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Abstract

Forest canopies represent an extensive organic surface available for partitioning of semivolatile organic pollutants with the atmosphere. To date, the ability of forests to sequester such compounds (the so called “forest filter effect”) has been investigated using indirect methods which yield time integrated deposition fluxes and scenario-dependent deposition velocities. In the present study, experimental data collected at three different alpine forest sites were used to assess the dynamics of PCB deposition fluxes (*F*; ng $m^{-2}d^{-1}$) during the growing season. Estimated values of *F* were consistent with previously reported data. Furthermore, this study showed that maximum levels of *F* in late spring can be a factor of 1.4-3.4 higher than their seasonal mean value. These data, in conjunction with a simple model framework which includes the main forcing parameters of air concentration, temperature, foliage structure and biomass dynamics, are used to estimate the plant-air mass transfer coefficient (k_U; m d^{-1}) and its variation with time in one of the forests. k_U did not appear to significantly vary during the season and its mean seasonal value ranged between 43-95 m d^{-1} for selected compounds. The proposed framework was successfully applied to predict the variation in canopy concentration with time in the other two forests.

Introduction

Persistent organic pollutants (POPs) can undergo long range atmospheric transport following emissions in source areas (1, 2). During their journey, these pollutants partition to available environmental media, including soils (3), water bodies (4) and vegetation (5). Because of their lipophilicity, the environmental stocks of organic carbon play a key role in this partitioning of POPs (6). Vegetation provides an important, carbon rich interface with which POPs interact (5, 7) given plant foliage efficiently accumulates compounds with LogK_{OA} > 6 and LogK_{AW} > -6 (8) from the atmosphere, showing bio-concentration factors or equilibrium plant-air partition coefficients (K_{PA}, defined on a volume/volume base) in the order of 10^6-10^8 (9-11).

Forests cover approximately one-third of the world's land area (12) and form one of the world's largest organic carbon stocks (13, 14). This, allied to their large unit area standing biomass and high carbon turnover rates, means that forest canopies have the potential to affect air-surface POP partitioning significantly. In a mature forest canopy, there is as much as 8 - 10 m^2 of organic leaf surface per unit of ground area which is available for POP exchange with air (15). In addition, the organic carbon pool of the forest canopy is structurally organized to optimize light harvesting and gas exchange (16), thereby inadvertently enhancing the rate of air-leaf gaseous exchange of POPs (17).

Horstmann and McLachlan (18,19) investigated the air-canopy exchange of POPs and showed that yearly averaged deposition fluxes to forest soils were 3-5 times higher than to bare soils. Additional experimental confirmation of this effect was obtained more recently (20, 21). Using these results, some global scale model assessments have been performed which, through arbitrarily attributing annual POP deposition velocities for different forests types (22-24), indicated that the presence of vegetation can significantly affect the global distribution of POPs (22-24). However, for regions experiencing significant seasonality, 'yearly averaged' characterisation of air-canopy exchange of POPs such as these ignore the potentially important effects of intra-annual changes in forest composition, biomass, boundary layer and surface roughness. To understand the importance of these dynamic effects requires studies which are able to resolve this temporal variability at the forest scale. To date, such studies have been notable by their absence in the POP literature.

This paper exploits a simple mass balance framework accounting for the role of vegetation structure, temperature and biomass growth, combined with data from a recent field study reporting the accumulation of POPs in the leaves of two alpine forests (11) over a single growing season, to attempt to resolve the temporal evolution of the air-canopy exchange flux of POPs, F (ng m^{-2} d^{-1}) and the effective air-canopy mass transfer coefficient, k_u (m d^{-1}).

Methods

Data source

Nizzetto *et al*. (11) provide experimental data from a field campaign performed in April-October 2005 where a range of PCBs were measured in the atmosphere and vegetation of two Italian alpine broadleaved forests, with one at 1100 m the other at 1400 m altitude (referred to as the 1100 and 1400 m site, hereafter). During the same period data were also collected in a third forest site located at an altitude of 1800 m on the same slope comprised exclusively of larch (*Larix deciduas*), a deciduous conifer. Figure SI 1 shows the forest composition and structure of the sites and Text SI 1 describes the characteristics of the dataset and provides some considerations of the spatial scale and the significance of the present calculations. Available data include: PCB canopy concentration (C_C; pg g^{-1} dw); air concentrations (C_A, pg m^{-3}); leaf area index (*LAI;* m^2 m^{-2}, referring to 1 side of the leaf); mean canopy specific leaf area (SLA_C; m^2 g^{-1} dw, referring to 1 side of the leaf); data on forest composition, and air temperature (T). Additionally ref. 11 reports estimates of the equilibrium leaf-air partition coefficients (K_{PA}; m^3 of air per g of leaf dw) for the dominant tree in the forest sites.

