

Fluxes of trichloroacetic acid through a conifer forest canopy

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“Capsule”: *Annualized within-canopy elimination of TCA is similar to that determined under controlled reductionist conditions.*

Abstract

Controlled-dosing experiments with conifer seedlings have demonstrated an above-ground route of uptake for trichloroacetic acid (TCA) from aqueous solution into the canopy, in addition to uptake from the soil. The aim of this work was to investigate the loss of TCA to the canopy in a mature conifer forest exposed only to environmental concentrations of TCA by analysing above- and below-canopy fluxes of TCA and within-canopy instantaneous reservoir of TCA. Concentrations and fluxes of TCA were quantified for one year in dry deposition, rainwater, cloudwater, throughfall, stemflow and litterfall in a 37-year-old Sitka spruce and larch plantation in SW Scotland. Above-canopy TCA deposition was dominated by rainfall (86%), compared with cloudwater (13%) and dry deposition (1%). On average only 66% of the TCA deposition passed through the canopy in throughfall and stemflow (95% and 5%, respectively), compared with 47% of the wet precipitation depth. Consequently, throughfall concentration of TCA was, on average, $\sim 1.4 \times$ rainwater concentration. There was no significant difference in below-canopy fluxes between Sitka spruce and larch, or at a forest-edge site. Annual TCA deposited from the canopy in litterfall was only ~ 1 –2% of above-canopy deposition. On average, $\sim 800 \mu\text{g m}^{-2}$ of deposited TCA was lost to the canopy per year, compared with estimates of above-ground TCA storage of ~ 400 and $\sim 300 \mu\text{g m}^{-2}$ for Sitka spruce and larch, respectively. Taking into account likely uncertainties in these values ($\sim \pm 50\%$), these data yield an estimate for the half-life of within-canopy elimination of TCA in the range 50–200 days, assuming steady-state conditions and that all TCA lost to the canopy is transferred into the canopy material, rather than degraded externally. The observations provide strong indication that an above-ground route is important for uptake of TCA specifically of atmospheric origin into mature forest canopies, as has been shown for seedlings (in addition to uptake from soil via transpiration), and that annualized within-canopy elimination is similar to that in controlled-dosing experiments.

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1. Introduction

It is well-known that trichloroacetic acid (TCA, CCl_3COOH) is present in rain deposition and in tree foliage, particularly in coniferous needles, in remote environments (McCulloch, 2002; Schöler et al., 2003). Some field studies have shown correlations between TCA

in needles and extent of needle loss (Frank et al., 1992) while others have shown none (Juuti et al., 1996). Although TCA is only one of many air pollutants or other stress factors that may be involved in tree damage, risk assessments are required for those chlorinated solvents that are known to contribute to production of TCA through photo-oxidation in the atmosphere (Ahlers et al., 2003).

TCA in the forest canopy can arise from direct transfer from the atmosphere, or by transport from the soil or soil water through the transpiration stream. The

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latter route can include TCA formed in situ in the soil or having entered the soil from atmospheric deposition. Soil formation of “natural” TCA has been implicated in direct and indirect experiments (Haiber et al., 1996; Hoekstra et al., 1999a) and indirect mass balance calculation (Hoekstra et al., 1999b). On the other hand, an above-ground route of TCA in the canopy can only arise for TCA of atmospheric origin, since TCA formed in soil or waters will not volatilise. Previously, such a route has been assumed to derive only from oxidation of emissions of anthropogenic C₂ chlorinated solvents, either in the atmosphere or within the plant foliage following uptake of the precursors (Frank, 1991). However, an excess of measured atmospheric TCA flux compared with currently-quantified precursor oxidation pathways (McCulloch, 2002) implies missing anthropogenic or natural sources of TCA or a precursor.

Both uptake routes for TCA into foliage have been demonstrated in seedling dosing experiments. For example, Matucha et al. (2001) have shown translocation of TCA to the needles of Norway spruce seedlings via the roots and transpiration stream, while both root-only and foliage-only routes have been shown for Scots pine (Sutinen et al., 1997) and Sitka spruce seedlings (Cape et al., 2003; Dickey et al., 2004). These experiments have all involved small seedlings <5–6-year old, and consequent TCA doses per unit mass of tree higher than environmental. Although a few previous data exist for ambient below-canopy throughfall TCA concentration (Hoekstra, 2003), there are no data that quantify the TCA flux through a mature forest canopy exposed only to ambient TCA deposition fluxes. To address this we made detailed measurements of the above-canopy wet and dry deposition of TCA, and the below-canopy throughfall, stemflow and litterfall fluxes of TCA for an entire year at two-weekly sampling resolution in a Sitka spruce plantation. The above-ground TCA reservoir was calculated from measurements of TCA concentrations in tree foliage and branchwood (three year classes) and stemwood, and compared with the annual input and output fluxes. Our study separates the loss to the canopy of direct atmospheric sources of TCA from the soil-derived contribution.

2. Materials and methods

2.1. Site description

Measurements were made in a remote upland forest (elevation ~320 m asl) within the Ballochbeatties catchment (4°29'W, 55°13'N) in the Southern Uplands of Scotland, 70 km south of Glasgow. Sampling locations are shown in Fig. 1. The climate is strongly maritime and annual precipitation is 2.5–3 m, with little seasonal

variation. The catchment was visited on 26 occasions over one year commencing in May 2001.

The forest was planted in 1964 and is dominated by Sitka spruce (*Picea sitchensis*), but also contains hybrid larch (*Larix × eurolepis*, 16% by area), lodgepole pine (*Pinus contorta*, 6%) and other conifer species (8%), sited largely on wet basin peat. Prior to monitoring, the diameter at breast height (DBH) was measured of each tree within ten 10 m × 10 m quadrats distributed to represent the forest tree species and site conditions. Measured DBH values ranged from 2.5 to 35.7 cm with a median of 10.5 cm ($n = 471$). The mean tree density and forest basal area calculated for the whole forest were 0.45 stems m⁻² and 53 m² ha⁻¹, respectively.

