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Fate of mercury in tree litter during decomposition

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Abstract. We performed a controlled laboratory litter incubation study to assess changes in dry mass, carbon (C) mass and concentration, mercury (Hg) mass and concentration, and stoichiometric relations between elements during decomposition. Twenty-five surface litter samples each, collected from four forest stands, were placed in incubation jars open to the atmosphere, and were harvested sequentially at 0, 3, 6, 12, and 18 months. Using a mass balance approach, we observed significant mass losses of Hg during decomposition (5 to 23 % of initial mass after 18 months), which we attribute to gaseous losses of Hg to the atmosphere through a gas-permeable filter covering incubation jars. Percentage mass losses of Hg generally were less than observed dry mass and C mass losses (48 to 63 % Hg loss per unit dry mass loss), although one litter type showed similar losses. A field control study using the same litter types exposed at the original collection locations for one year showed that field litter samples were enriched in Hg concentrations by 8 to 64 % compared to samples incubated for the same time period in the laboratory, indicating strong additional sorption of Hg in the field likely from atmospheric deposition. Solubility of Hg, assessed by exposure of litter to water upon harvest, was very low (<0.22 ng Hg g^{-1} dry mass) and decreased with increasing stage of decomposition for all litter types. Our results indicate potentially large gaseous emissions, or re-emissions, of Hg originally associated with plant litter upon decomposition. Results also suggest that Hg accumulation in litter and surface layers in the field is driven mainly by additional sorption of Hg, with minor contributions from "internal" accumulation due to preferential loss of C over Hg. Litter types showed highly species-specific differences in Hg levels during decomposition suggesting that emissions, retention, and sorption of Hg are dependent on litter type.

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1 Introduction

Atmospheric deposition of mercury (Hg), a potent neurotoxin, enters remote ecosystems primarily through atmospheric deposition (Fitzgerald et al., 1998; Mason and Sheu, 2002). Terrestrial ecosystems serve as important receptors of Hg and as sources of Hg to aquatic systems (Lorey and Driscoll, 1999; Harris et al., 2007), and present large storage pools for atmospheric Hg depositions which accumulate in surface litter and soil pools (Grigal, 2003). There are several important deposition pathways for atmospheric Hg, including wet deposition resulting from uptake of reactive gaseous Hg and precipitation scavenging of particulates (Lindberg et al., 1992), plus dry deposition of gaseous elemental, reactive gaseous, and particulate-bound Hg (Zhang et al., 2009; Fu et al., 2010). Vegetation also plays an important role in deposition of atmospheric Hg (Lindberg, 1996; Grigal, 2003; Driscoll et al., 2007), both through uptake of atmospheric Hg to leaves and other plant tissues and consecutive input as plant detritus (e.g., litterfall deposition), plus by wash-off of Hg previously deposited on plant surfaces (i.e., throughfall deposition). A series of field investigations have shown that litterfall alone accounts for 30 to 60 % of total atmospheric Hg inputs in forests (Schwesig and Matzner, 2000; St. Louis et al., 2001; Rea et al., 2002; Sheehan et al., 2006; Demers et al., 2007) and that leaf litterfall inputs often exceed direct wet deposition inputs by a factor of two or more (Iverfeldt, 1991; Lindberg, 1996; Grigal et al., 2000; St. Louis et al., 2001). Laboratory studies confirm that the main source of Hg in aboveground biomass is from atmospheric uptake (Ericksen et al., 2003; Frescholtz et al., 2003; Millhollen et al., 2006a, b; Rutter et al., 2011). Field studies show uptake of atmospheric gaseous Hg during peak vegetation periods, particularly when leaf areas are at maximum expansion (Obrist et al., 2006; Fritsche et al., 2008b). Uptake of Hg by vegetation may occur both through stomatal processes (Ericksen et al., 2003; Stamenkovic and Gustin, 2009; Rutter et al., 2011) and non-stomatal sorption to plant surfaces (Rea et al., 2000; Stamenkovic and Gustin, 2009).

There are many open questions about the fate and dynamics of Hg bound to leaves and other plant tissues once tissues are exposed in the environment as litter and in the form of soil organic carbon (C), particularly in regards to potential emission or re-emission fluxes to the atmosphere. Since Hg in litter and soils is strongly bound to organic matter (Aastrup et al., 1991; Meili, 1991; Grigal, 2003; Obrist et al., 2009), its behavior and mobility is also associated with the dynamics of C (Mierle and Ingram, 1991; Johansson and Iverfeldt, 1994; Joslin, 1994; Driscoll et al., 1995; Lee et al., 1998; Kolka et al., 1999; Grigal, 2002). Organic C also is subject to mineralization, however, and a hypothesized fate of Hg contained in organic C includes release from the matrix as C decomposes (Grigal, 2003; Obrist, 2007). A few recent studies indicate correlations between CO_2 and Hg^0 emission fluxes from soils, indicative of some gaseous losses of Hg in volatile form upon C mineralization (Wickland et al., 2006; Fritsche et al., 2008a; Obrist et al., 2010), and it has been proposed that Hg losses from soils may be in the range of a few percent of total Hg originally bound to organic C fractions (Obrist et al., 2010).

Exposed surface litter and organic C pools in the field strongly bind atmospheric Hg deposition, thereby reducing input and transfer of atmospheric Hg deposition to water bodies (Harris et al., 2007; Graydon et al., 2009). As a result, field observations generally show strong Hg enhancement in surface litter and soil organic C fractions, greatly exceeding Hg concentrations of the original plant detritus inputs (Lindberg and Harris, 1974; Nater and Grigal, 1992; Hall and St. Louis, 2004; Demers et al., 2007; Tsui et al., 2008; Obrist et al., 2011). Continued sorption of atmospheric Hg to litter and soil organic C pools in the field, however, complicates the study of fate of Hg associated with litter and soil organic C, as newly sorbed Hg is difficult to separate from Hg originally associated with plant tissues.

Our goal was to address the fate of Hg originally bound to forest litter during decomposition under tightly controlled environmental conditions in which we minimized additional Hg sorption from the atmosphere and from other sources. A set of 25 litter samples each of four different forest litter types were incubated for time periods of 0, 3, 6, 12, and 18 months. After each period, litter was harvested and analyzed for total Hg, soluble Hg, C, N, and dry mass to assess concentration changes and respective mass losses through time. In a field control component, the same litter samples were exposed in surface litter horizons at respective collection sites using litter bags for a period of 12 months. The hypotheses of this study were that (1) during laboratory decomposition, Hg associated with forest floor litter is subject to gaseous losses as evident by a mass loss of Hg through time; (2) dry mass and C mass of litter are preferentially lost compared to Hg mass, resulting in an increase in Hg concentrations and Hg/C ratio through time; (3) Hg concentration and Hg/C ratio of field control samples will be higher after one year of decomposition compared to samples exposed in the laboratory, re-

flecting additional sorption of Hg in the field (e.g., from atmospheric deposition) ; and (4) Hg bound to litter also may be subject to mobilization in soluble form during decomposition.