Estimation of POP fluxes to the canopy, F

Because of the discrete, unevenly sampled nature of the canopy characteristics measurements, experimental results for C_C, *LAI* and *SLA* were interpolated using low order polynomials (Figure 1). This allowed the functions describing their seasonal variability to be obtained on a daily resolution, and time derivatives to be calculated.

The accumulation of POP in the canopy per unit of ground surface at a given time, *U* (ng m^{-2}) is given by,

$$U = BC_C = \frac{LAI}{SLA_C} C_C \times \frac{1}{1000} \qquad 1)$$

where *B* is the canopy biomass (g m^{-2}, dw) and 1000 is the scaling factor which provides the correct unit fo *U*. Finally, $F = dU/dt$ (ng m^{-2} d^{-1})

Effective air-canopy mass transfer coefficient estimates, k_u

The accumulation of atmospheric POPs by vegetation can be described by considering the forest canopy as a single homogenous compartment in contact with the air, with diffusive exchange of POPs between the air and the canopy described by a standard linear gradient analogue. Thus, the air-canopy exchange flux of POPs, *F* can be described as follows (16):

$$F = k_U 2LAI \left(C_A - \frac{C_C}{K_{PA}} \right) \qquad 2)$$

Obviously equation 2 only attempts to describe the uptake of gaseous compounds and not of those associated to particles. However, it was shown that in these sites the particle phase concentration of the selected compounds is negligible (11, 25). The coefficient 2 is needed to account for both the sides of the leaves (see above).

Although conceptually simple, equation 2 captures both the mass transport characteristics of the air-canopy exchange in addition to the effects of canopy growth dilution on C_c. Remembering the definition of *F*, equation 2 can be rewritten as follows:

$$\frac{dC_C}{dt} = k_U 2SLA_C\left(C_A - \frac{C_C}{K_{PA}}\right) - k_G C_C \qquad 3)$$

with $SLA_C = \frac{LAI}{B}$ and k_G (the growth dilution rate, d^{-1}) defined as $\frac{dB}{dt}\frac{1}{B}$.

In summary, the following assumptions have bveen made in the present analysis:

i) Given the small proportion of the atmospheric PCB which is particle bound (11-25), aerosol deposition (wet and dry) onto canopy surfaces was assumed to be negligible;

ii) During the sampling campaign precipitation averaged 500 mm (21). Even assuming a worst case scenario (i.e: that this amount of water is at equilibrium partitioning with the atmosphere and that after the impact with the canopy surface, the load of pollutants is instantaneously transferred to the leaves) wet deposition is not expected to produce any significant effect on C_C and hence has been ignored

iii) because the time frame of the study only covered the active growing season, and taking into account the persistence and hydrophobicity of the chemicals being considered (26), loss of POPs from the canopy due to reaction or wash-out is negligible;

iv) POP loss from the canopy due to cuticular wax erosion has been hypothesized in previous studies (18, 21) although it is not clear if this can significantly influence canopy PCB concentration in deciduous forests. This loss process are driven primarily by a leaf mass export from the canopy. Recent studies (27, 28) showed that only a small fraction of the total PCBs in the leaf foliage is expected to be stored in cuticular waxes. Finally, it has been shown that the total deposition of PCBs during spring and summer is negligible compared to the litter fall period in deciduous stands (20).

v) Although non-leaf surfaces (i.e. tree bark and soil) can also accumulate significant amounts of POPs directly from the atmosphere (29), these are considered negligible compared to that accumulated by foliage, given the latter's larger surface area (18, 21) and that changes in bark mass are very small compared to changes in leaf area.