2.2. Above-canopy measurements

The dry deposition and rain and cloud wet deposition fluxes of TCA were measured two-weekly as part of a catchment-scale study (Stidson et al., 2004). Rainfall depth was measured at two sites (Fig. 1) using ARG100 tipping bucket raingauges with rims ~0.4 m above the ground. Samples for TCA analysis were collected in adjacent bulk precipitation gauges consisting of a 150 mm diameter funnel, 1.5 m above ground, draining into a polypropylene bottle. Cloudwater was collected by a passive harp wire device, shaped like an inverted cone of polypropylene filaments, as described by Crossley et al. (1992). Cloudwater deposition to the forest canopy was calculated from the corrected cloudwater depth adjusted for the capture efficiencies of the cloud collector (0.29) and the forest canopy (0.05).

Air was sampled for TCA at a location 4 km NE of the catchment due to the requirement for mains power. Atmospheric concentration was assumed constant over this distance. The method followed that detailed in Heal et al. (2003b) in which total atmospheric TCA (gas and particle-bound) was collected by drawing air through two 47 mm diameter open-face Na₂CO₃-impregnated Gelman A/C filters in parallel. Total flow rate through both filters was approximately 20 L min⁻¹, measured cumulatively with an in-line gas meter.

2.3. Below-canopy measurements

Four of the quadrats described in Section 2.1 were selected as sites for sampling (Fig. 1); three of Sitka spruce and one of larch, in approximate proportion to the overall distribution of species in the forest. Two of the Sitka sites were situated within the forest (Sitka North and Sitka South) and the third was situated along a forest edge (Sitka Edge) to assess for edge effects.

Throughfall precipitation was collected at each site using inclined guttering draining into a lidded collection tank (total area of guttering per site: 0.92–0.95 m²). Nine Sitka spruce trees, representative of the size

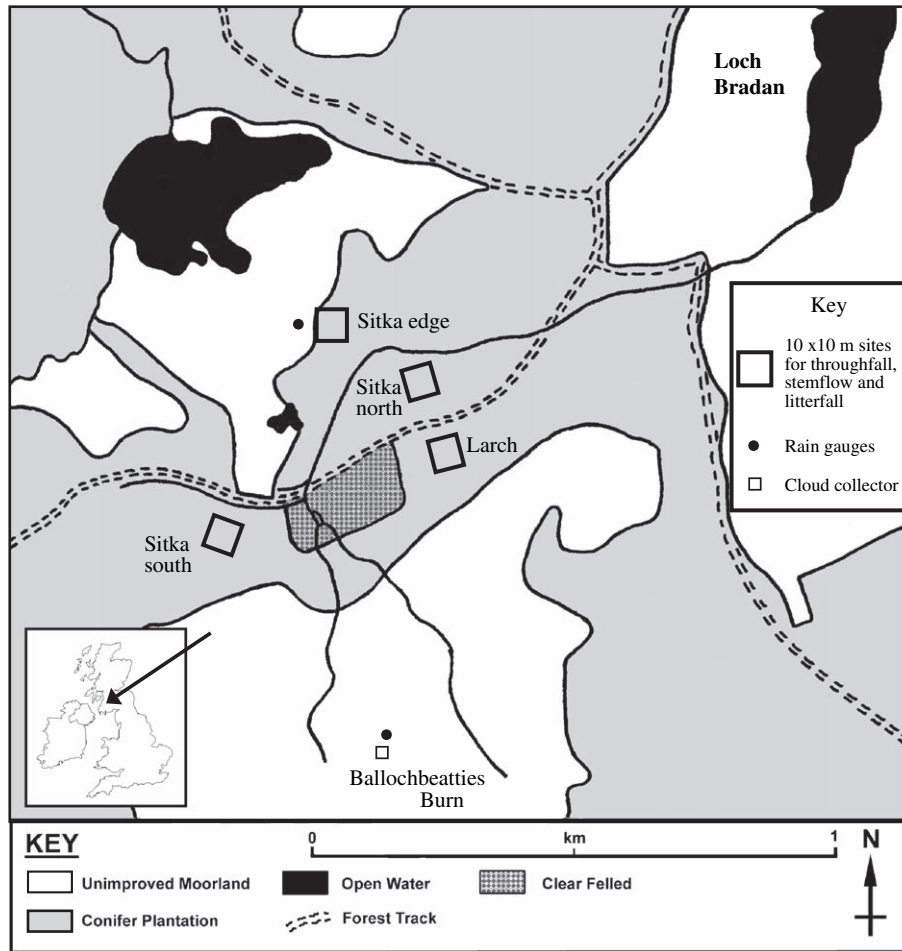


Fig. 1. Location of forest sampling sites in the Ballochbeatties catchment, SW Scotland.

distribution in the catchment, were selected for stemflow collection by selecting trees whose DBH values equalled the median value of the nine evenly spaced noniles in the distribution of all ranked Sitka spruce DBH values from the initial DBH survey. Three larch trees for stemflow sampling were similarly selected. Stemflow was channelled into a covered collection tank using a flexible plastic gutter (2 cm diameter) wrapped around each tree and sealed with silicon sealant to the bark.

Throughfall and stemflow were measured two-weekly for volume and TCA concentration. Throughfall depth at each site was calculated directly using the known collector surface area. For the five two-week periods when throughfall collection tanks overflowed, throughfall depth was extrapolated from the strong linear relationship between rainfall and throughfall in the rest of the dataset ($r^2 = 0.93$, $n = 21$). The mean of the nine Sitka spruce stemflow volumes was assumed to represent the mean stemflow volume per tree (since trees for stemflow measurement were selected to characterise the overall distribution in the forest), and was multiplied by the catchment average stem density of Sitka spruce to obtain a spatially averaged Sitka spruce stemflow depth. A

spatially averaged Larch stemflow depth was similarly derived. Average stemflow depth derived by this approach differed by less than 6% from an alternative approach that used the significant relationship that existed between individual tree stemflow depth and $(DBH)^2$ to derive stemflow depths for the distribution of all tree sizes in the catchment. The impact of different scale-up methodology was negligible since stemflow was only a small proportion of below-canopy aqueous flux (see Section 3).

Below-canopy litterfall was collected two-weekly at each site in guttering of twice the area of those for throughfall, and weighed and analysed for TCA.

2.4. Forest canopy measurements

Foliage was sampled using extending pruners from three randomly selected trees near each site, from branches below the third whorl at a height of ~ 4 m, on three occasions (September 2001, January 2002 and May 2002). Samples were separated into needles and branchwood from the current growing season (C) and the previous two growing seasons (C + 1, C + 2) which were

then pooled by site. Stemwood cores (4 mm diameter) were extracted with a borer at 1.3 m above the ground, in May 2002, from eight trees (two per site) whose DBH values matched the trees for stemflow measurement. All samples were stored frozen until analysis.