2 Materials and methods

2.1 Litter collection

We collected fresh surface litter from Oi litter horizons from four different US forest sites: a mixed deciduous forest near Bartlett, New Hampshire; an aspen stand near Reno, Nevada; a pine forest in the Sierra Nevada Mountains near Georgetown, California; and a blue oak forest in the Sierra Nevada foothills near Marysville, California. We will refer to these four different litter types as species throughout the text. The deciduous forest in Bartlett is located at 44°03′ N, and 71°17′ W, at an elevation of 94 m, with annual precipitation of 1270 mm and mean annual temperature of 4.5 °C. Dominant tree species comprising surface litter at the Bartlett site are American beech *(Fagus grandifolia)*, yellow birch *(Betula alleghaniensis)*, sugar maple *(Acer saccharum)*, and eastern hemlock *(Tsuga Canadensis)*. The aspen stand near Reno, located at a latitude of 39°23′ N, longitude of 119°50′ W, and at an elevation of 1821 m, shows 241 mm of annual precipitation and a mean annual temperature of 10.5 °C. The dominant aspen species here is *Populus tremuloides*. The pine forest near Georgetown, California, is located at 38°54′ N and 120°39′ W, at an elevation of 1302 m, and experiences annual precipitation averaging 1660 mm and a mean annual temperature of 13.7 °C. Dominant tree species include ponderosa pine *(Pinus ponderosa)* and sugar pine *(Pinus lambertiana)*, with lesser contributions of white fir *(Abies concolor)*, incense cedar *(Calocedrus decurrens)*, Douglas fir *(Pseudotsuga menziesii)*, and California black oak *(Quercus kelloggii)*. The oak forest in California, dominated by blue oak *(Quercus douglasii)*, is situated at 39°15′ N, and 121°17′ W, is at an elevation of 193 m and shows annual precipitation of 775 mm and a mean annual temperature of 16.9 °C. Other species on the site include interior live oak, *(Q. wislizenii)* and foothill pine *(Pinus sabiniana)*.

All sites are considered remote locations not affected by known, specific point sources of Hg. All litter samples were collected within days to a few weeks after the occurrence of leaf litterfall in late summer and fall of 2008. Litter samples were comprised predominantly of leaves from the dominant tree species, with smaller contributions from other trees and from understory vegetation. Woody litter components, which were a minor part of surface litter, were removed from samples in order to facilitate comparison of Hg patterns in foliar litter across the four sites, and the remaining leaf litter was mixed well (but not crushed) prior to use in the laboratory and field decomposition studies.

2.2 Controlled laboratory incubation study

For the controlled laboratory incubation study, we prepared 100 glass jars of 960 ml volume (wide-mouth, clear USP Type III soda-lime glass with PTFE-lined lids). All glass jars were cleaned with chelating soap and dilute nitric acid (5 %), dried, and weighed. A 2.7 cm diameter hole was drilled in the lids of the jars and covered with a Teflon® filter membrane (pore size 0.2 μm). This allowed air exchange between the jars and the atmosphere, and, at the same time, avoided deposition of dust (including particulate-bound Hg) and likely minimized any transfer and deposition of reactive gaseous Hg to jars. Each of 25 glass jars was filled with homogenized litter samples from the four sites, with an initial starting weight (fresh mass) of 30 g of litter (15 g for blue oak litter). Immediately after sample preparation, litter from the first five of the 25 replicate jars was harvested for determination of dry mass and initial C, N, and Hg concentrations (i.e., time: $t = 0$ month). The 20 remaining jars of each species were placed in an environmentally-controlled chamber at the Desert Research Institute (EcoPODS) at a constant temperature of 25 °C throughout the experiment. Walls and the ceiling of the chamber were covered by black cloth to allow decomposition under dark conditions. Five replicate glass jars from each species were harvested after 3, 6, 12, and 18 months of incubation (i.e., 4 species × 5 harvest times × 5 replications = 100 incubation samples total), and analyzed for dry mass, C, N, and Hg concentration as described below. Litter samples were kept moist by additions of ultra-purified Millipore water (15 ml each) every three weeks. We assured that during harvest, all material from the jars were carefully removed, including small litter fractions that were washed to the bottom of the incubation jars.

We calculated total mass of the respective elements through time. Harvested litter samples also were used for determination of Hg solubility: ultra-purified Millipore water (500 g) was added to half of the harvested litter samples, and after one hour of exposure in water, 26.5 ml aliquots of solution were extracted for measurement of soluble Hg. Aliquots were filtered with 0.45 μm pore size filters (PTFE membrane; PP housing), preserved by adding 1 % concentrated hydrochloric acid, and stored at 5 °C until analysis.

2.3 Field study

We conducted a field component using the same litter species to assess changes of Hg, C, and N concentrations plus their stoichiometric relationships after one year of decomposition. Samples for field decomposition were packed in mash bags made from nylon screen. All bags were washed prior to use with a chelating soap bath for 48 h and were tested for Hg concentrations, which averaged $15.0 \pm 7.0\,\mu g\,Hg\,kg^{-1}$. Hence, mash Hg concentrations were lower than all litter concentrations observed (see results), and hence litter bags were unlikely a significant source of Hg to litter in the field.

We measured litter concentrations of C, N, and Hg prior to field exposure. Litter bags were exposed in the field for one full year through placement in the surface Oi litter horizons of the respective collection sites. Hg, C, and N concentrations were re-measured after collection to assess concentration changes. Mass balances of litter bags were not quantified in the field study due to potential losses of small litter fractions from bags during field exposure and transport. It is important to note that environmental conditions at the field sites differed from those of the controlled laboratory incubation study, including temperatures, rainfall patterns, relative humidities, and solar radiation exposures.

2.4 Sample analyses for C, N, total Hg, and soluble Hg

Upon harvests, litter samples were freeze dried using a freeze dryer (Model Micro Modulyo-115, Thermo Scientific, Waltham, MA, USA) for 48 h. After freeze drying, dry weights of each litter sample contained in glass jars were determined. Half of the well-homogenized litter samples were then milled using stainless steel coffee mills and kept frozen until analysis, while the other portions were used for determination of soluble Hg. Milled samples were analyzed for total Hg using a Model MA-2000 Total Mercury Analyzer (Nippon Inc., Takatsuki, Japan) according to US EPA Method 7473. The analyzer was calibrated using 0.1 ppm and 0.01 ppm Hg stock solutions made from 1000 ppm $HgCl_2$ standard in 0.001 % L-cysteine solution according to the manufacturer guidelines. National Institute of Standards and Technology (NIST) solid standard reference materials (# 1575: Pine leaves: $39.9\,\mu g\,Hg\,kg^{-1}$; and # 1515: Apple Leaves: $44.4\,\mu g\,Hg\,kg^{-1}$) were measured at the beginning of each analytical run and repeated after every six samples. When analysis of NIST standards deviated more than 5 % from their values, the analyzer was recalibrated and all samples were re-run. Across all sample analyses, NIST standard samples averaged $39.7 \pm 1.2\,\mu g\,Hg\,kg^{-1}$ (mean ± standard deviation; $n = 27$; 99 % recovery) for pine leaves, and $44.8 \pm 0.9\,\mu g\,Hg\,kg^{-1}$ (mean ± standard deviation; $n = 41$; 101 % recovery) for apple leaves. All samples were analyzed in duplicates, and analyses were repeated when the coefficient of variability of samples exceeded 10 %. Total C and N in litter samples were analyzed using a Leco Turspec carbon/nitrogen analyzer (LECO, St. Joseph, Michigan, USA) at the Soil Forage and Water Analysis Laboratory at Oklahoma State University (http://www.soiltesting.okstate.edu/), which guarantees accuracy and precision of test results through daily analysis of quality control samples. All instruments used for analysis were calibrated with certified standards and maintained in accordance with specification. Using standards every 10 samples, specific quality control for C/N analysis included frequent blank test and sample checks.

Water samples for determination of soluble Hg were analyzed according to US EPA Method 1631 for Total Mercury

Table 1. Dry mass, C mass, C concentration, Hg concentration, Hg mass, Hg/C ratio, N mass, N concentration, C/N ratio, and Hg/N ratio of laboratory samples.