Providing K_{PA} is known, all terms in equation 2 are known other than k_U which can, as a result, be determined. Ref. 11 reports estimates of K_{PA} values for the dominant species at the 1100 m and 1400 m forests. These values were derived based on the same dataset used in the present study to calculate F. In order to estimate k_U, it is important to use values derived from an independent dataset. For this reason, the K_{PA} values estimated for larch at the 1400 m site (11) were used in equation 1 together with C_C and the biophysical parameters of the larch stand at 1800 m (figure 1) to derive the k_U value for this site. The effect of temperature on K_{PA} was accounted for using the Van't Hoff equation with the enthalpy of plant-air phase transfer taken from ref. 30.

Propagation of uncertainties

The propagation of uncertainty was assessed using a simple Monte Carlo framework. The uncertainty in C_C and SLA_C estimates were assumed to be represented by the covariance matrix estimates of the polynomial parameters when fitted to the observed time series data in Figure 1. The uncertainty on LAI was obtained from the standard deviation of repeated (n = 10) measurements (11). The uncertainty in the measured C_A values was assumed to be described by the relative standard deviation of the reproducibility study presented in ref. 25. Finally, the uncertainty on K_{PA} estimates was that reported in ref. 11.

To translate these uncertainties into the final estimates of F and k_U, N = 10^4 repeat calculations were made for each time-step. For each calculation the observed terms in equations 1 and 2 were generated using the polynomial parameter combinations drawn randomly from the relevant covariance matrix, assuming normality in all cases.

Results

Figure 1 shows the least squares fits of low order polynomials used to capture the seasonal trends in the experimental observations. Calculations were performed for PCBs 101, 118, 138, 153 and 180 (as an example Figure 1 shows results for PCB 138 at the 1800 m site). This approach was not suitable to describe the behaviour of C_C for tri- and tetra-CB which showed more complex/uncertain dynamics (11). Therefore, these compounds were not considered in the present study. All variations in the observed terms with frequencies higher than the seasonal trend described by the polynomial fits are treated as noise. Thus the present approach only attempts to capture seasonality when estimating F and k_U.

PCB air-canopy exchange flux (F)

Figure 2 shows estimates of F derived for PCB 138 at the three forest sites. F was maximum in late spring, when a considerable amount of leaf biomass was already available for exchange, but C_C was still far from reaching partitioning equilibrium. F tended to decrease after this, reaching a minimum in mid summer when higher temperatures inhibited the canopy capacity for taking up POPs from the air. Similar behavior was previously described in a model simulation of the canopy uptake of POPs (31).

After this period, the estimates of C_C and B derived from the associated polynomials introduced significant uncertainty into the estimates of F, preventing any meaningful analysis. However, F is expected to tend to zero when the canopy approaches equilibrium partitioning with the air, although the decrease in temperature occurring at the end of the season could have enhanced deposition fluxes until litter fall. Given the large amount of leaf surface available at this stage, this effect could generate significant late season deposition fluxes. During the spring maximum (i.e the period of leaf growth), F for PCB 138 reached 0.9-1.1, 0.8-1.5, and 0.8-1.6 ng m^{-2} d^{-1} for the 1100, 1400 and 1800 m sites respectively. Table 1 reports overall mean and peak F values for other selected compounds. These fluxes are high but consistent with previously reported data obtained using deposimeters (20) although the estimates made here have resolved their seasonality, showing maximum daily F values a factor 1.4-3.4 higher than the overall mean value.

Air-canopy mass transfer coefficient (k_U)

The k_U estimates obtained here can be regarded as a measure of the average overall mass transfer coefficient for PCBs between air and vegetation (per unit of leaf surface) at the canopy spatial scale and on a time scale of weeks. Therefore, differences due to particularly dynamic atmospheric conditions (i.e. storms, strong wind speeds, diel variability of the turbulence in the atmospheric boundary layer) will not emerge from the dataset.

Results of the calculation of k_U for PCB 138 are reported in Figure 3 as an example. Considering the uncertainty amplified when rearranging equation (2), no significant seasonal trends were observed. However, there appears to be a tendency (especially observed for PCB 138, 153 and 180), toward high median values coinciding with the phase of biomass development and lower values during the warmest part of the year. After the end of June the estimation of k_U became compromised during certain periods. This was mainly dependent ($P<0.05$) on the value of the concentration gradient $\left(C_A - \frac{C_C}{K_{PA}}\right)$ tending to zero and hence generating critical numerical limits when rearranging equation 2. This not only occurred as the canopy approached equilibrium, but also in warmer conditions because the concentration gradient is negatively correlated to the temperature. It is possible to show that when the vegetation reaches 65 percent POP saturation the quality of the estimates of k_U generally drops (see figure SI2).