2.5. TCA analysis

TCA concentration in all samples was determined following the method of Plümacher and Renner (1993), by thermal decarboxylation of TCA to chloroform (CHCl_3) and quantification of the latter by headspace gas-chromatography with electron capture detection (Perkin–Elmer HS40/Austosystem). Full details of the methodology as applied in this work for determination of TCA in air and aqueous samples, and in needle and branchwood samples, respectively, are given in Heal et al. (2003b) and Heal et al. (2003a). In brief, samples were sealed in headspace vials, heated to 100 °C for 1.5 h to achieve decarboxylation, and re-equilibrated at 60 °C before transfer of an aliquot of headspace to the GC. Background CHCl_3 was quantified in replicate samples equilibrated in parallel to 60 °C only. Direct calibration using standard addition of TCA solutions rather than CHCl_3 solutions avoided any potential bias arising from incomplete decarboxylation of TCA to CHCl_3 although experiments showed that decarboxylation was stoichiometric (Heal et al., 2003b).

Aqueous and air-filter samples were analysed as collected; foliage and branchwood samples were ground to a powder under liquid nitrogen (and stemwood to pieces approximately 1 mm in diameter) prior to analysis. All samples were analysed in triplicate, except the air filters for which only duplicate samples were available. Random analytical uncertainties in measurement of TCA in aqueous samples and air filters averaged around 20–30%. Random analytical uncertainty for foliage samples was lower (typically 15–20% on average) due to the higher analyte concentrations. Concentrations of TCA in biomass were expressed as dry mass using the measurement of mass loss on drying for 6 days at 60 °C.

The decarboxylation method has the advantage of being a whole-sample technique whereas extraction-derivatisation techniques, whilst specific for TCA, must assume that all intrinsic matrix-bound TCA is extracted into solution. The decarboxylation method does not directly quantify TCA so it is possible that other compounds in the sample matrix might yield CHCl_3 under the sample decarboxylation conditions and be erroneously quantified as TCA. However, all samples were always blank-corrected for CHCl_3 quantified at 60 °C so that only CHCl_3 produced by the sample during 1.5 h above 60 °C is quantified as TCA. Although we do not believe the possibility of erroneous TCA quantification to be a significant issue for aqueous and needle matrices, this potential bias cannot be

excluded when interpreting the TCA data presented here.

3. Results

The hydrological inputs and outputs to the forest were well-characterised and balanced (Heal et al., 2004), so calculation of fluxes of TCA in aqueous media was not subject to bias arising from incomplete hydrological capture. Uncertainties in data arising from TCA analysis have been discussed in Section 2.5, with further discussion of overall uncertainties in Section 4.

3.1. Above-canopy TCA concentrations and fluxes

The time-series of two-weekly air, rain and cloud volumes and TCA concentrations contributing to total annual above-canopy TCA deposition are reported in Stidson et al. (2004). Only the annual summary is given here (Table 1). Annual rainfall was 2.50 m with a further 0.41 m calculated for cloud deposition to the canopy. Two-weekly rainwater and cloudwater TCA concentrations varied from 0.32 to 2.3 $\mu\text{g L}^{-1}$ (median 0.81 $\mu\text{g L}^{-1}$) and from <0.1 to 3.4 $\mu\text{g L}^{-1}$ (median 0.81 $\mu\text{g L}^{-1}$), respectively. The concentration of total gas and particle-bound TCA in air was low, ranging from 5 to 130 pg m^{-3} ($n = 24$).

Overall, the total above-canopy deposition flux of TCA was 2.4 $\text{mg m}^{-2} \text{y}^{-1}$ (comprising 0.02 $\text{mg m}^{-2} \text{y}^{-1}$ from air, 2.1 $\text{mg m}^{-2} \text{y}^{-1}$ from rain and 0.3 $\text{mg m}^{-2} \text{y}^{-1}$ from cloud) (Stidson et al., 2004). The dry deposition flux is an estimated maximum calculated from measured air concentrations assuming a deposition velocity of $2 \times 10^{-2} \text{ m s}^{-1}$. Rainwater flux was calculated using the mean depth and TCA concentrations from the two sites. The above-canopy flux did not vary seasonally, reflecting the uniform wet precipitation for this catchment.

3.2. Below-canopy TCA concentrations and fluxes

The annual throughfall depth was, on average, 45% of the total wet deposition onto the canopy and hardly differed across the four sites (range: 43–46%). The concentration of TCA in throughfall collected every two-weeks (Fig. 2a) ranged from 0.33 to 3.0 $\mu\text{g L}^{-1}$ (median 1.2 $\mu\text{g L}^{-1}$, $n = 98$). Hoekstra (2003) recently summarised from the literature a median canopy-drip concentration of 0.83 $\mu\text{g L}^{-1}$. TCA concentrations in throughfall did not vary significantly between sites or throughout the year, with the exception of a peak in September 2001, the reason for which is unknown, but is not thought to be related to chemical analytical problems.

The annual depth of stemflow under Sitka spruce and larch was 2.8% and 1.7%, respectively, of the total wet

Table 1

Summary of annual above- and below-canopy aqueous and TCA fluxes, and the TCA content in the above-ground forest biomass, at four forest sites in the Ballochbeatties catchment for the period May 2001–May 2002 (data for TCA flux are reported with significant figures that imply an associated uncertainty for the values in the approximate range 5–20%; true uncertainty in flux is likely to be greater, as discussed fully in the text)