Time in months	Dry mass (g)				C mass (g)				C concentration (%)			
	Mixed deciduous	Aspen	Pine	Oak	Mixed deciduous	Aspen	Pine	Oak	Mixed deciduous	Aspen	Pine	Oak
0	24.1±0.4	23.9±0.3	21.3±0.6	11.1±1.2	11.7±0.3	11.3±1.0	10.8±0.3	5.3±0.6	48.6±0.7	47.3±0.5	50.8±0.5	47.9±0.1
3	22.2±0.5	22.5±0.9	20.9±0.4	10.6±1.1	11.0±0.1	10.2±0.4	10.6±0.3	5.1±0.6	49.7±0.5	45.5±0.8	50.7±0.4	48.2±0.6
6	21.8±0.5	21.3±0.4	20.6±0.4	10.4±1.2	10.9±0.2	10.2±0.2	9.3±0.2	4.4±0.5	50.3±0.4	47.7±0.2	45.0±0.5	42.5±0.6
12	19.9±0.5	16.8±1.0	19.9±0.5	9.5±0.6	9.5±0.2	7.7±0.5	9.7±0.2	4.4±0.3	47.7±0.4	45.7±0.3	48.9±0.3	46.2±0.4
18	19.4±0.3	16.4±0.9	19.7±0.6	8.6±0.7	9.6±0.2	7.5±0.5	10.1±0.3	4.1±0.3	49.6±0.4	45.9±0.6	51.3±0.5	47.4±0.8

Time in months	Hg concentration ($\mu g\,kg^{-1}$)				Hg mass (ng)				Hg/C ratio ($\mu g\,kg^{-1}$ C)			
	Mixed deciduous	Aspen	Pine	Oak	Mixed deciduous	Aspen	Pine	Oak	Mixed deciduous	Aspen	Pine	Oak
0	32.4±4.2	50.2±1.6	39.3±2.5	40.7±1.5	782±97	1198±30	834±57	452±48	66.8±8.9	106.1±3.3	77.4±5.6	84.9±3.3
3	35.5±1.7	54.6±1.5	37.9±3.0	40.8±1.2	788±53	1228±52	792±61	430±37	71.5±4.0	119.9±5.0	74.8±6.3	84.8±2.6
6	35.0±3.4	55.1±2.9	38.4±2.3	36.1±1.8	764±71	1174±44	790±46	378±55	69.7±7.3	115.6±6.3	85.3±5.0	84.9±3.9
12	34.9±2.1	61.8±3.1	37.9±1.8	39.0±2.7	700±62	1036±52	754±42	372±24	73.2±5.0	135.3±7.4	77.5±3.7	84.4±5.2
18	35.5±1.6	62.1±5.0	40.3±3.8	40.3±3.8	690±26	1016±31	792±84	348±36	71.7±3.5	135.6±12.2	78.6±7.5	84.9±9.0

Time in months	N mass (g)				N concentration (%)				C/N ratio			
	Mixed deciduous	Aspen	Pine	Oak	Mixed deciduous	Aspen	Pine	Oak	Mixed deciduous	Aspen	Pine	Oak
0	0.13±0.01	0.16±0.013	0.09±0.01	0.09±0.01	0.56±0.05	0.67±0.06	0.45±0.03	0.81±0.05	87.8±8.7	70.6±5.7	113.3±6.7	59.2±3.4
3	0.14±0.01	0.17±0.013	0.08±0.01	0.09±0.01	0.64±0.03	0.74±0.04	0.39±0.03	0.83±0.09	77.6±4.4	62.1±4.5	130.8±8.8	58.7±6.9
6	0.12±0.01	0.16±0.012	0.08±0.01	0.08±0.01	0.56±0.04	0.77±0.07	0.41±0.05	0.80±0.05	89.4±7.7	62.4±5.2	111.2±13.8	53.0±4.1
12	0.13±0.02	0.17±0.012	0.09±0.00	0.08±0.01	0.65±0.06	1.00±0.09	0.43±0.02	0.86±0.06	73.8±6.5	45.9±3.9	114.4±5.3	54.1±3.5
18	0.21±0.01	0.23±0.01	0.16±0.01	0.12±0.02	1.07±0.03	1.40±0.12	0.83±0.05	1.35±0.19	46.2±1.4	33.2±3.0	61.8±3.3	35.9±5.8

Time in months	Hg/N ratio ($\mu g\,kg^{-1}$ N)			
	Mixed deciduous	Aspen	Pine	Oak
0	5809±378	7481±592	8754±701	5027±335
3	5542±340	7434±364	9749±582	4963±464
6	6195±383	7188±168	9434±632	4498±348
12	5386±337	6193±215	8850±375	4552±307
18	3313±185	4475±187	4836±220	3019±334

in Water using dual stage gold pre-concentration. We used a Tekran 2600 Mercury Analyzer (Tekran Inc., Toronto, Canada). Bromine monochloride (0.5 % BrCl) was added to each sample 12 h prior to analysis for sample digestion. Immediately prior to sample analysis, we added 0.25 % hydroxylamine hydrochloride (HH) to samples to ensure full destruction of the free halogens. We used a 3 % solution of freshly prepared stannous chloride, purged with a slow flow of ultra-high purity (UHP) argon at $20\,ml\,min^{-1}$, to reduce Hg in samples to gaseous Hg, which was separated by a liquid-gas separator and loaded on gold traps of the analyzer. After thermal desorption, Hg was analyzed using atomic fluorescence spectroscopy. The analyzer was calibrated with standards of 0.5, 5, 10, 25, and 50 ppt of Hg in solution of 0.5 % BrCl, and 0.25 % HH. Quality control included three calibration blanks (consisting of 0.5 % BrCl and 0.25 % HH reagent), Ongoing Precision and Recovery (OPR) of 5 ppt Hg after every six samples (average recovery 97±9 %; $n = 21$), and matrix spikes of at least two samples per analytical run. Detection limit of the system was estimated at <0.5 ppt, based on 3× standard deviation of the reagent blanks.

2.5 Statistical analyses

All numbers in text, figures, and tables (Table 1) are shown as mean ± 1 standard deviation of five replicate samples for the laboratory study, and mean ± 1 standard deviation of 15 replicate samples for the field study. Statistical analyses of laboratory samples (Table 2) were performed using analysis of variance (ANOVA) and Bonferroni post-hoc comparison tests to analyze for statistical effects of variables: *Time*, *Species*, and *Time × Species* interactions. Dependent variables tested were dry mass, C mass, C concentrations, Hg mass, Hg concentrations, Hg/C ratio, C/N ratios, and total soluble Hg (per unit dry mass). We performed Bonferroni post-hoc tests when the significant *Time × Species* interactions indicated different time trends among species to assess which of the species showed statistical changes. For field litter samples, paired Student t-tests were performed to assess differences in Hg concentrations, Hg/C ratios, and C/N ratios prior to and after exposure. Linear regression analyses were performed to assess the relationships of Hg concentrations and respective C/N ratios (Fig. 3). All statistical tests were performed with STATA Version 9 (Stata Corporation,

Table 2. Results of statistical Analysis Of Variance (ANOVA) and Bonferroni post-hoc tests to test for effects of incubation time (continuous variable), species (categorical variable), and interactions for the dependent variables: dry mass, Hg mass, Hg concentration, Hg/C ratio, C mass, C concentration, C/N ratio, N mass, N concentration, and soluble Hg.

		Dependent Variables							
		Dry mass (g)	Hg mass (ng)	Hg concentration ($\mu g\,kg^{-1}$)	Hg/C ratio	C mass (g)	C concentration (%)	C/N ratio	Soluble Hg ($ng\,g^{-1}$ dry mass)
ANOVA tests	*Variable Time*	$DF=1, P<0.01$	$DF=1, P<0.01$	$DF=1, P<0.01$	$DF=1, P<0.01$	$DF=1, P<0.01$	$DF=1, P=0.64$	$DF=1, P<0.01$	$DF=1, P<0.01$
	Variable Species	$DF=3, P<0.01$	$DF=3, P<0.01$	$DF=3, P<0.01$	$DF=3, P<0.01$	$DF=3, P<0.01$	$DF=3, P<0.01$	$DF=3, P<0.01$	$DF=3, P<0.01$
	Interaction Time × Species	$DF=3, P<0.01$	$DF=3, P<0.01$	$DF=3, P<0.01$	$DF=3, P<0.01$	$DF=3, P<0.01$	$DF=3, P=0.64$	$DF=3, P<0.01$	$DF=3, P<0.01$
Bonferroni tests	*Significant effect of Time in*	Mixed Deciduous Aspen Pine Oak	Mixed Deciduous Aspen Oak*	Aspen	Aspen	Mixed Deciduous Aspen Pine Oak	N/A	Mixed Deciduous Aspen Pine Oak	Mixed Deciduous Aspen Oak

* Significant post-hoc test at significance level = 0.10, but not at 0.05.