During August-September when the canopy POP saturation is high, the value of the concentration gradient is mainly influenced by the temperature dependence of K_{PA}. . Given there is no reason to expect that k_U falls close to zero in August and September, these low values are probably a result of the fact that the temperature dependence of the larch needle K_{PA} is different from that assumed from ref. 30 highlighting an area that needs developing in the analysis. At the beginning of the season the k_U estimates are much less influenced by this possible artefact because the level of equilibrium saturation is still low. Despite this limitation, the median value of k_U was always the same order of magnitude as the seasonal mean value.

The best estimates of k_U were mainly obtained between May and the end of June when C_C was still far from approaching partitioning equilibrium. In this phase, the 95 percent confidence interval on the k_U estimates was approximately a factor of 2 around the median values. The overall means of k_U values calculated for selected compounds in the period between 2 May -16 June are reported in Figure 3 and ranged between 43-95 m d^{-1}. Considering the uncertainty, no significant differences ($P<0.05$) were observed among different compounds.

Other studies attempted to provide estimates of the POP transfer rate between the air and the forest canopy (18-21) in the form of mean seasonal deposition velocities v (m d^{-1}). Remembering its definition (18) v can be regarded as the velocity of the transfer of POPs between air and the forest per unit of ground surface. The value of v estimated for selected compounds has been reported previously for the same forest canopy at 1800 m site (21). This was obtained using deposimeters, a method that can account for the effect of different loss processes from the canopy (i.e. wax erosion and wash out). It is possible to show that for compounds which do not reach the partitioning equilibrium within the growing season

$$v = 2LAI\left(\overline{k_U}\right) \qquad 4)$$

where $\overline{k_U}$ is the mean seasonal value of k_U. Using the data of PCB 180 (a congener that did not reach partitioning equilibrium (11) as an example) good agreement is obtained between the estimated value of v through equation 4 (620 m d^{-1} ranging 390 – 850 m d^{-1}) and the one measured (590 m d^{-1}) (21). This supports the aforementioned assumption regarding loss processes.

A limitation in estimating k_U using the present approach is the need to know the value of K_{PA} a priori. There is still only limited K_{PA} data for specific canopies (11, 18, 20). However, under the conditions of this study, the adopted framework is not particularly influenced by the uncertainty on the K_{PA} value. In fact, even adopting values reported for other forests/species (18, 20) (which, once corrected for temperature are higher by a factor ~4 compared to that used here) the seasonal mean value of k_U only changes by about 20%.

Testing the predictive capability of the modelling framework

The proposed framework was tested by comparing predicted and observed C_C values in the 1100 and 1400 m forests, over time. Calculations were performed using equation 3 by introducing the seasonal mean value of k_U derived from the 1800 m site data for selected compounds (Figure 3). Given that the 1100 m and 1400 m sites are multi-species forests, the adopted K_{PA} value for the prediction represented the weighted average of the dominant species, aggregated as a function of their relative abundance in the canopy. The reported experimental C_C values therefore also represent the mean canopy concentrations. Text SI 2 explains the method used for determining the forest composition, while Figure SI1 schematizes forest composition and structures.

The performance of the predictions is reported in Figure 4. Predictions successfully described the experimental observations at both sites. The ratio between predicted and observed C_C for all the considered compounds was 1.06±0.46 and 1.03±0.21 at the 1100 m and 1400 m sites, respectively. Standard sensitivity analysis showed that the most influential parameters in determining C_c were k_U and *SLA*. Despite this, equation 3 successfully predicted C_C for forest canopies with different structures (e.g. SLA_C varied by a factor of 2 between the 1400 m and the 1800 m sites and maximum *LAI* ranged between 4.1 and 5.4) and under different temperature conditions (mean seasonal temperature ranged at the three sites between 17 and 12°C).