	Sitka north	Sitka south	Sitka edge	Larch	Mean ^c
Above-canopy hydrology					
Rainwater depth (m)	2.50	(all sites)			
Cloudwater depth (m)	0.41	(all sites)			
Below-canopy hydrology					
Throughfall depth (m)	1.34	1.33	1.29	1.25	1.30
Stemflow depth (m) ^a	0.082	0.082	0.082	0.049	0.075
Throughfall as % (throughfall + stemflow) depth	94	94	94	96	95
(Throughfall + stemflow) as % (rain + cloud) depth	49	48	47	45	47
Above-canopy TCA flux					
TCA input flux ($\mu\text{g m}^{-2}$)	2400 (all sites)				
Below-canopy TCA flux (aqueous)					
Throughfall flux ($\mu\text{g m}^{-2}$)	1500	1500	1400	1600	1500
Stemflow flux ($\mu\text{g m}^{-2}$)	90	90	110	60	90
Total below-canopy aqueous TCA flux ($\mu\text{g m}^{-2}$) ^c	1600	1600	1500	1700	1600
Throughfall flux as % of total below-canopy flux ^c	95	94	93	97	95
Below-canopy/above-canopy TCA flux (%) ^c	66	67	63	70	66
Annual TCA uptake by canopy ($\mu\text{g m}^2$)	800	800	900	700	800
Below-canopy TCA flux (litterfall)					
Litterfall TCA flux ($\mu\text{g m}^{-2}$)	20	30	20	25	25
Litterfall as % (throughfall + stemflow) TCA flux	1.3	2.0	1.2	1.5	1.5
Above-ground TCA storage					
TCA in above-ground biomass ($\mu\text{g m}^{-2}$) ^b	400	(all Sitka sites)		300	

^a Stemflow depth is derived as a single average value applicable to all Sitka spruce sites.

^b Derived from data in Table 4. Data are average values for all Sitka spruce sites.

^c TCA data in these rows and column are rounded to two significant figures after calculation using data with a greater number of significant figures.

deposition onto the canopy. The two-weekly concentration of TCA in stemflow (Fig. 2b) ranged from 0.23 to 2.8 $\mu\text{g L}^{-1}$ (median 1.2 $\mu\text{g L}^{-1}$, $n = 94$). The two peaks at 3.2 and 5.0 $\mu\text{g L}^{-1}$ are considered genuine, although the reason for the higher concentration is unknown. Stemflow TCA concentrations did not vary significantly between sites or throughout the year, and were not significantly different from concentrations in throughfall.

The two-weekly fluxes of TCA in throughfall and stemflow for each site are shown in Fig. 3a and b, respectively. Throughfall and stemflow TCA fluxes did not vary significantly between sites (no evidence of forest “edge” effects). Both fluxes were controlled by the corresponding aqueous depths; since wet deposition depth did not vary significantly with season, neither did throughfall nor stemflow TCA flux. The total annual throughfall and stemflow TCA fluxes through the canopy at each site are given in Table 1. The mean throughfall and stemflow TCA fluxes for all four sites were 1.5 and 0.09 $\text{mg m}^2 \text{y}^{-1}$, respectively. Stemflow constituted only 5% of below-canopy aqueous TCA flux. Mean annual below-canopy transmission (in throughfall and stemflow) of total above-canopy TCA flux was 66%, compared with a mean below-canopy transmission of only 47% for hydrological flux (Table 1). Sitka spruce and larch sites were similar.

The dry mass, TCA concentration and TCA flux of litterfall for two-weekly collection periods at each site are summarised in Table 2. For Sitka spruce sites, the mass of litterfall was relatively constant throughout the year, except during a period of high winds in January 2002. Litterfall mass at the Sitka edge site was lower than at the other spruce sites because of smaller trees. The mass of larch litterfall increased dramatically during the autumn, as expected for a deciduous species. The annual production of Sitka spruce litterfall ($\sim 230 \text{ g m}^{-2}$ dry weight, averaged over the three sites) was similar to the values of 220 and 320 g m^{-2} reported in other UK upland Sitka spruce plantations (Owen, 1954; Adams et al., 1980).

The TCA concentration in two-weekly samples of litterfall (Fig. 4) varied from 26 to 580 ng g^{-1} dry weight ($n = 96$) (N.B. a lot of samples were very wet). TCA concentrations in litterfall did not vary with season but concentrations at the Sitka edge site were significantly higher than at other sites. The flux ($\mu\text{g m}^{-2}$) of TCA in litterfall for each site for each two-weeks is shown in Fig. 5, calculated as the product of litterfall dry mass and TCA dry mass concentration. The peak in TCA litterfall flux at Sitka south in January 2002 was due to the wind-induced high litterfall at that time. Interestingly, the consistently higher TCA concentration in

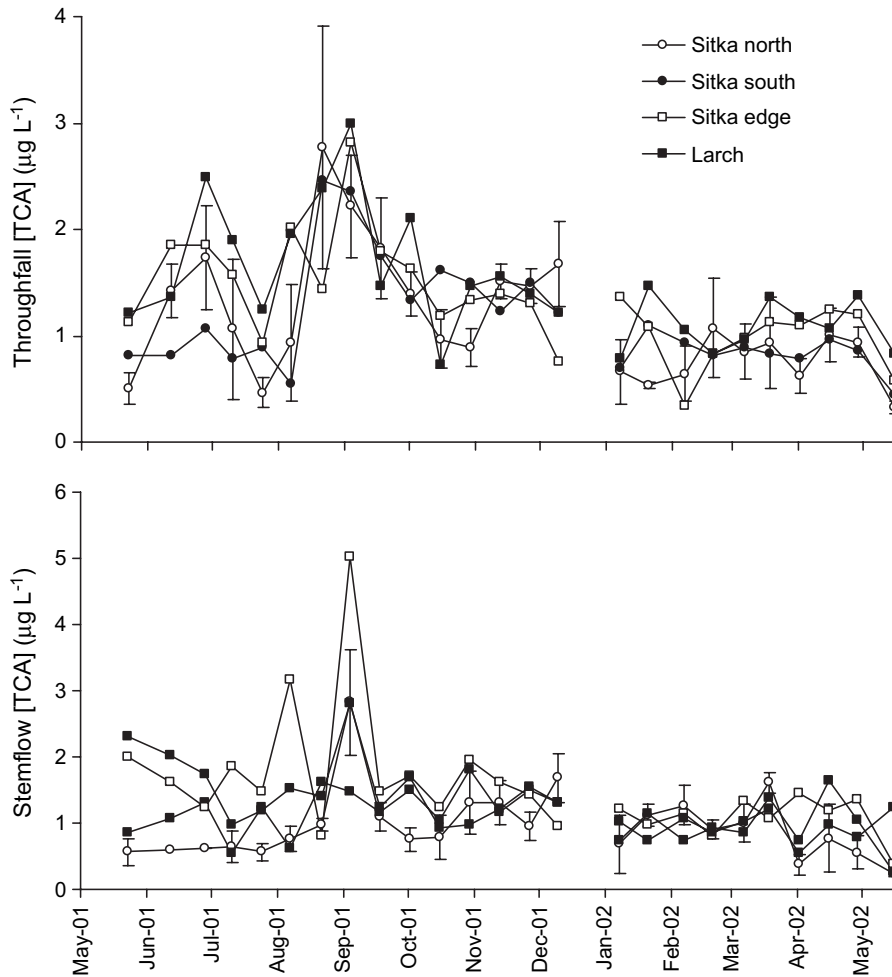


Fig. 2. Concentrations of TCA in (a) throughfall and (b) stemflow measured approximately two-weekly at four forest sites, May 2001–May 2002. The absence of data in mid-December 2001 reflects two-weeks with no precipitation. For clarity, error bars (± 1 sd of triplicate TCA analyses) are shown for data from the Sitka north site only, but are typical of other measurements.