College Station, Texas, USA). We considered statistically significant effects when *P*-values were lower than 0.05.

3 Results

### 3.1 Laboratory decomposition study: Hg, C, and N concentration and mass changes

At the start of the experiment, initial litter dry mass across all jars were 24.1 ± 0.4 g in mixed deciduous litter, 23.9 ± 0.3 g in aspen litter, 21.3 ± 0.6 g in pine needle litter, and 11.1 ± 1.2 g in oak leaves (Fig. 1; Table 1). In all four litter species, changes in dry mass showed relatively consistent temporal trends with increasing time of incubation. Pine needle litter showed small mass losses with each subsequent time interval, averaging 2, 3, 7, and 8 % loss of the initial (i.e., 0 month) dry mass after 3, 6, 12, and 18 months of incubation, respectively. All other litter types showed more substantial mass losses with time: dry mass decreased by 8, 10, 17, and 19 % in mixed deciduous litter and by 6, 11, 30, and 31 % in aspen litter. We also observed similar mass reductions in oak litter accounting for 5, 7, 15, and 22 % loss of initial mass. ANOVA tests (Table 2) including data of all litter species showed significant effects of *Time*, *Species*, and *Time × Species* interactions on dry mass, indicative of significant mass losses in time across all samples. Bonferroni post-hoc tests following the ANOVA showed that a significant effect of *Time* was evident in all four litter species.

Associated with dry mass losses, we observed C mass losses (Fig. 1; Table 1) with increasing time of incubation, and C mass losses were in a similar range as those observed for dry mass. Mass losses of C, however, were less consistent in time, likely due to sample variability of C analyses. Similar to dry mass, ANOVA tests showed significant effects of *Time*, *Species*, and *Time × Species* interactions on C mass across all litter samples, and Bonferroni post-hoc tests also showed that the significant effect of *Time* occurred in all four litter species.

The similar behavior of dry mass and C mass losses was due to relatively constant C concentrations in time (Fig. 1; Table 1). Small, inconsistent, and not statistically significant changes in C concentrations by the end of the experiment (after 18 months) included an increase of 2 % and 1 % in mixed deciduous and pine litter as well as a decrease by 3 % and 1 % in aspen and oak litter. ANOVA tests on C concentrations showed a significant effect of *Species*, but no significant effect of *Time*.

Initial Hg concentrations (i.e., 0 month; Fig. 2; Table 1) in litter samples averaged $32.4 \pm 4.2\,\mu g\,kg^{-1}$ in mixed deciduous litter, $50.2 \pm 1.6\,\mu g\,kg^{-1}$ in aspen litter, $39.3 \pm 2.5\,\mu g\,kg^{-1}$ in pine litter, and $40.7 \pm 1.5\,\mu g\,kg^{-1}$ in oak litter. Using all data, ANOVA tests showed statistically significant effects of *Time*, *Species*, and *Time × Species* interaction on Hg concentration. Changes in Hg concentrations, however, were highly species-specific: Bonferroni post-hoc tests showed that the *Time* effect was driven solely by one species, aspen litter, which showed a strong increase in Hg concentration through time. All other species showed no significant *Time* effects on Hg concentrations using Bonferroni post-hoc tests. Hg concentration in aspen litter increased by 24 % after 18 months of incubation, but Hg concentrations remained within 1 to 10 % of the original concentrations for the other three species.

Total Hg mass contained in incubation jars (Fig. 2; Table 1), calculated by multiplication of Hg concentrations by dry mass, averaged 782 ± 97 ng, 1198 ± 30 ng, 834 ± 57 ng, and 452 ± 48 ng at the start of the experiment for mixed deciduous, aspen, pine, and oak litter, respectively. After 18 months of incubation, Hg mass was reduced by 92 ng, 182 ng, 42 ng, and 104 ng in mixed deciduous, aspen, pine, and oak litter, respectively. These Hg mass losses accounted for 5 to 23 % of the initial Hg mass present at the start of the incubation. ANOVA tests including all data showed significant effects of *Time*, *Species*, and *Time × Species* interactions, indicative of significant mass losses of Hg across all litter samples. Hg mass losses were species-specific, and Bonferroni post-hoc tests showed that the significant effect of *Time* was driven by significant Hg mass losses in mixed
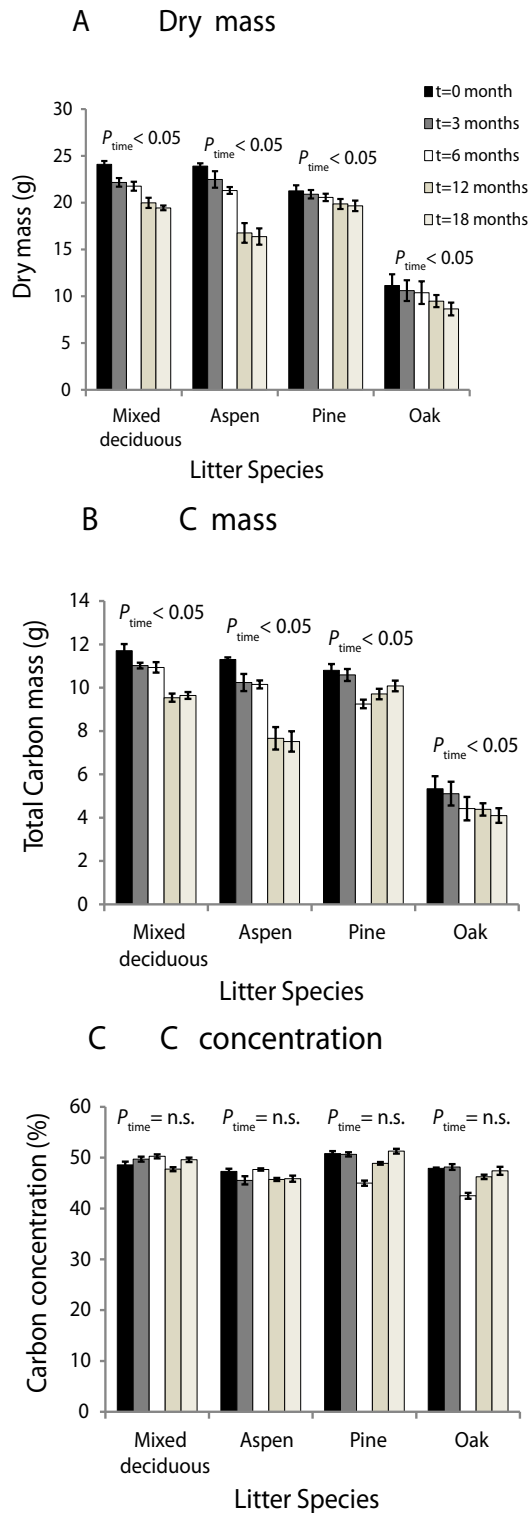
Fig. 1. Development of dry mass, carbon (C) mass, and C concentrations throughout 18 months of litter decomposition in a controlled laboratory study. Bars represent means ± standard deviations of five replicate samples. *P*-values are effects of *Time* for individual species based on Bonferroni post-hoc analyses (Table 2).

deciduous litter, aspen litter, and to a smaller degree in oak litter (at the 10 % significance level). No *Time* effect, based on Bonferroni post-hoc tests, was observed for Hg mass in pine litter.

3.2 Stoichiometric relationships between Hg, C, and N

Hg/C ratios showed only minor changes during the 18 months of laboratory decomposition in most litter species (Fig. 2; Table 1). Overall, ANOVA tests showed significant effects of *Time*, *Species*, and *Time × Species* interaction on Hg/C ratios. As with Hg concentrations, the significant increase in Hg/C ratios, however, was driven entirely by aspen as indicated by Bonferroni post-hoc tests, while no significant *Time* effect was evident for the other three litter species. In aspen, Hg/C ratios increased from $106.1 \pm 3.3\,\mu g\,kg^{-1}C$ at the start of the experiment to $135.6 \pm 12.2\,\mu g\,kg^{-1}$ C at the end of the experiment.

In regards to C/N ratios, ANOVA tests showed significant effects of *Time*, *Species*, and *Time × Species* interaction, in support of decreases in C/N ratios in time across all laboratory samples. Post-hoc Bonferroni tests showed that the *Time* effects were significant in all four litter species, although occurring to various degrees. Regression analyses between Hg concentrations and C/N ratios in laboratory samples (Fig. 3c) showed significant increase in Hg concentrations with decreasing C/N ratios in aspen and pine litter samples (significant negative slope of linear regression; $r^2 = 0.77$ and $r^2 = 0.22$, respectively), while the two other litter species showed no significant regression slopes.

3.3 Field litter decomposition patterns

Paired Student t-tests of Hg concentrations of samples prior to and after exposure for one full year in the field showed that Hg concentration increased significantly across all species. When each species was analyzed independently, three of four showed significant Hg concentration increases after field exposure, and only in pine litter was the effect not statistically significant. Increases in Hg concentrations during the one-year field exposure (i.e., from time $t = 0$ month to time $t = 12$ months, Fig. 3a) accounted for $23\,\mu g\,kg^{-1}$ in mixed deciduous (+67 %), $15\,\mu g\,kg^{-1}$ in aspen (+28 %), and $21\,\mu g\,kg^{-1}$ in oak (+62 %) compared to concentrations of the samples prior to the field exposure. Final concentrations of Hg in the field (i.e., after one year of exposure) were higher in all litter types compared to the concentrations after laboratory exposure for one year (+64 % in mixed deciduous, +62 % in oak, +10 % in aspen, and +8 % in pine). However, given that field decomposition likely proceeded at different rates than decomposition in the laboratory, we analyzed Hg concentrations as a function of C/N ratios to standardize Hg concentrations to the degree of decomposition. C/N ratios can be used as a proxy for the degree of litter decomposition with generally decreasing C/N ratios with increasing stage of decomposition
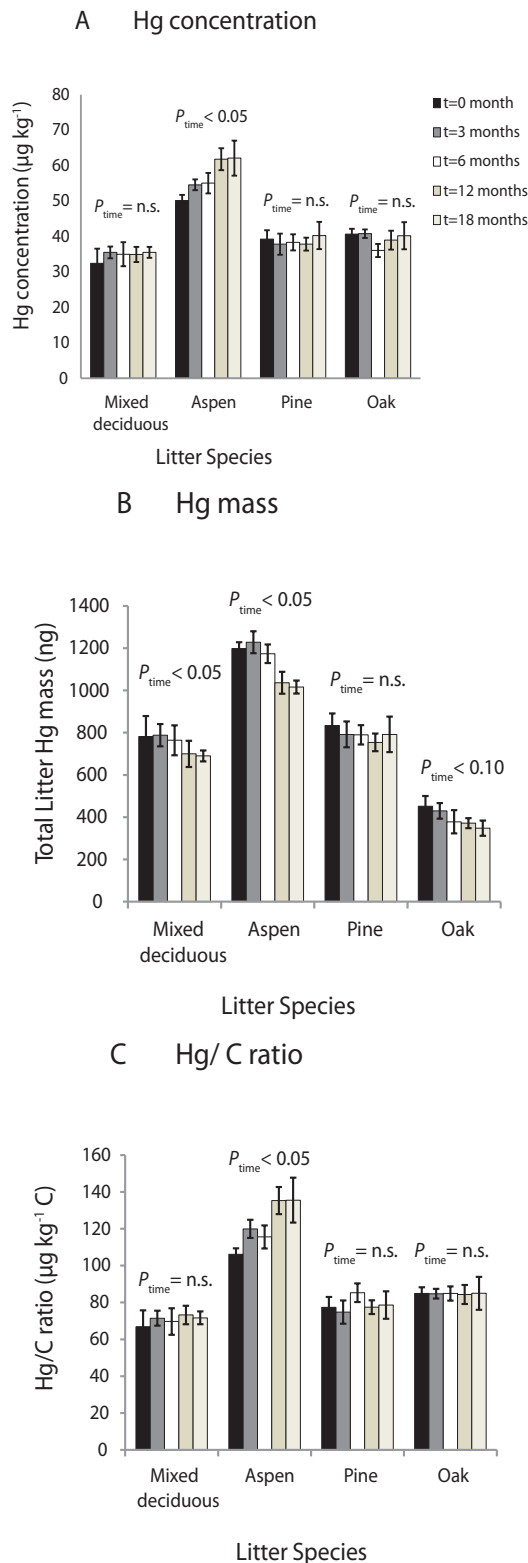
Fig. 2. Development of Hg concentration, Hg mass, and Hg/C ratio throughout the 18 months of litter decomposition in the controlled laboratory study. Bars represent means ± standard deviations of five replicate samples. *P*-values are effects of *Time* for individual species based on Bonferroni post-hoc analyses (Table 2).

(see discussion below). Figure 3c shows that for field samples of mixed deciduous and oak litter, Hg concentrations fall above the regression line between Hg concentrations and C/N ratios of laboratory samples, indicating that even when adjusted for differences in decomposition rates (i.e., C/N ratios), field samples show enhanced Hg levels compared to laboratory samples. However, in aspen and pine litter, data points for field and laboratory samples follow a similar regression line between Hg and C/N ratios.

As with Hg concentrations, Hg/C ratios of field samples were significantly enriched after field exposure (Fig. 3b), and individual analysis showed that the increase was significant in all species but pine. C/N levels decreased significantly during exposure in the field in all litter species, with the strongest decrease observed in mixed deciduous, aspen, pine, and to a lesser degree in oak. C/N ratios of field samples after 12 months of exposure were significantly lower than C/N ratios observed in laboratory samples after 12 months of exposure, with field C/N ratios decreased by 23 to 42 % compared to those exposed in the laboratory (Fig. 3c; Table 1).

3.4 Solubility of Hg in decomposing litter

Concentrations of soluble Hg – measured during one-hour exposure of half the harvested samples to 500 ml of Hg-free water and standardized to the amount of dry mass – were highly variable across different litter species (Fig. 4). For example, the initial amount of soluble Hg per unit of dry litter mass accounted for 0.22 ± 0.02 ng g^{-1} in oak litter, but only for 0.07 ± 0.01 ng g^{-1} in pine litter. The amount of soluble Hg generally decreased in all species throughout the experiment (Fig. 4). After 18 months, concentrations of soluble Hg were negligible and mainly below the detection limit of the analyzer ($\sim$0.5 ng l^{-1}, based on three times standard deviation of reagent blanks), except in mixed deciduous litter. Overall, ANOVA tests showed significant effects of *Time* and *Species* on soluble Hg per unit of dry litter mass (both when only samples above the detection limit were considered and when samples below the detection limit were considered as zero values; Table 2). ANOVA tests indicated no *Time* × *Species* interaction when only samples above the detection limits were considered, but indicated species-specific responses when all samples were considered (i.e., samples below detection limit set as zero), with Post-hoc Bonferroni tests showing significant *Time* effects in mixed deciduous, aspen, and oak litter, but not in pine litter (Table 2).

4 Discussion

4.1 Changes in dry mass as well as concentration and mass changes of C and N

Significant dry mass losses, with relatively consistent temporal decreases in all four litter species through time (Fig. 1), show that sampling replications and time of exposure (i.e.,
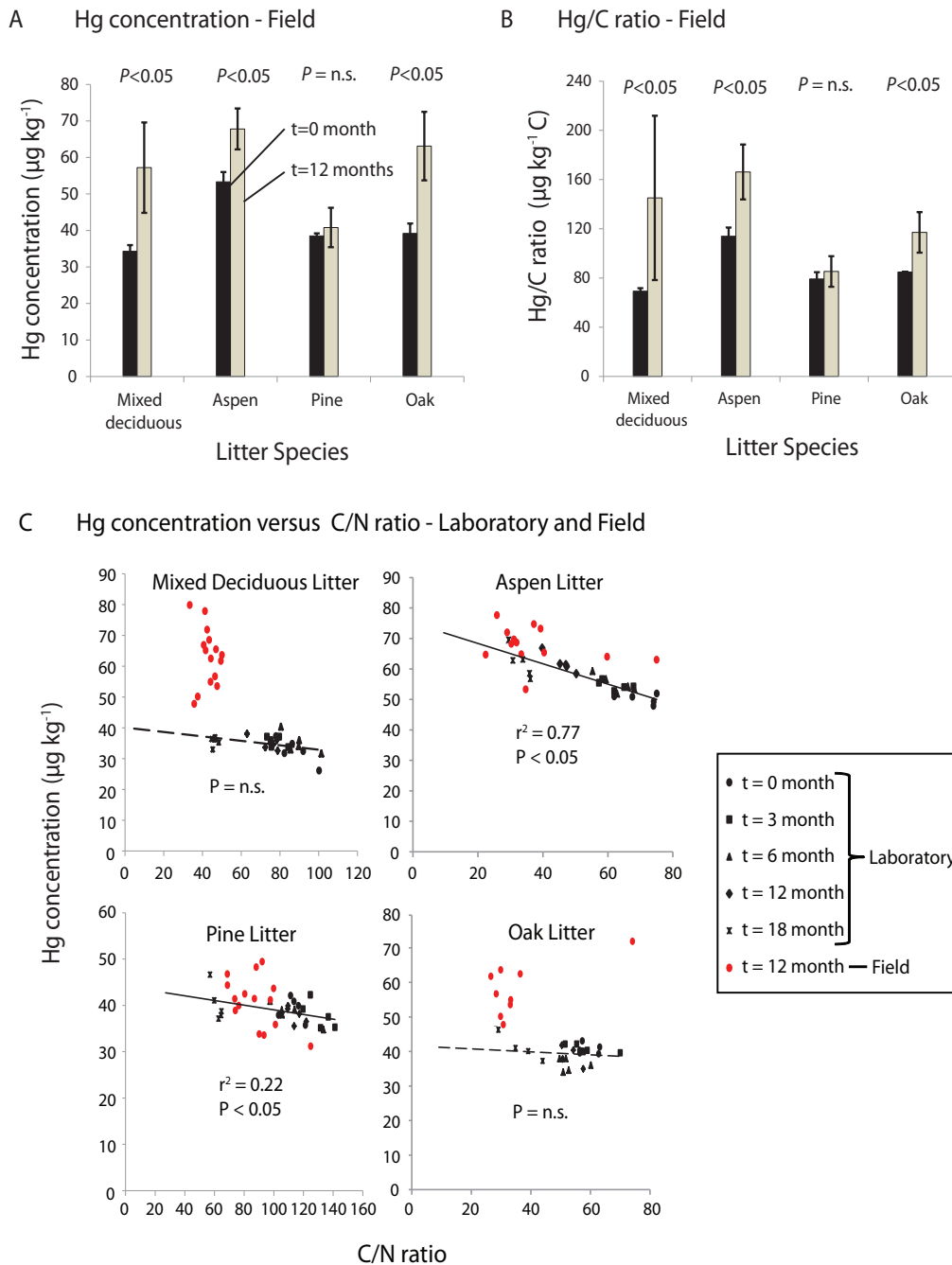
Fig. 3. (A): Hg concentrations of field samples prior to ($t = 0$ month) and after ($t = 12$ months) one year of exposure in the field. Bars represent means $\pm$ standard deviations of 15 replicate samples. P-values are based on paired t-tests. **(B)**: same as panel A for Hg/C ratios. **(C)**: scatter plots of Hg concentration and C/N ratios of all litter samples in the laboratory decomposition study (black symbols). Samples at different harvest times are marked with different symbols. Regression line marks linear trendline (solid line when $P < 0.05$) between Hg and C/N ratios in laboratory samples. Red symbols are Hg concentrations, and C/N ratios of samples exposed in the field. In two species, points fall clearly above trendlines for laboratory samples.

18 months) yielded substantial and detectable mass losses during the laboratory incubation study. Rates of mass decreases were different among litter species, and aspen leaf litter showed the strongest dry mass decrease (31 % after

18 months) while pine litter showed only small losses (8 %). Many field studies have shown that different litter types are subject to different decomposition rates. For example, studies have shown that deciduous litter decomposed faster than

Soluble Hg
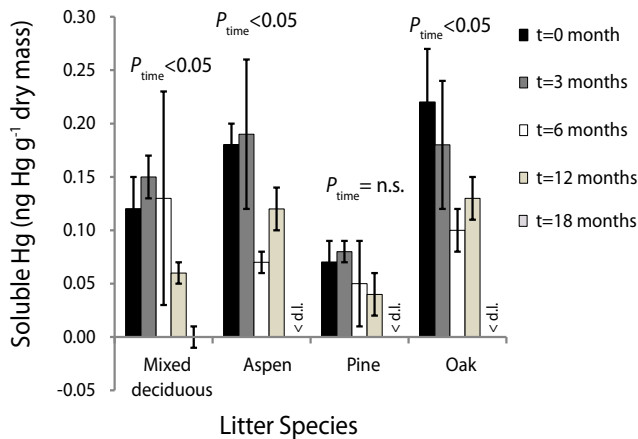
Fig. 4. Development of soluble Hg per unit dry mass throughout the 18 months of litter decomposition in the controlled laboratory study. Bars represent means ± standard deviations of five replicate samples. *P*-values are effects of *Time* for individual species based on Bonferroni post-hoc analyses (Table 2). <d.l. refers to values below the limit of detection.

coniferous litter (Kaneko and Salamanca, 1999; Hall and St. Louis, 2004), while others found the opposite (Demers et al., 2007). Some studies observed inconsistent trends or time-dependent trends, e.g., where initial differences between litter species disappeared during longer time periods (Moore et al., 1999; Sundarapandian and Swamy, 1999; Prescott et al., 2000). In general, these field studies showed higher mass losses (e.g., up to full mass loss after one year; Sundarapandian and Swamy, 1999) than we observed during our controlled laboratory study. Possible reasons for the slower decomposition rates in the laboratory study include an artificial environment without presence of underlying soil substrates, which may have reduced diversity and mass of microbial communities (Couteaux et al., 1995). Although we regularly watered samples every 2–3 weeks, the moisture conditions for mineralization (Horner et al., 1988) may have been unfavorable compared to a field environment as well. Associated with dry mass losses, we observed similar losses of C mass, although C mass losses were less consistent in time. C concentrations did not significantly change throughout the experiment, and remained within 97 to 102 % of the original C levels after 18 months of decomposition.

Lower C/N ratios in the field control samples (Fig. 3c) compared to laboratory samples after one year of decomposition suggest that litter samples experienced higher decomposition rates under field conditions than during laboratory incubation. C/N ratios reflect the degree of decomposition with high C/N ratios associated with fresh and undecomposed organic C, while lower C/N ratios are indicative of older and more decomposed fractions (Paul and Clark, 1989). In our

study, the highest C/N ratios were observed in pine litter. This is similar to other studies that reported higher C/N ratios of coniferous trees over deciduous (Finzi et al., 1998; Smolander et al., 2005), and may be linked to its correspondingly slow decomposition rate and low N availability. (Webster and Benfield, 1986; Bryant et al., 1998).

4.2 Concentration and mass changes of Hg plus stoichiometric relationships to C and N

Across all litter types, litter incubated under controlled laboratory conditions exhibited significant Hg mass losses through time (Fig. 2), with losses after 18 months ranging from 5 to 23 % of the initial Hg mass present at the start of the experiment. We ensured that all dry mass was harvested from sample jars and was well homogenized prior to analysis; even if small fractions of dry mass were lost during harvests, any losses would have been constant throughout the experiment (i.e., including at the initial harvest at time = 0 months) and hence would not likely explain mass losses in time. Hg losses were relatively consistent and linear in time. At the level of individual species (post-hoc test after ANOVA), significant mass losses were observed in the three deciduous species but were not significant in pine litter. The lack of mass loss in pine may be associated with its correspondingly slow rate of decomposition.

Because litter samples were kept in glass jars that only allowed mass losses by air exchange through a 0.2 μm Teflon® filter membrane in the lid, we attribute the observed Hg mass losses from litter to gaseous evasion to the atmosphere, most likely in elemental form. We originally hypothesized (Hypothesis 1) that C mass loss due to mineralization (as CO_2) would result in corresponding losses of Hg associated with organic C, and our experimental results are in support of this hypothesis. Percentage Hg mass losses, however, were generally smaller than observed dry mass and C losses; for example, Hg mass losses after 18 month were 12 %, 15 %, and 5 %, compared to dry mass losses of 19 %, 31 %, and 8 % (percentage loss of original mass). The percentage Hg mass lost per unit C loss in these three litter species was between 48 to 63 %. Only in oak litter did we observe almost identical mass losses of dry mass and Hg mass (i.e., 100 % Hg lost per dry mass loss). Differences among species indicate that ratios of Hg subject to evasion versus retention is species-specific, a notion also supported by observed Hg concentration changes in time: ANOVA results showed overall significant *Time* and *Time × Species* effects on Hg concentration, but post-hoc tests showed that the *Time* trend was driven by one litter species only (aspen) that showed a significant increase in Hg concentration (+24 % of the original concentration after 18 months). Hg concentrations of the other litter species remained close to starting levels (within 1 to 10 %). Aspen litter also showed the lowest fraction of Hg loss, consistent with a Hg concentration increase in time. We conclude that dry and C mass are preferentially lost over Hg

mass during decomposition in most species (in support of Hypothesis 2), but that losses can be similar in others (e.g., aspen).

Evaporation of gaseous Hg from soils and surface litter is considered an important source of Hg to the atmosphere; and many studies have quantified such emissions, in particular from soils, along with its controlling factors (Hanson et al., 1995; Carpi and Lindberg, 1997; Gustin et al., 1997; Poissant and Casimir, 1998; Engle et al., 2001; Zhang et al., 2001; Ericksen and Gustin, 2004; Xin and Gustin, 2007; Kuiken et al., 2008a, b). Only a few studies have performed corresponding measurements of both Hg^0 and CO_2 efflux rates in order to assess potential relationships between C mineralization and Hg emissions, and to quantify if and to what degree Hg emissions may be due to loss of the organic C matrix with which Hg is associated. Fritsche et al. (2008a) reported correlations between Hg^0 and CO_2 emissions from soils upon stimulation and inhibition of soil respiration using experimental treatments. Wickland et al. (2006) reported a correlation between in situ field soil respiration and Hg^0 emission rates in boreal forest soils. Previously, Rogers and Mc-Farlane (1979) reported declines in Hg^0 emissions following soil sterilization, albeit without directly measuring CO_2 respiration rates. Obrist et al. (2010) observed relationships between CO_2 and Hg^0 efflux rates in controlled laboratory studies and also showed that Hg/C ratios in surface emission only accounted for $\sim 3\%$ of the Hg/C ratio present in soils. They also showed that experimental treatments (such as implementation of anaerobic conditions) easily disrupted this CO_2-Hg^0 flux relationship. Significant Hg mass losses observed in the present laboratory study suggested that gaseous losses of Hg during decomposition potentially may be much larger in litter than relatively small Hg losses associated with mineralization in soils. We propose that a significant fraction of Hg associated with surface forest litter – ranging from 48% to full loss and depending on species – may be subject to evaporation losses once litter is subject to decomposition, at least under the conditions implemented in our controlled laboratory study.

Our observations of significant Hg mass losses, and relatively constant Hg concentrations and Hg/C ratios, during decomposition contrast observations made in the field, both from previous studies and our field control. Demers et al. (2007) observed that total litter Hg increased by 134% and 128% of its initial mass in deciduous and coniferous litter after two years of exposure in a mixed deciduous and coniferous forest, while at the same time litter dry mass decreased by 33% and 43%, respectively. Similarly, Hall and St. Louis (2004) reported that Hg mass in deciduous and coniferous litter exposed in forests increased by 147%, and 37% compared to initial Hg mass after the 798 days of decomposition in a boreal, upland forest, while dry mass declined by 57 to 46%, respectively. Hayes et al. (1998) showed no Hg mass change in spruce litter in the field during 2.5 yr of exposure, despite 20 to 40% dry mass losses.

Along with Hg mass increases, Hall and St. Louis (2004) observed Hg concentration increases during field exposure (151 to 474% after 798 days of field exposure), and Demers et al. (2007) observed Hg concentration increases of 109 to 127% after two years of field exposure. In our study, field control samples exposed at the respective sampling locations showed consistently higher Hg concentrations and higher Hg/C ratios after one year compared to levels observed prior to field exposure. Also, litter Hg concentrations were enhanced by 8 to +64% compared to samples incubated for the same time period in the laboratory (Fig. 3a). We graphed Hg concentrations versus respective C/N ratios (Fig. 3c) to quantify Hg concentration changes per unit change C/N ratio. As discussed above, we thereby use C/N ratios as a relative measure of the degree of decomposition, with higher C/N ratios representing less decomposed litter samples and lower C/N ratios indicative of more decomposed litter samples. We thereby can account for potentially different decomposition rates of field and laboratory samples and "standardize" Hg concentrations to the degree of decomposition. Results show that two species (mixed deciduous and oak litter) showed particularly pronounced Hg concentration enhancements in the field compared to the laboratory, as evident by data points above the linear trendline drawn for laboratory samples. In aspen litter, however, where we already observed Hg concentration enhancement in the laboratory, the regression line was similar between laboratory and field samples, and in pine litter we observed inconsistent and variable patterns.

The above patterns suggest pronounced sorption of additional Hg in litter exposed in the field (in support of Hypothesis 3), leading to over 60% concentration enhancements in the field compared to litter exposed in the laboratory where atmospheric Hg inputs were minimized by 0.2 µm Teflon® membranes covering litter jars and addition of Hg-free water. Our results, however, also indicate that Hg accumulation in the field may strongly dependent on litter types or on location of field exposure. We did not directly measure Hg deposition at the field sites, but National Atmospheric Deposition Program data indicate that wet deposition in the area of our field sites ranged between 4 to 6 µg Hg m^{-2} yr^{-1} (NADP, 2009). Additional Hg deposition can be expected in forest sites due to throughfall deposition (Iverfeldt, 1991; St. Louis et al., 2001; Lindberg, 1996) and dry deposition (Driscoll et al., 2007; Lyman et al., 2007; Selin et al., 2007). Previous litter studies have attributed increases in Hg concentrations in the field to significant sorption of Hg from the surrounding environment (e.g., Hall and St. Louis, 2004; Demers et al., 2007), although these studies have not looked at the potential for "internal" Hg accumulation due to preferential losses of C over Hg in decomposing litter. Our field and laboratory comparisons support the notion that sorption of Hg in field litter is the main reason for Hg accumulation in litter, although our results also suggest that preferential release of C over Hg leads to additional "internal" Hg accumulation in

some species. Further, it is possible that tissues in the field equilibrate Hg concentrations with those of the surrounding substrates: Hall and St. Louis (2004) observed that litter with initial Hg concentration of less than $30 \, \text{ng} \, \text{g}^{-1}$ showed increases in Hg concentration, while litter with Hg concentrations more than $30 \, \text{ng} \, \text{g}^{-1}$ generally showed a decrease compared to initial concentration. In our study, we did not find indication for such a "compensation" point. The notion of significant sorption of Hg in decomposing litter is in good agreement with many studies that report strong accumulation of Hg in litter and surface soil layers in the field (Mierle, 1990; Aastrup et al., 1991; Nater and Grigal, 1992; Munthe et al., 1998; Grigal, 2003; Friedli et al., 2007; Obrist et al., 2011).

It is important to note that artificial laboratory conditions also may have contributed to differences between laboratory and field litter samples, including different temperatures, solar radiation, humidities, and differences in watering (e.g., Millipore water versus rainwater, drying-wetting cycles). For example, laboratory samples were kept under darkness while litter samples in the field may have experienced light exposure. Laboratory samples hence may have been shielded from photoreduction processes (e.g., Graydon et al., 2008). This effect, however, actually should have decreased Hg levels of field-exposed litter. Light exposure may possibly only affect very top-surface leaves and may be important for short time periods (until burial by new leaves). Light exposure also may play a role in litter decomposition (e.g., through reduction in litter decomposition rate; Austin and Vivanco, 2006).

We observed pronounced differences in Hg accumulation patterns between the four litter species; for example, aspen litter showed Hg concentration increases both in the field and during laboratory exposure, while pine litter showed a lack of accumulation under both exposures. This may be caused by pine litter's low decomposition rate (note its slow mass loss in Fig. 1), possibly caused by relatively high C/N ratios as discussed above. Previous studies have shown strong links between Hg concentrations and organic matter degradation in soils and lake sediments (Grondin et al., 2005; Teisserenc et al., 2011). Obrist et al. (2011) observed increasing Hg accumulation in litter and soils from southern to northern latitudes using data of 14 forest sites, which they attribute in part to potentially slower decomposition rates – and hence longer exposure – of organic carbon pools in northern latitudes. Given that we only evaluated four litter types, it is not possible to assess if Hg accumulation patterns are specific to particular litter types (such as coniferous versus deciduous litter). Aside from C/N ratios, for example, litter species differ in many other biogeochemical processes (tanning and lignin contents, mineralization rates, microbial biomass, dissolved C and N dynamics; Finzi et al., 1998; Côté et al., 2000; Smolander et al., 2005), and such parameters could affect the capacity of litter to retain and sorb Hg.

4.3 Solubility of Hg in litter during decomposition

When harvested litter was submerged in water for quantification of Hg solubility, the amount of soluble Hg (filtered by $0.45 \, \mu\text{m}$ membrane) per litter dry mass strongly decreased in time. At the start of the experiment, soluble Hg averaged between 0.07 and $0.22 \, \text{ng} \, \text{Hg} \, \text{g}^{-1}$ dry mass, depending on species. This amount, although highly variable, decreased to close to detection limit (about $0.05 \, \text{ng} \, \text{Hg} \, \text{g}^{-1}$ dry mass) to $0.13 \, \text{ng} \, \text{Hg} \, \text{g}^{-1}$ dry mass after 12 months. After 18 months, most litter samples showed no soluble Hg concentrations above the detection limit anymore. These results indicate that the fraction of Hg available for mobilization as soluble Hg decreases with increasing time of decomposition.

Comparisons of these results with other studies are challenging since we are not aware of studies that addressed Hg solubility of variously decomposed litter substrates. In a controlled litter incubation study, Tsui et al. (2008) submerged forest litter samples in different stream water for 66 days and observed that soluble Hg (both total Hg and methylated Hg) in water samples increased significantly with time of exposure. The Tsui et al. study demonstrated that litter in streams and lakes decomposing under hypoxic conditions contribute Hg to water bodies and showed that the contributions are highly dependent on stream water chemistry. The experimental conditions between Tsui et al.'s study and ours, however, are not comparable – given that we decomposed litter under aerobic conditions and assessed Hg solubility at the time of harvests, while Tsui et al.'s study assessed the cumulative amount of soluble Hg released under anaerobic decomposition. In the field, Hall and St. Louis (2004) reported Hg concentration increases in tree litter submerged in flooded reservoirs whereby litter seemed to reach equilibrium conditions with the surrounding water. In sphagnum tissues, Heyes et al. (1998) and Hall and St. Louis (2004) reported Hg mass losses from litter submerged in wetland and flooded reservoirs, respectively.

Possible reasons for declines in soluble Hg release with increasing stage of decomposition include gaseous losses of Hg (see above) that may have depleted Hg that was initially present in soluble form. Other reasons include the possibility that decomposition may have led to increased surface area as well as increased presence of humic and fulvic substances, which may result in more efficient binding of Hg in decomposing litter fractions. Allard and Arsenie (1991) showed that humic and fulvic acids have strong sorption capacity for Hg, thereby reducing its mobility, and humic matter is known to play a major role in controlling solubility and mobilization of Hg in freshwater systems (Mierle and Ingram, 1991; Weber, 1993). Ericksen et al. (2003) showed that about 1.5 to 3 % of total Hg present in fresh leaves was water soluble and easily rinsed from the leaves. In our study, the fraction of soluble Hg, as a percentage of total Hg, only ranged between 0.2 and 0.6 % at the beginning of the experiment, and this further declined with time. Reasons for reduced solubility

in our study may include different tissue types, leaf age, and stage of decomposition (e.g., fresh leaves versus surface Oi litter), and that litter was subject to precipitation wash-off prior to collection in the field while leaves used by Ericksen et al. (2003) were grown in environmentally controlled growth chambers without experiencing rain.

5 Summary

The results of our laboratory incubation study showing substantial Hg mass losses in decomposing litter are important in regards to atmospheric emissions of Hg from terrestrial ecosystems. Such releases back into the atmosphere can be considered re-emission fluxes of Hg that was originally sorbed from the atmosphere and then deposited by leaf litterfall. The issue of re-emission processes is of high interest since thousands of tons of Hg are contained and stored in surface litter and surface soils (e.g., Grigal et al., 2003; Obrist, 2007), including substantial amounts of past anthropogenic emissions due to increased atmospheric Hg pollution during the last 150 yr (Fitzgerald et al., 1998; Schuster et al., 2002). Substantial re-emission of Hg contained in terrestrial storage pools, particularly during mineralization processes, could have important consequences for global environmental change due to predicted changes in terrestrial C storage (Grigal, 2003; Obrist, 2007). Recent studies using stable isotopes (Hintelmann et al., 2002; Ericksen et al., 2005; Harris et al., 2007; Graydon et al., 2009) showed that most of newly deposited Hg, when applied via wet deposition, is retained in watersheds and soils, and that atmospheric re-emission may account for less than 10 % in the first year after application (Ericksen et al., 2005; Harris et al., 2007). Our study points toward potentially stronger re-emission, up to 23 % of Hg within 18 months, of Hg that is originally associated with plant litter. Our study, however, cannot address the degree to which re-emission will reach the atmosphere in the field, or to what degree artificial laboratory conditions might have biased our results. Our laboratory litter samples, for example, were kept in an artificial environment, were removed from soils, kept in darkness, and watered regularly with Millipore water, and all these conditions may affect re-emission losses of Hg. In a field study, for comparison, we found that gaseous Hg/C ratios in emissions only accounted for a few percent of the Hg/C ratios of the soil pool (Obrist et al., 2009), while in this laboratory study, we observed up to equivalent loss of Hg and C upon decomposition in litter. Smith-Downey et al. (2010) estimated the fraction of re-emissions of Hg released from soil organic carbon upon decomposition to 16 %. Our results also indicate that litter types show highly species-specific behaviors: evasion losses of Hg were variable by species (ranging from 5 to 23 %), and so was sorption of new Hg litter observed in the field, indicating that different plant tissues show inherently different behaviors regarding sorption, retention, and re-emission of Hg.

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