Further work

The framework presented here offers an extension to the somewhat static analyses of air-canopy POP exchange presented to date (18, 20, 21, 32) by attempting to recover the seasonal characteristics of F and k_U for an Alpine forest area. One obvious limitation of the present framework is the need to assume values of K_{PA} a priori, whereas it is clear from equation 2 that identifying this value is in fact part of the problem. Fortunately, in relation to the present results, the sensitivity analysis indicates that the current framework is not sensitive to this when the canopy is far from the partitioning equilibrium.

Both the framework and the results from this study should be useful when incorporating vegetation compartments in regional or global fate dynamic models. Additionally, given the intimate association between the canopy carbon stock and POP turnover shown here, studies such as this should seek to further exploit the extensive network of tower-based carbon flux monitoring sites (33) when developing POP modelling and monitoring programs.

Supporting information available

Supporting information is available free of charge at http://pubs.acs.org including considerations on the spatial scale of the study and information on the forest composition.

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Table 1. Calculated values of U_{max} (ng m^{-2}), mean and max *F* (ng m^{-2} d^{-1}) for selected compounds. U_{max} is the maximum reached amount of a given compound sequestered in the canopy.

	1100 m			1400 m			1800 m		
	U (max)	*F* (mean)	*F* (max)	*U* (max)	*F* (mean)	*F* (max)	*U* (max)	*F* (mean)	*F* (max)
PCB 101	108	0.62	0.87	126	0.63	1.05	174	1.09	2.69
PCB 118	64	0.26	0.45	50	0.34	0.72	79	0.46	0.98
PCB 138	97	0.70	1.04	126	0.70	1.05	123	0.74	1.69
PCB 153	161	1.05	1.64	84	0.67	1.51	144	0.84	2.87
PCB 180	66	0.39	0.58	43	0.34	0.65	65	0.38	0.65

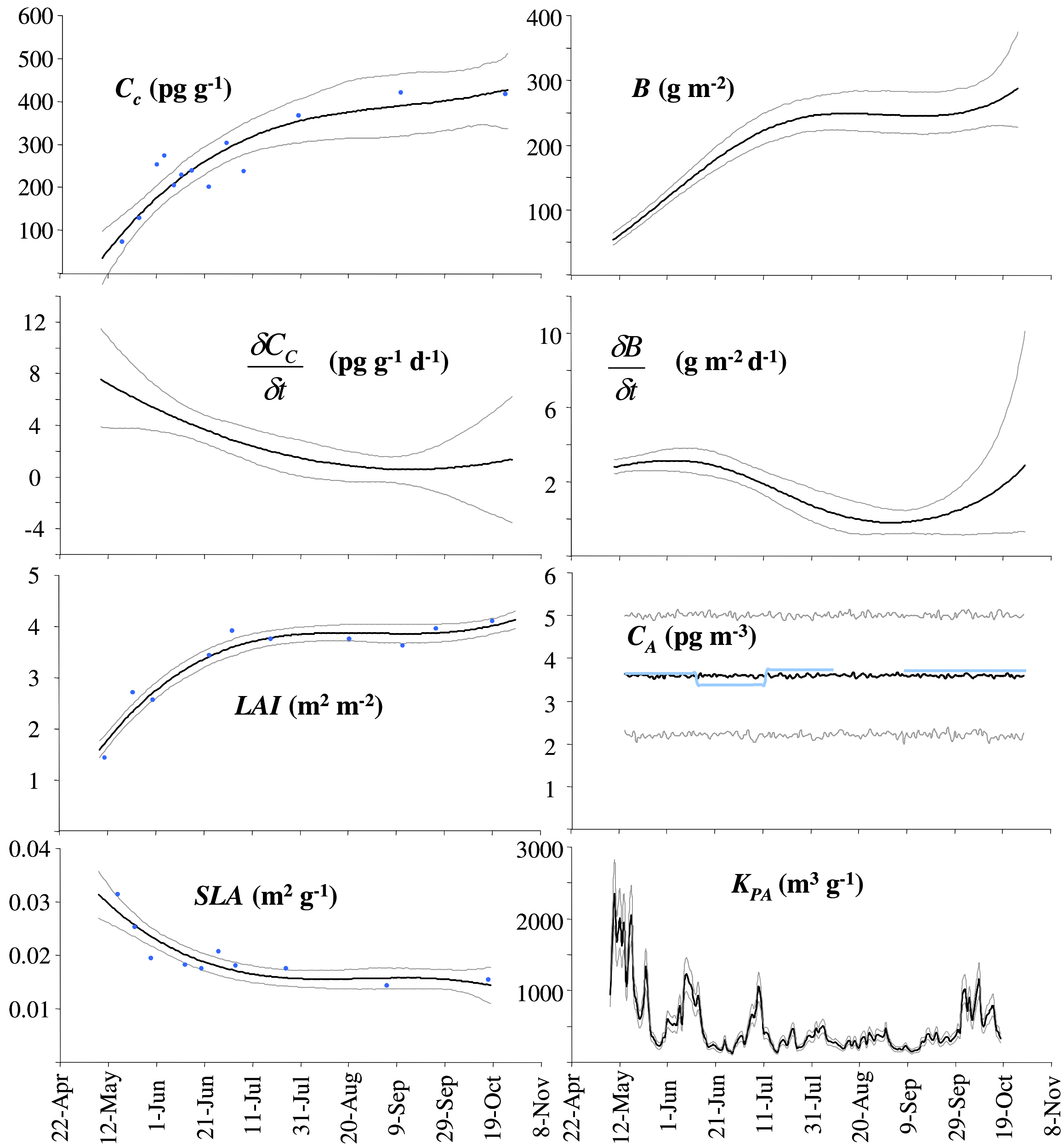

Figure 1. Experimental and modeled parameters for the calculation of k_U. The figure presents data for PCB 138 and the properties of the 1800m forest. Dots are experimental observations (11), the black line represents the median optimum fitted value of the modeled parameters, grey lines are 95% confidence interval. Blue lines in the C_A plot are measured mean values (11, 25).

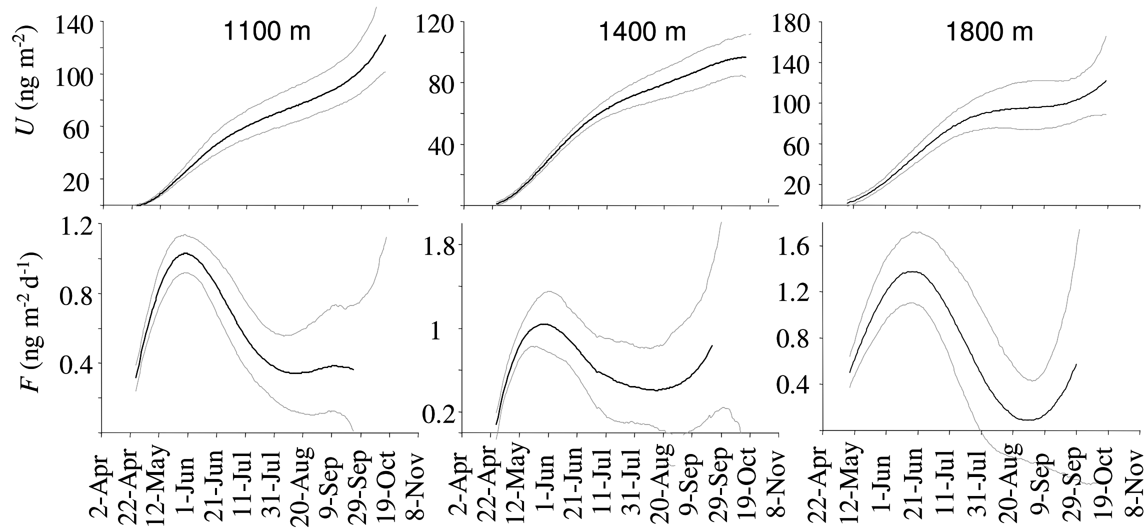

Figure 2. Plots to show how the amount (*U*) and the air-canopy exchange flux (*F*) vary seasonally for the two forested sites using as an example PCB 138. Note: the black line is the median, grey lines represent the 95% confidence boundaries.

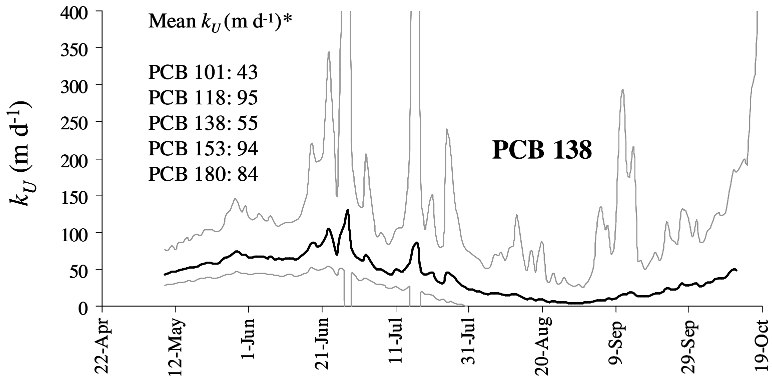

Figure 3. Derived values of k_U through the season at the 1800 m site (the example refers to the calculation for PCB 138). The median value is shown in black, while the grey lines represent the 95% confidence bounds of N = 10^4 Monte Carlo simulations.

* Averal mean for the best estimates (2 May- 16 June).

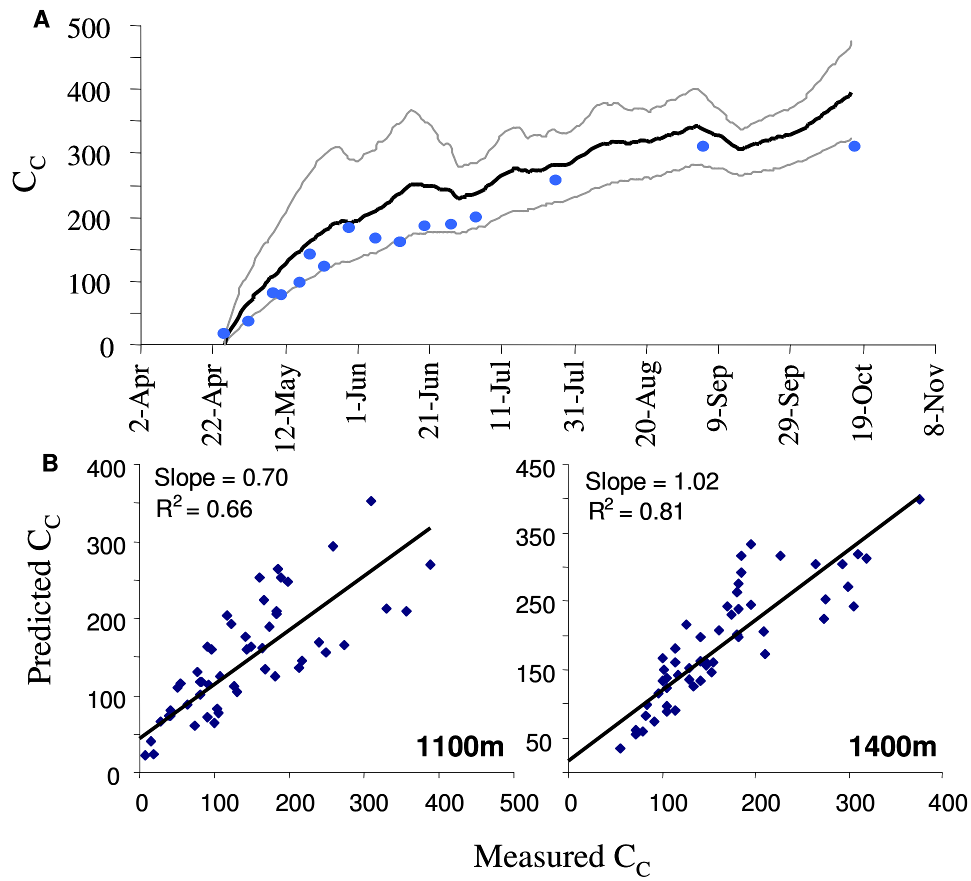

Figure 4: Assessment of the predictive ability for equation 2. A: comparison between experimental C_C (pg g^{-1} dw) (points) and predicted C_C with time (black line: median of the predictions; grey line 95% boundaries of predictions). Data refers to PCB 138 in the 1100 m forest. B: Predicted C_C (pg g^{-1} dw) vs observed for the 1100 m and 1400 m forest sites. Figure includes results for PCB: 101, 118, 138, 153 and 180. Calculations were performed using the seasonal mean k_U values reported in Figure 3.