litterfall at the Sitka edge site than at other sites (Fig. 4) was offset by the lower litterfall mass at this site resulting in no difference in flux of TCA in litterfall between the sites. The total annual loss of canopy TCA in litterfall at each site is given in Table 1. The mean value was $25 \mu\text{g m}^{-2} \text{y}^{-1}$.

3.3. Comparison of canopy TCA fluxes with the above-ground forest TCA reservoir

The concentrations of TCA measured in needles, branchwood and stemwood are shown in Table 3. Concentrations in Sitka spruce needles ranged from 35 to 220 ng g^{-1} dry weight (median 100 ng g^{-1}) (or $14\text{--}120 \text{ ng g}^{-1}$ fresh weight, median 50 ng g^{-1}), while larch needles had a median TCA concentration of 160 ng g^{-1} dry weight. Branchwood TCA concentrations were much lower than in needles, with median values for Sitka spruce and larch of 15 and 29 ng g^{-1} dry weight, respectively. In Sitka spruce, TCA concentration always

increased with age of needle, and nearly always increased with age of branchwood. TCA concentrations in stemwood ranged from 2 to 22 ng g^{-1} dry weight, with median values of 11 and 6 ng g^{-1} dry weight for Sitka spruce and larch, respectively. Fig. 6 demonstrates an inverse, although not quite statistically significant, relationship between stemwood TCA concentration and tree DBH ($r = 0.67$, $n = 8$, $P = 0.07$).

Above-ground forest biomass in individual needle, branchwood and stemwood compartments was estimated by combining data from the measured distributions of planting density and DBH values with allometric equations for Sitka spruce and hybrid larch from a wide range of literature sources. Dry mass per m^2 values are given in Table 4, which also includes the estimated TCA mass in each compartment calculated by multiplying these data by the median value of the associated concentration data. The estimated total TCA mass stored in above-ground tree biomass was ~ 400 and $\sim 300 \mu\text{g m}^{-2}$ for Sitka spruce and larch, respectively.

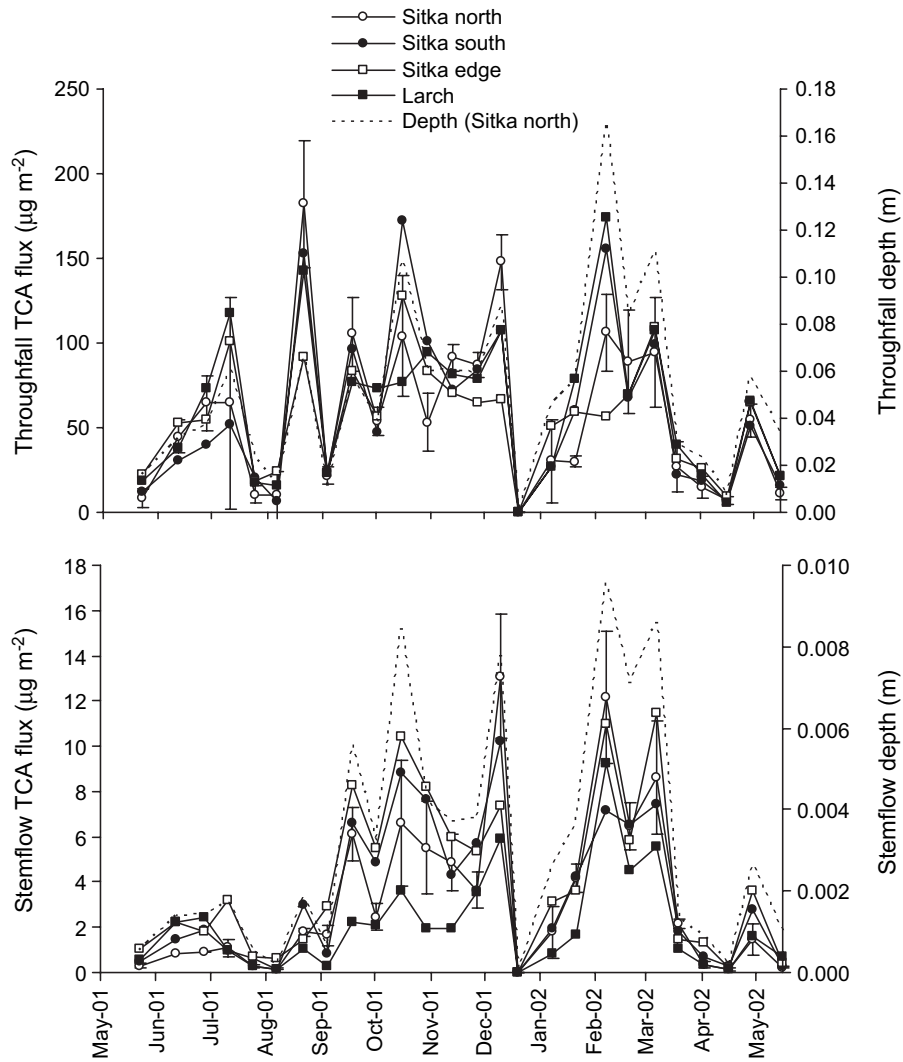


Fig. 3. Fluxes of TCA in (a) throughfall and (b) stemflow determined approximately two-weekly at four forest sites, May 2001–May 2002. For clarity, error bars (± 1 sd of triplicate analyses of TCA concentration) are shown for data from the Sitka north site only, but are typical of all sites. The dashed lines show throughfall and stemflow depths for the Sitka north site.

4. Discussion

Concentrations of TCA measured in needles in this forest are comparable to the range of previous studies (McCulloch, 2002; Schöler et al., 2003), although slightly

higher than the general average. This probably reflects the generally higher rate of wet deposition of TCA also observed at this site, which exceeds that expected from known anthropogenic precursor oxidation routes (McCulloch, 2002). The source of extra atmospheric

Table 2

Summary data for dry mass of litterfall, measured litterfall TCA concentrations and litterfall TCA flux for ~14 day sampling periods ($n = 26$) (data are quoted to two significant figures to illustrate raw data values; as detailed in the text, the replicate analytical uncertainty for an individual determination of TCA concentration in foliage and branchwood averaged around 15–20%; uncertainty in TCA flux will be greater because of additional uncertainty associated with measurement of dry mass of litterfall)

		Sitka north	Sitka south	Sitka edge	Larch
Dry mass (g m^{-2})	Median	6.3	8.3	3.0	3.9
	Min, max	1.8, 56	2.3, 100	0.6, 19	0.9, 72
[TCA] (ng g^{-1} dry mass)	Median	85	80	200	90
	Min, max	33, 150	30, 200	65, 580	26, 240
TCA flux ($\mu\text{g m}^{-2}$)	Mean	0.8	1.2	0.7	1.0
	Min, max	0.18, 4.6	0.13, 14	0.19, 3.0	0.09, 5.8

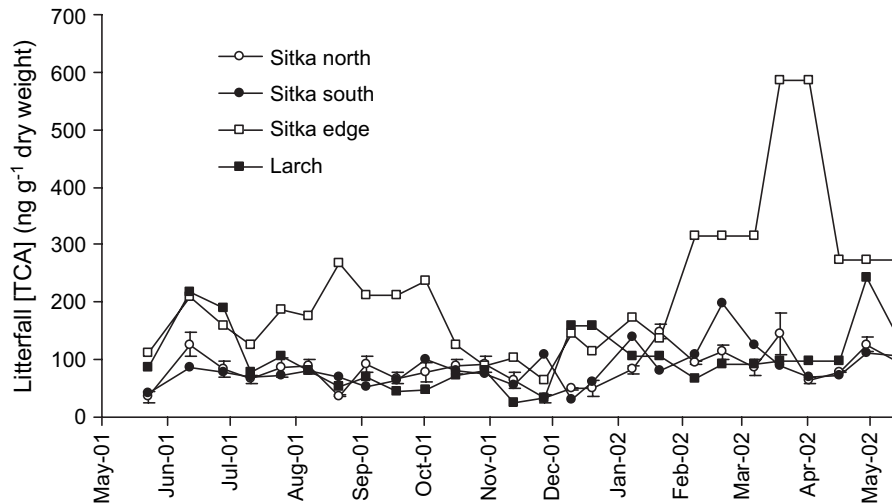


Fig. 4. Concentrations of TCA in litterfall measured approximately two-weekly at four forest sites, May 2001–May 2002. For clarity, error bars (± 1 sd of triplicate TCA analyses) are shown for data from the Sitka north site only, but are typical of all measurements. Litterfall samples from the Sitka edge site were pooled from some sampling periods in January–May 2002 to provide sufficient material for TCA analysis.

TCA in the comparatively remote region of southern Scotland is not known. However, heterogeneous oxidation has not been well-characterised, allowing the possibility that more TCA is formed from chlorinated solvents via the aqueous (rain and cloud) phase than previously proposed. In addition, marine algae in temperate waters have been shown to be an atmospheric source of tri- and tetra-chloroethene (Abrahamsson et al., 1995). Both may be relevant explanations of additional TCA in an atmosphere dominated by maritime meteorology. It has been speculated that TCA may be produced in situ in foliage after absorption of chlorinated gases, but there is no field evidence for this process at environmental conditions.

The observation of increasing TCA concentration with needle age in Sitka spruce has been previously

reported for other conifers, e.g. (Frank et al., 1992; Frank et al., 1994). The concentration of TCA in needles must reflect the net kinetics of uptake into the needle and internal elimination. Thus, higher concentrations of TCA in older needles may indicate one or a combination of: greater rate of direct uptake of TCA from atmosphere through older needles (greater disruption to cuticle); additional active translocation of TCA from younger to older needles; greater translocation from roots because of greater transpiration rates; slower rates of elimination of TCA. The last two of these seem most likely. There was a similar, although less universal, trend for TCA concentrations in branchwood to increase with year class which has not been reported before, and presumably arises for the same reason. Stemwood concentrations have also not been previously reported. The apparent

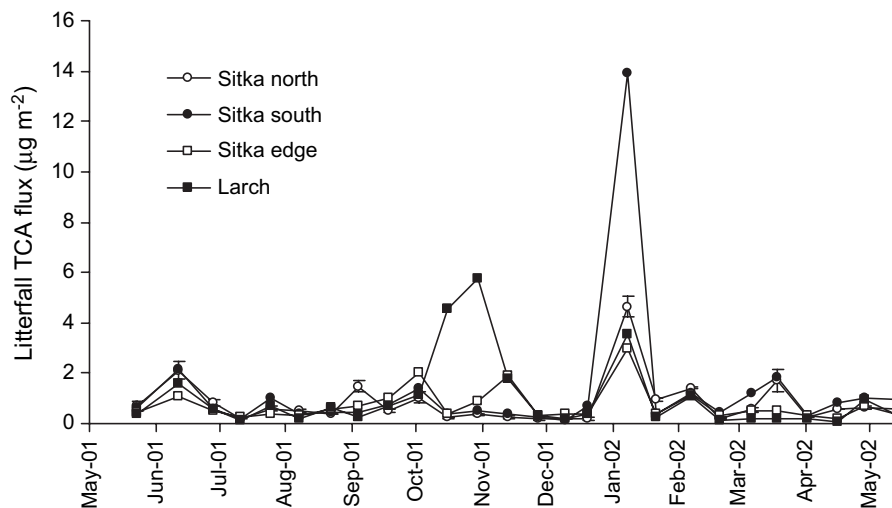


Fig. 5. Fluxes of TCA in litterfall determined approximately two-weekly at four forest sites, May 2001–May 2002. For clarity, error bars (± 1 sd of triplicate analyses of TCA concentration) are shown for data from the Sitka north site only, but are typical of all sites.

Table 3

Dry mass TCA concentrations in needles, branchwood and stemwood of Sitka spruce (from three different sampling sites), hybrid larch and lodgepole pine (data are quoted to two significant figures to illustrate raw data value; as detailed in the text, the replicate analytical uncertainty for an individual determination of TCA concentration in foliage, branchwood and stemwood averaged around 15–20%; additional methodological uncertainty is also discussed in the text)

Sampling date		[TCA] (ng g ⁻¹ dry weight)		
		18-Sep-01	21-Jan-02	16-May-02
Needles				
Sitka north	C	35	100	93
	C + 1	86	110	100
	C + 2	120	160	140
Sitka south	C		51	63
	C + 1	66	99	64
	C + 2	97	140	78
Sitka edge	C	36	120	160
	C + 1	82	200	200
	C + 2	150	210	220
Larch		190		140
Lodgepole pine	C		25	
	C + 1		54	
	C + 2		84	
Branchwood				
Sitka north	C	12		9
	C + 1	12	38 ^a	9
	C + 2	18		13
Sitka south	C		15 ^b	14
	C + 1	12		69
	C + 2			21
Sitka edge	C	11	58	20
	C + 1	18	35	10
	C + 2	26	170	14
Larch		30		28
Lodgepole pine	C			
	C + 1		26	
	C + 2		49	
Stemwood				
Sitka	Median	11		
Larch		6		

^a Pooled sample of C and C + 1.

^b Pooled sample of C, C + 1 and C + 2.

trend for lower stemwood TCA concentration with increasing tree size is probably due to the greater proportion of heartwood to sapwood in larger trees, and the consequent lower proportion of active transpiration stream containing TCA (the whole radius of stemwood was analysed for each tree).

The TCA concentration in foliage and litterfall were higher at the Sitka edge site than at the other sites. This is in agreement with Frank et al. (1992) who reported that, for Norway spruce and Scots pine needles in Finland, TCA was preferentially deposited on trees in open stands that received a high inflow of winds. Edge trees capture a greater proportion of cloud droplets and fine rain and have a larger canopy area per tree. Foliage

was not sampled at sufficient temporal resolution to observe any seasonal trends, although strong seasonality is not expected for this site because of the fairly uniform deposition of TCA throughout the year.

The deposition of TCA to the canopy was dominated by rainwater (86%), compared with cloudwater interception (13%) and dry deposition (1%). Dry deposition of TCA, gas or particle-bound, was therefore a negligible source of TCA to the canopy in this forest (but note that this catchment has high annual rainfall and few periods of any length without rain). Only 63–70% (average 66%) of total TCA deposition passed through the canopy in throughfall and stemflow, the majority, 95% on average, in throughfall. Since only 47% of the total wet precipitation passed through the canopy as throughfall and stemflow, the below-canopy aqueous TCA concentration was, on average, a factor $0.66/0.47 = 1.4$ greater than above-canopy aqueous TCA concentration. This enhancement in below-canopy throughfall TCA concentration is due to the evaporative loss of rain and cloudwater from the canopy; but overall there was a net loss of TCA flux through the canopy. TCA fluxes were generally similar in different conifer tree species and were not influenced by forest edge effects (Table 1). Above and below-canopy TCA fluxes for each site over the year of sampling are shown in Fig. 7. In general, trends in above- and below-canopy TCA fluxes were similar throughout the year, presumably reflecting the generally even wet deposition flux to this catchment throughout the year, although there is some suggestion of greater net uptake in winter and lower uptake during summer.

A further 1–2% of annual TCA deposition reached the forest floor from the canopy in the form of foliage litterfall. Even though litterfall is a small component of the annual below-canopy flux, the lifetime of litter from conifers on the forest floor is long. The depth of litter on the forest floor was many cm, and TCA concentrations measured in the soil litter layer in the same plots were of the same magnitude as TCA concentrations in litterfall (median soil litter TCA concentration, 200 ng g⁻¹ dry weight, $n = 12$ (Stidson et al., 2004)). This indicates a slow rate of degradation of TCA in fallen foliage so that, over many years, the accumulation of litterfall may represent an important source of TCA to the soil system.

The persistent difference between above and below-canopy TCA flux is clear evidence of loss of TCA to the canopy arising from transport of TCA into the needles and branchwood, and/or TCA loss on the canopy surface, for example by degradation by microorganisms. These field observations are consistent with controlled-dosing experiments which clearly demonstrate an above-ground route of TCA uptake into foliage of Sitka spruce (Cape et al., 2003; Dickey et al., 2004) and other conifer seedlings (Sutinen et al., 1997; Schröder et al., 1997). These experiments indicate that uptake through the

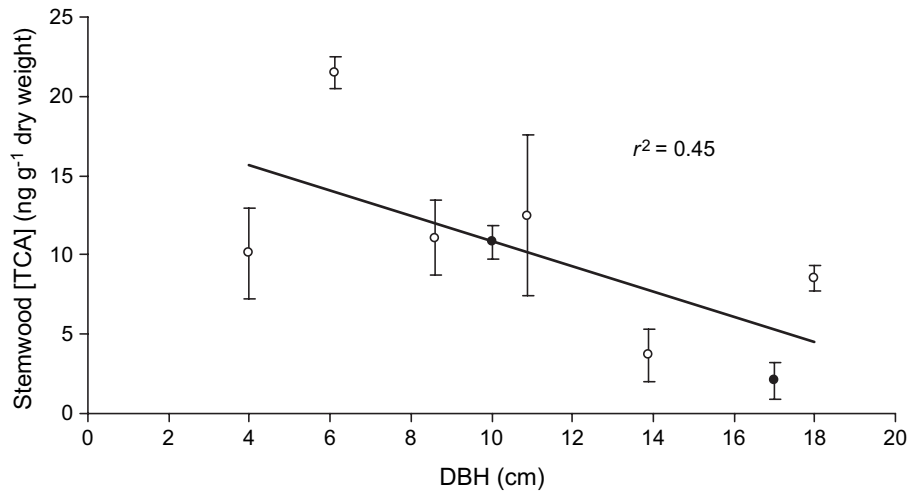


Fig. 6. The relationship between stemwood TCA concentration and tree diameter at breast height (DBH). Open and closed circles represent Sitka spruce and hybrid larch trees, respectively. The trendline is for all data and has significance value $P = 0.07$. Error bars are ± 1 sd of triplicate TCA analyses.

branchwood is likely to be an important route for the above-ground uptake of TCA (Dickey et al., 2004). Kinetic modelling of seedling dosing data also suggests that loss of TCA on the foliage surface is also an important process occurring in parallel to uptake into the foliage (Heal et al., 2003a). For comparison, chloride and sulphate ions are generally regarded as being conserved through the canopy, although there is some evidence of sulphate uptake, again particularly through branchwood (Percy and Baker, 1989). Nitrate ions are actively taken up by leaves and/or surface microbes. The data here for TCA imply behaviour intermediate between chloride and nitrate. Transfer of TCA from solution into foliage and wood may be driven by concentration gradients increasing as water on the tree surfaces evaporates.

The mean annual effective loss of TCA to the forest canopy was $\sim 800 \mu\text{g m}^{-2}$ (Table 1), compared with estimated above-ground forest biomass TCA reservoirs of $\sim 400 \mu\text{g m}^{-2}$ for Sitka spruce and $\sim 300 \mu\text{g m}^{-2}$ for larch. The uncertainties in these values are now considered. The above- and below-canopy TCA flux values,

from which the value for uptake is derived, are dominated by the contributions from rainwater and throughfall, respectively. The depths of these quantities are relatively accurately determined (estimated better than $\pm 10\%$); the greater uncertainties associated with estimating depths of cloudwater and stemflow have comparatively small influence. Because cloud water was measured at the upper end of the catchment, the calculated cloud input to the forest canopy should be regarded as an upper limit. The largest uncertainty in the flux values is contributed by the TCA analytical variability (20–30%, on average) and any potential bias in the analytical method (see Section 2.5). If total uncertainty in each of the above- and below-canopy TCA fluxes is estimated at $\pm 35\text{--}40\%$, the estimated total uncertainty in canopy uptake TCA flux is $\sim \pm 50\%$. The uncertainty in TCA reservoir is dominated by uncertainty in allometric equations for estimation of forest biomass. It is not possible to put an accurate figure on this uncertainty, but $\pm 50\%$ is assumed adequate.

Using the above data, the ratio between above-ground TCA reservoir and annual TCA loss to the forest canopy

Table 4

Calculated mass of TCA reservoir in above-ground forest biomass compartments of Sitka spruce and hybrid larch (the significant figures quoted for the data in the first three columns do not reflect presumed precision but are included here to illustrate the raw data used; the data in the final column for total TCA stored have been rounded to one significant figure)

			Median [TCA] (ng g^{-1} dry weight)	Dry mass in catchment (kg m^{-2})	Storage of TCA ($\mu\text{g m}^{-2}$)	Sum of stored TCA ($\mu\text{g m}^{-2}$)
Sitka	Needles	C	78	0.4	31	400
		C + 1	99	0.4	39	
		C + 2	140	0.8	110	
	Branchwood (C, C + 1, C + 2)	15	3.7	55		
	Stemwood	11	16	160		
Larch	Needles		160	0.5	82	300
	Branchwood		29	3.2	91	
	Stemwood		6	18	120	

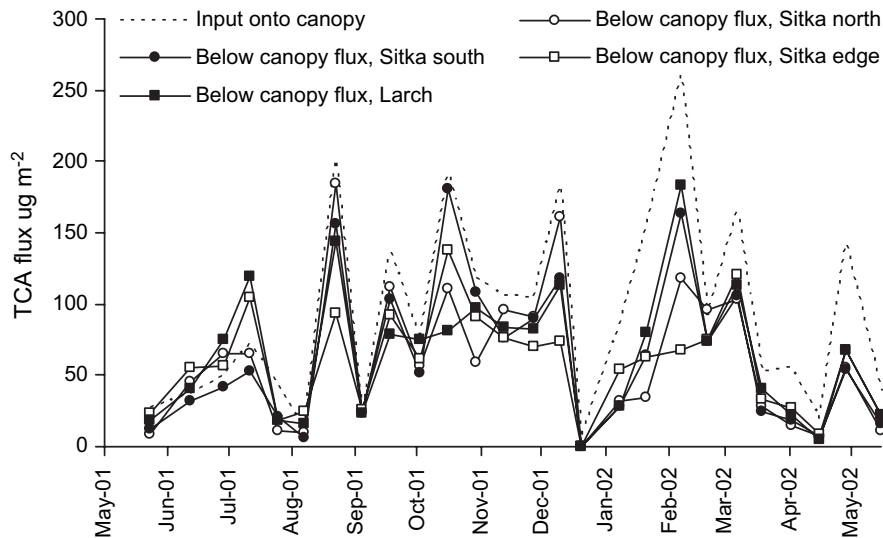


Fig. 7. Total two-weekly above-canopy and below-canopy TCA fluxes per at all sites, May 2001–May 2002.

is calculated to be in the range 0.5 ± 0.3 y. This figure represents the average (steady state) residence time for atmospherically supplied TCA in the forest canopy, if it is assumed that the only source of TCA in the canopy is capture from precipitation and that transfer into the foliage is 100%. If it is assumed that only a proportion of the TCA flux captured from precipitation passes into the foliage (the rest being degraded externally), then the average residence time of TCA in the canopy will be greater than 0.5 y. On the other hand, assuming there is an additional source of TCA to the foliage by uptake through the transpiration stream from a below-ground source in the soil, as seems likely from other studies showing root uptake, then the average residence time of TCA in the canopy will be shorter (note that a below-ground source does not have to imply in situ natural production of TCA, but could be TCA in throughfall reaching the soil). In reality, there is likely to be both transpiration uptake of TCA from soil and external foliage loss processes, which have opposing effects on the average residence time of TCA in the canopy.

The loss process for TCA within the foliage is presumed to be metabolic degradation. The estimated residence time derived above (with its uncertainty) corresponds to an average first-order lifetime for within-foliage degradation in the range 70–300 days, equivalent to a half-life for within-foliage degradation in the range 50–200 days. These field-derived values agree well with estimates for within-foliage degradation half-lives of ~50 days (during a growing season) and ~300 days (over winter) derived from single and multiple TCA dosing experiments to Sitka spruce saplings in a greenhouse (Heal et al., 2003a; Dickey et al., 2004). An appropriately annualized half-life for within-foliage degradation would be expected to lie somewhere between the two extremes derived from the dosing experiments. In conclusion, the

field measurements indicate an above-ground route of uptake of ambient atmospheric TCA into mature forest canopies, and associated elimination rates, in line with extrapolation of artificial dosing experiments on small seedlings.

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