadia National Park, Maine, USA. *Environ. Monit. Assess.* 126, 69–80.

Obrist, D. (2007): Atmospheric mercury pollution due to losses of terrestrial carbon pools? *Biogeochemistry* 85, 119–123.

Obrist, D., Johnson, D. W., Lindberg, S. E. (2009): Mercury concentrations and pools in four Sierra Nevada forest sites, and relationships to organic carbon and nitrogen. *Biogeosciences* 6, 765–777.

Obrist, D., Johnson, D., Lindberg, S., Luo, Y., Hararuk, O., Bracho, R., Battles, J., Dail, D., Edmonds, R., Monson, R., Ollinger, S., Pallardy, S., Pregitzer, K., Todd, D. (2011): Mercury distribution across 14 U.S. forests. Part I: Spatial patterns of concentrations in biomass, litter, and soils. *Environ. Sci. Technol.* 45, 3974–3981.

Pokharel, A. K., Obrist, D. (2011): Fate of forest litter during decomposition. *Biogeosciences* 8, 2507–2521.

Poulain, A. J., Roy, V., Amyot, M. (2007): Influence of temperate mixed and deciduous tree covers on Hg concentrations and photoredox transformations in snow. *Geochim. Cosmochim. Acta* 71, 2448–2462.

Rasmussen, P. (1995): Temporal variation of mercury in vegetation. *Water Air Soil Pollut.* 80, 1039–1042.

Rasmussen, P., Mierle, G., Nriagu, J. (1991): The analysis of vegetation for total mercury. *Water Air Soil Pollut.* 56, 379–390.

Rea, A. W., Keeler, G. J., Scherbatskoy, T. (1996): The deposition of mercury in throughfall and litterfall in the Lake Champlain watershed: A short-term study. *Atmos. Environ.* 30, 3257–3263.

Rea, A., Lindberg, S., Scherbatskoy, T., Keeler, G. (2002): Mercury accumulation in foliage over time in two northern mixed-hardwood forests. *Water Air Soil Pollut.* 133, 49–67.

Schuster, E. (1991): The behavior of mercury in the soil with special emphasis on complexation and adsorption processes–a review of the literature. *Water Air Soil Pollut.* 56, 667–680.

Schwesig, D., Krebs, O. (2003): The role of ground vegetation in the uptake of mercury and methylmercury in a forest ecosystem. *Plant Soil* 253, 445–455.

Schwesig, D., Matzner, E. (2000): Pools and fluxes of mercury and methylmercury in two forested catchments in Germany. *Sci. Total Environ.* 260, 213–223.

Siwik, E. I. H., Campbell, L. M., Mierle, G. (2009): Fine-scale mercury trends in temperate deciduous tree leaves from Ontario, Canada. *Sci. Total Environ.* 407, 6275–6279.

St Louis, V., Rudd, J., Kelly, C., Hall, B., Rolfhus, K., Scott, K., Lindberg, S., Dong, W. (2001): Importance of the forest canopy to fluxes of methyl mercury and total mercury to boreal ecosystems. *Environ. Sci. Technol.* 35, 3089–3098.

Teisserenc, R., Lucotte, M. M., Houel, S., Carreau, J. (2009): Linking the nature of terrigenous organic matter inputs and mercury concentrations in boreal lake sediments. Conference on Mercury as a Global Pollutant, June 7–12, 2009, Guiyang, China.

Witt, E. L., Kolka, R. K., Nater, E. A., Wickman, T. R. (2009): Influence of the forest canopy on total and methyl mercury deposition in the boreal forest. *Water Air Soil Pollut.* 199, 3–11.

Yin, Y. J., Allen, H. E., Li, Y. M., Huang, C. P., Sanders, P. F. (1996): Adsorption of mercury(II) by soil: Effects of pH, chloride, and organic matter. *J. Environ. Qual.* 25, 837–844.

© 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim