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ARTICLE *in* ENVIRONMENTAL SCIENCE AND TECHNOLOGY · FEBRUARY 2008

Impact Factor: 5.33 · DOI: 10.1021/es070764f · Source: PubMed

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Received March 31, 2007. Revised manuscript received October 6, 2007. Accepted October 19, 2007.

The uptake kinetics and storage of PCBs by isolated cuticles and cuticular waxes from *Hedera helix*, *Prunus laurocerasus*, and *Ilex aquifolium* were studied. Small chambers were used, allowing variation in plant uptake parameters to be studied by having the same air boundary layer in each chamber. During the 64 day study tri- and tetrachlorinated biphenyls generally reached equilibrium in waxes but not in whole cuticles. Differences between species were observed. Higher chlorinated PCB congeners did not approach equilibrium in either sample type. Although PCBs showed higher affinity for waxes than whole cuticles, the latter dominated the total uptake capacity on a surface area basis, because of the large amount of nonwax cuticular components. Mass transfer coefficients (MTCs) for PCB uptake (into both cuticles and waxes) indicated partition dependence up to log octanol/air partition coefficients (K_{OA}) of 8.5−10, depending on species and sample type. For cuticles, higher MTCs occurred at the beginning of the experiment than later. This was not seen in reconstituted waxes, a difference which may be explained by the dispersion of intracuticular waxes within cuticles. For more lipophilic compounds, uptake appeared to be limited by diffusion processes, which may be influenced by plant physiology. Leaf surface area is, therefore, likely to control the ability of vegetation to scavenge these compounds from the air in many field situations.

Introduction

Vegetation is a dynamic environmental compartment which takes up semivolatile organic chemicals (SVOCs) from the atmosphere (directly from the gas phase, or as particles containing bound chemical). It can play an important role in the environmental fate of SVOCs (*1, 2*), influencing concentrations in the air (*3*) and in wildlife (*4*) and contributing to their global cycling. Uptake from the air is the major pathway for the accumulation of SVOCs in plant foliage (*5*), although there are still uncertainties in understanding and quantifying the processes involved. In particular, an understanding of the kinetics of SVOC uptake by vegetation is required, as it appears that the leaves of some plant species may reach equilibrium (or at least steady state) with air during one growing season, whereas others do not (*2, 6*).

Gas phase SVOCs need to move through the bulk air and the air-side boundary layer surrounding leaf surfaces, before partitioning to the plant material. On entering the leaf cuticle they may remain in the waxy and polymeric cuticular components or diffuse deeper into the leaf to reach intracellular storage compartments (*7, 8*). Which of these steps limits uptake depends on the properties of the compound, the plant and the environment. McLachlan (*7*) developed a framework for the interpretation of uptake observations that can help to distinguish between different controlling processes. The uptake of SVOCs by vegetation from the gas-phase is often described using a two-resistance model, with an air side resistance due to the air boundary layer surrounding the leaves and a plant side resistance resulting from limited diffusion of compounds within the vegetation (*9*). For polychlorinated biphenyls (PCBs), field experiments provide evidence that diffusion through the air boundary layer limits the uptake rate and can prevent plants from reaching equilibrium within a growing season (*10*). On the air side, wind speed may be an important variable, since boundary layer thickness decreases with increasing wind speed. However, particularly for the less chlorinated PCB congeners, studies have also indicated the importance of plant side resistance (*11, 12*). Cuticle thickness and other properties (such as the crystallinity of the epicuticular waxes) may influence the role of the cuticle as a barrier (*13*).

A simplified way of describing vegetation is required to use mathematical models for the fate of SVOCs in the environment, and this has often meant a one-compartment model to describe the plant (either by total plant weight or by its lipid content) (*14*). Generally, no distinction has been made between cuticular and intracellular lipids, even though the latter may not receive significant amounts of compounds entering the leaf mainly through the cuticle (*15*). Other leaf constituents, such as cutin, are generally not taken into account. However, experimental results show that two-compartment models, consisting of a fast equilibrating surface compartment and an internal reservoir compartment that needs much longer to achieve equilibrium, can explain uptake phenomena better (*11, 16*). It is still uncertain which constituents of the leaf (i.e., cuticular waxes alone, or along with other cuticular constituents) form the surface (rapidly reacting) compartment.

The aim here was to study the uptake kinetics and storage of PCBs in isolated cuticles and cuticular waxes. Small, identically designed chambers were used, where the air boundary layer was fixed, to allow comparison of varying plant-side resistances with different isolated cuticle compartments from different species. PCBs were chosen, because they provide a range of vapor pressures and partition coefficients over several orders of magnitude within a single chemical family, to allow the influence of compound properties to be assessed.

Materials and Methods

Preparation of Cuticles and Waxes. Cuticles were isolated from mature leaves of *Hedera helix* (common ivy, hereafter called ivy), *Prunus laurocerasus* (cherry laurel, hereafter called laurel) and *Ilex aquifolium* (common holly, hereafter called holly) using an enzyme method described in detail elsewhere (*17*). These species were chosen because detailed information about composition of cuticles and cuticular waxes is available from the literature. Figure 1a gives a schematic of a leaf section, showing which parts have been isolated by enzymolysis. Briefly, the method involved the following: 15 × 15 mm squares were cut from the leaves (avoiding the main veins) and immersed in an aqueous enzyme solution (2% pectinase and 2% cellulase in 0.001 M NaN_3, buffered to pH

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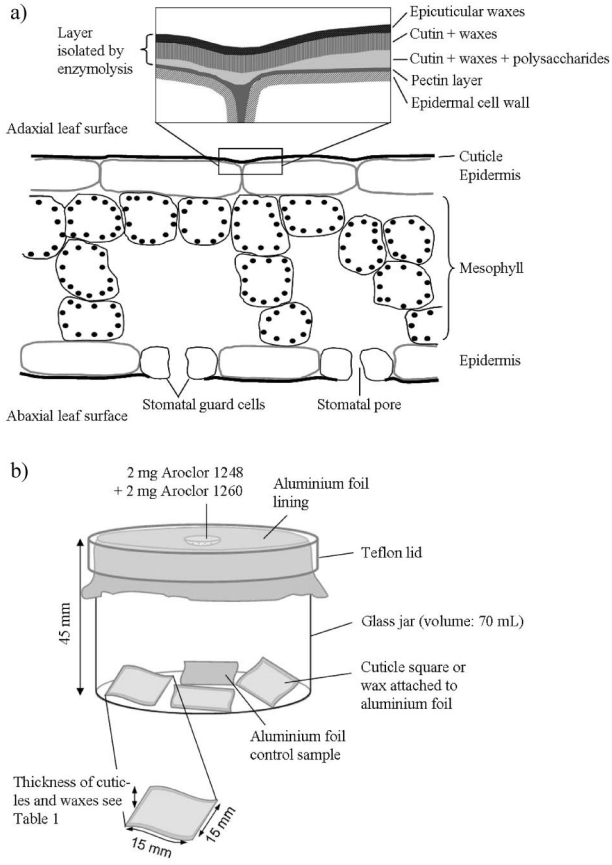

FIGURE 1. Schematic of (a) a leaf section, illustrating the parts isolated by enzymolysis in detail, (b) the experimental setup of the small chambers for the uptake of PCBs by cuticle and wax samples.

3 with 0.01 M citric acid and 0.01 M KOH). The leaf squares were placed in a reduced-pressure desiccator for 3 h to improve the infiltration of the enzyme solution. After an incubation period of 5−7 days, cuticles could be separated easily and any remaining tissue was removed carefully with a stream of deionized water. Only adaxial cuticles, where no (or very few) stomata can be found, were used for the following experiments. Cuticles were soaked in 0.01 M $Na_2B_4O_7$ solution (pH 9) for 3 days with frequent solution changes to remove substances that were released from leaf tissues during enzymatic isolation and may have been absorbed by the cuticles (*17*). After washing with deionized water, cuticles were laid flat (with the epicuticular surface outermost) on to small, preweighed, aluminum foil squares and stored until further use in a jar containing a desiccant (silica gel).

Cuticular waxes were extracted from isolated dry cuticle squares by soaking in dichloromethane (changed every 1.5 h) for 6 h with gentle automatic shaking. All extracts of the same batch of cuticles were pooled, reduced to a known volume and aliquots (each equivalent to one cuticle square) of this wax solution were applied with a syringe to preweighed aluminum foil squares of the same area as the cuticle squares. The amount of wax applied to each square corresponded to the average amount extracted from one cuticle. For the uptake experiment, aluminum foil pieces were only used if an even wax layer had formed after evaporation of the solvent, i.e. no spots or patches were visible, because varying thickness and surface morphology may influence sorption kinetics.

The weight of each cuticle was determined directly, prior to the start of the uptake experiment. The weights of the wax layers were calculated as a proportion of the residue left from the wax solution equivalent to 10 wax squares, because of the small amount of wax on each aluminum square. Unusually light and heavy dry cuticles were discarded to achieve a cuticle weight standard deviation below 10% for each species, for the entire study.

Uptake Experiment. The experiment was conducted using small, uniformly designed chambers, so all samples experienced an air side boundary layer of the same thickness. This unmixed layer, where substances can move by diffusion only, was thicker than under real environmental conditions due to the sealed design of the chambers. The fixed air-side resistance allowed the effect of varying plant-side resistances to be studied (by using different cuticle compartments and plant species) as well as the influence of varying chemical properties. Contamination chambers were cylindrical glass jars (height: 45 mm, volume: 70 mL) with aluminum foil lined Teflon lids. In each chamber 2 mg of each of Aroclor 1248 and 1260, dissolved in hexane, were applied directly to the aluminum foil lid-lining (see Figure 1b for a schematic of the experimental setup). After the solvent had evaporated the chambers were sealed for three days to allow the glass walls to become saturated with PCBs prior to the start of the experiment.

Three cuticle or wax squares were placed on the bottom of each chamber (to act as triplicate samples for one time point), together with one aluminum foil control sample. Chambers were stored at 20 ± 1.5 °C until sampling. The sampling points were 1, 2, 4, 8, 16, 32, and 64 days after the beginning of the experiment. Care was taken to minimize the time the chambers were opened and to keep them closed tightly throughout the experiment. Day 0 was represented by cuticles and waxes not exposed to PCBs in the chambers. At the end of the exposure period, samples were removed from the chambers and stored in solvent rinsed aluminum foil at −20 °C until analysis.

Analysis. Prior to extraction, samples were spiked with ^{13}C-labeled PCB congeners ($^{13}C_{12}$ PCB 28, 52, 101, 138, 153, 180, 209) to assess their recoveries in the method. Samples (including blanks and controls) were Soxhlet extracted for 16 h with dichloromethane (DCM). Extracts were then rotary evaporated and cleaned on chromatography columns packed with acidified silica (8 g; 2:1 silica/H_2SO_4 by weight) underneath activated silica (8 g; Merck), eluted with hexane. Extracts were further cleaned by gel permeation chromatography (GPC) using Biobeads SX3 (BioRad laboratories) eluted with hexane/DCM (1:1). Finally, dodecane containing PCB 30 and $^{13}C_{12}$ PCB 141 internal standards was added and the samples were reduced to a final volume of 25 μL prior to GC injection. The samples were injected splitless and analyzed for a total of 34 PCBs (trichlorinated: PCBs 18, 22, 28 + 31; tetrachlorinated: PCBs 41 + 64, 44, 49, 52, 56 + 60, 70, 74; pentachlorinated: PCBs 87, 90 + 101, 95, 99, 105, 110, 118; hexachlorinated: PCBs 138, 141, 149, 151, 153; heptachlorinated: PCBs 170, 174, 180, 183, 187); octachlorinated: PCBs 194, 199, 203 on a Finnigan Trace GC-MS operated in electron ionization (EI+) mode, using selected ion monitoring (SIM). Separation was carried out on a CP-Sil8 capillary column (Chrompak/Varian, Palo Alto, CA, 5% phenyl, 95% dimethylpolysiloxane, length 50 m, diameter 0.25 mm) using helium as carrier gas.

Quality Control. Recoveries of all ^{13}C labeled PCBs were 71–122% with averages between 86 and 98% for individual congeners. No trend could be observed between the degree of chlorination and recovery rates. All reported values are blank corrected using the average concentrations of the aluminum foil control samples, but not corrected for the recovery rates of labeled compounds. PCB concentrations in control samples showed only small variations and were <10% of the concentrations in plant material samples after one day of exposure for low chlorinated PCBs and <20% for higher chlorinated congeners. They did not increase after

TABLE 1. Average Weight of Cuticle and Wax Samples in the Present Study and from the Literature

	common ivy	cherry laurel	common holly
cuticle weight (mg)	1.68	1.94	4.91
standard deviation (%)	7.24	9.33	7.67
cuticle thickness (μm)	6.78	8.04	19.9
cuticle thickness observed in other studies (μm)	1.96[a] 4.91[b]	0.7[c]	10[a]
wax weight (mg)	0.07	0.33	0.93
wax layer thickness (μm)	0.34	1.63	4.59

[a] Ref *18*. [b] Ref *19*. [c] Ref *20*.

the first sampling day, indicating that they had reached equilibrium with the air quickly. Reported results were calculated from the average concentrations of the triplicate samples. Standard deviations between triplicate samples were usually between 3 and 16%, but higher in samples taken on day 0 and day 1 (2−47%).

Results and Discussion

Characterization of Plant Material and Experimental Conditions. *Isolated Cuticles and Waxes.* Average weights of cuticles and wax samples are given in Table 1, together with their estimated thickness, assuming a density of 1.1 g/cm^3 for whole cuticles (*21*) and 0.9 g/cm^3 for waxes. These estimates should be regarded as approximate, since densities may vary between species and even single leaves. Ivy leaves had the thinnest cuticle and the lowest amount of extractable wax, whereas laurel had slightly thicker cuticles but much more extractable wax. Holly had the thickest cuticle and the highest amount of wax of the three species. The cuticle thicknesses obtained in this study appear to be relatively high compared to those reported in other studies (see Table 1). The fact that mature leaves were used may explain this, since significant changes occur in cuticles during leaf development (*19, 22*).

Temperature and PCB air concentrations. Changes in temperature can affect uptake of PCBs by cuticular material since the vapor pressure, cuticle/air- and wax/air-partition coefficients, and diffusion coefficients are all temperature dependent. The average temperature (the mean of the lowest and highest temperatures observed each day) was stable (20 ± 1.5 °C) throughout the experiment. It was therefore assumed that there are no temperature-related variations in mass transfer in the study. Since it is not possible to make measurements of PCB concentrations in air in the sealed chambers used, concentrations were estimated applying the ideal gas law and Raoult's Law using the vapor pressure of the individual PCB congeners at 20 °C (*23*) and their mole fraction in the Aroclor mixture which was determined by gas-chromatographic analysis. These data are shown in Supporting Information (SI) Table S1 along with octanol/air partition coefficients (K_{OA}) at 20 °C. Note that these concentrations assume that diffusion throughout the chamber occurs more rapidly than through the leaf parts.

PCB Uptake by Whole Cuticles and Cuticular Waxes. SI Figure S1 shows typical concentration-time plots for a number of PCB congeners in laurel cuticles. Similar patterns were seen for the other species and in waxes (not shown). Concentration-time plots of single congeners for cuticles and waxes of all three species are presented in Figure 2. Trichlorinated biphenyls (tri-CBs) generally reached equilibrium in cuticular waxes within 64 days for ivy and laurel, and were close to equilibrium at 64 days for holly (see Figure 2a). It can be assumed that the flattening of the uptake curves indicated approaching equilibrium rather than the end of an initial surface saturation phase since, as Barber et al. (*6*) indicated, such a rapid initial phase lasts only a few hours. Tetra-CBs also appeared to approach equilibrium after 64 days, but the more chlorinated PCBs required more time (Figure 2). PCBs did not reach equilibrium in the whole cuticles within 64 days, but for tri- and tetra-CBs a leveling of the concentration−time curve was seen (Figure 2).

The absolute amount of PCBs taken up after the same exposure time was similar for waxes and cuticles for all three species when equilibrium was not approached. This indicates either an air-side limited uptake process or, if wax/cuticle side limited, similar transport velocities within the different sample types and species.

It is clear, from comparing weight corrected PCB concentrations in the cuticles and waxes (see SI Table S2) that PCBs have a much higher affinity for waxes than for the other cuticular constituents. However, the amount of PCBs that can accumulate in complete cuticles far exceeds the amount taken up by cuticular waxes because of the much higher mass of the nonwax cuticle components, as shown in Figures 1b−e. This has also been seen for PAHs in pepper cuticles (*26, 27*).

Species Differences in PCB Equilibrium Concentrations. Only lower chlorinated PCB congeners reached equilibrium in waxes, so this interspecies comparison is focused on these compounds. There were differences in the amount of PCBs taken up by waxes by different plants on both a pg/sample and pg/mg wax basis. In general, the amount of PCBs accumulated per sample was in the order ivy wax < holly wax < laurel wax. However, ivy accumulated the highest PCB concentrations per mg wax (SI Table S2). It is clear, therefore, that both the amount of wax present (or rather, extractable with dichloromethane) and the composition of the waxes influence the capacity to accumulate PCBs. In particular, differences in polar wax components between species may explain variations, since these substances lower the lipophilicity of the whole wax mixture. It has been shown that cuticular waxes from mature leaves, such as the leaves used in this study, contain significant amounts of polar compounds (*22, 28, 29*).

Logarithmic plots of the wax-air partition coefficient K_{WA} against K_{OA} show slopes above 1 for compounds that reached equilibrium (1.5 to 1.9; see Figure 3). K_{WA} was calculated as the quotient of concentrations of individual PCBs in the wax (C_W in ng/cm^3) and in the air (C_A in ng/cm^3) (using the average of all sampling events when equilibrium was apparently achieved and assuming a density of 0.9 g/cm^3 for the waxes). Slopes that differ from 1 indicate that octanol is not an ideal surrogate to model the uptake capacity of cuticular waxes for PCBs. However, since K_{OA} is the only partition coefficient available for a wide range of SVOCs, its use is likely to continue, but perhaps with due consideration of species differences. Furthermore, different intercepts of the regression lines among the three species may indicate variability in the percentages of octanol-like substances in cuticular waxes, with very low intercepts resulting from relatively high contents of more polar compounds. This could be important when results for the same species at different times in the growing season are compared. An increase in the relative proportion of polar wax components with increasing age of the leaves (as observed for ivy) (*22*) may promote revolatilization from the cuticular wax as its constitution changes, even if the total wax content only undergoes minor changes.

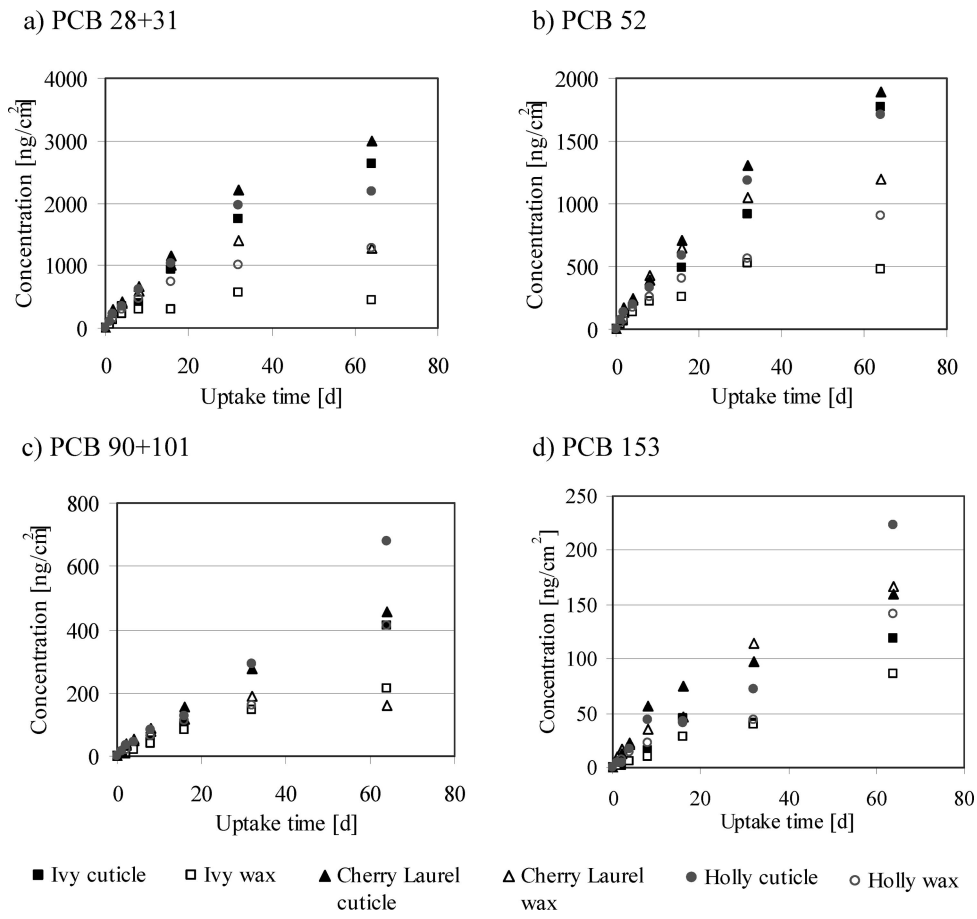

FIGURE 2. Concentrations [ng/cm²] of selected PCB congeners, taken up by cuticle and wax samples, against the uptake time (single congeners in cuticles and waxes for all the three species studied).

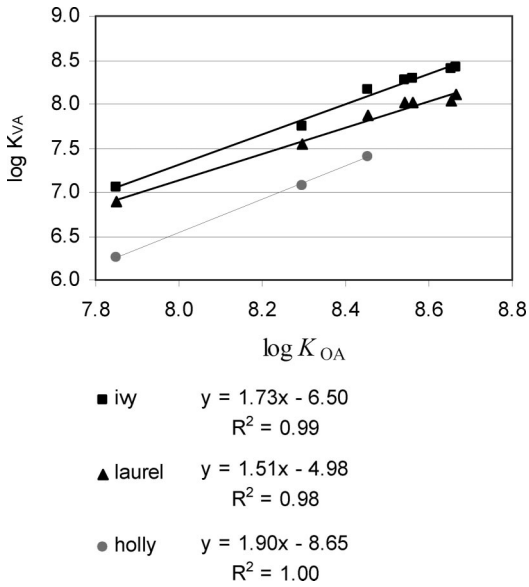

FIGURE 3. Log K_{VA} against log K_{OA} for tri and tetra-CBs in waxes.

Mass Transfer Coefficients (MTCs): Calculation. To describe the uptake of PCBs by cuticles or waxes from the gas phase, a two-resistance model can be used (*7*).

$$d(VC_V)/dt = Av_A(C_A - C_V/K_{VA}) \quad (1)$$

where C_V and C_A are as defined above, A is the surface area and V the volume of the vegetation (compartment), K_{VA} is the vegetation/air-partition coefficient and t is time. After integration of eq 1, the concentration in the vegetation (compartment) can be calculated at any time from the following:

$$C_V = K_{VA}C_A(1 - \exp[-Av_A t/(VK_{VA})]) \quad (2)$$

The overall MTC v_A comprises v_{AA}, the mass transfer coefficient for transport through the air (both laminar and turbulent, if applicable), and v_{AV}, the mass transfer coefficient for transport from the vegetation (compartment) surface to the place where contaminants are stored (*7*).

$$v_A = (1/v_{AA} + 1/(K_{VA}v_{AV}))^{-1} \quad (3)$$

According to equation 1, v_A can be obtained from plots of the uptake experimental data expressed as $[VC_V/(A(C_A - C_i/K_{VA}))]$ against time if V, A, K_{VA}, and C_A are constant. As long as the vegetation compartment is far from equilibrium with the air, C_V/K_{VA} is much smaller than C_A and eq 1 can be simplified:

$$d(VC_V)/dt = Av_A C_A \quad (4)$$

Since cuticles did not reach equilibrium for any PCB congeners in the uptake experiment equation 4 was used to calculate overall MTCs for the uptake of PCBs for each sampling day using the time and concentration difference from the previous sampling day. C_V was replaced by the concentration of target compounds in the cuticle (C_C) here. As long as log v_A versus log K_{OA} plots for compounds that experience predominantly K_{OA} controlled uptake show similar slopes, the uptake slowdown due to approaching equilibrium is presumably negligible. Many of the concentration-time

plots showed a flattening of the curve for the latest data points (see Figures 1)a−d. Therefore only the results of the first 8 days are considered for further discussion (detailed concentration-time plots of this period can be found in SI Figure S2).

Waxes reached equilibrium for tri and tetra-CBs, so K_{WA} was calculated and υ_A could be determined using equation 1 where K_{VA} was replaced by the wax−air partition coefficient K_{WA} and C_V by the concentration of target compounds in the wax (C_W). It should be noted that υ_A is very sensitive to experimental and analytical variability at concentrations close to the estimated equilibrium concentration, because of the way it is calculated. For higher chlorinated PCBs it was not possible to estimate K_{WA}, although the concentration−time curve flattened significantly. Thus eq 4 was used for penta-, hexa-, and hepta-CBs, and for tetra-CBs in the case of holly, but only data for the first two days were used to minimize the error due to the convex curves. SI Tables S3 and S4 give υ_A values for all PCB congeners monitored in cuticles and waxes, and K_{WA} for waxes, if applicable.

Mass Transfer Coefficients: Significance. Assuming that K_{VA} in eq 3 can be expressed by the following function:

$$K_{VA} = mK_{OA} \tag{5}$$

A plot of log υ_A against log K_{OA} can give information about the process(es) limiting the uptake of pollutants from the air if a sufficient range of lipophilicity is covered (*7*). For substances with relatively low K_{OA}, the term $1/(K_{VA}\upsilon_{AV})$ will contribute significantly to υ_A, so υ_A should increase with increasing K_{OA}. The MTC of transport through the air, υ_{AA}, is mainly influenced by the thickness of the air boundary layer and the diffusion coefficient of the pollutant in air.

Since the diffusion coefficients of POPs in air only vary within a factor of about 2, due to the limited range of molecular weights (*30*), υ_{AA} will be relatively similar for all PCB congeners and, compared to υ_{AA}, $1/(K_{VA}\upsilon_{AV})$ becomes negligible for substances with high K_{OA} values. Thus, υ_A should be independent of K_{OA} for highly lipophilic compounds, as long as particle binding does not play a major role.

Figure 4 shows plots of log υ_A against log K_{OA} between day 1 and day 2 of the experiment for cuticles and waxes of the three plant species studied. At this early stage the influence of approaching equilibrium conditions was lowest. Interspecies variations of υ_A are most likely the result of plant/cuticle specific properties such as K_{VA}, diffusion coefficients and distances in cuticles/waxes.

Wax and cuticle samples from laurel and holly show a K_{OA} dependence of υ_A up to log K_{OA} values of about 9.5, whereas the uptake into ivy samples seems to be K_{OA} independent from log K_{OA} of about 8.5. This difference may be explained by the higher weight based equilibrium concentration in ivy waxes than in the other two species, which is either caused by less polar wax components in general or a lower content of polar substances in the cuticular wax from ivy, as discussed earlier. Both decrease plant side resistance compared to laurel and holly, where the possible presence of more polar wax components results in lower K_{WA} for PCBs and perhaps longer effective diffusion distances within the wax/cuticle.

Equilibrium is not approached, even for the less chlorinated congeners, indicated by the log υ_A−log K_{OA} regression curves remaining parallel. υ_A values in waxes are generally similar to $\upsilon_{A,\ 0-1}$ and $\upsilon_{A,\ 1-2}$ in cuticles, but higher than υ_A in cuticles at later stages. This may be explained by the preparation of the cuticles and reconstituted cuticular waxes, which contain both epicuticular and intracuticular waxes. After reconstituting, the intracuticular waxes in particular may form a more compact film than in whole cuticles, potentially shortening the transport distances for lipophilic compounds within reconstituted waxes, and therefore, increasing υ_{AV}. The relatively high υ_A in cuticles seen at the beginning of the experiment may be caused by the epicuticular waxes that, for the plants studied, form an even, glossy top layer without crystals (*31*). These may become saturated with PCBs after a short period of exposure. Other explanations for this effect are that a layering of chemically distinguishable cuticular waxes (i.e., possibly varying in their sorptive and diffusional properties), which was observed in *Prunus laurocerasus* (*32*), gets lost by reconstituting waxes, and the specific surface area of the waxes may also change during this procedure. The observation that such systematic differences between early and later υ_A do not exist if the uptake is independent from K_{OA} supports this interpretation. This supports findings by Barber et al. (*12*) where a two-phase uptake process of PCBs into leaves was observed.

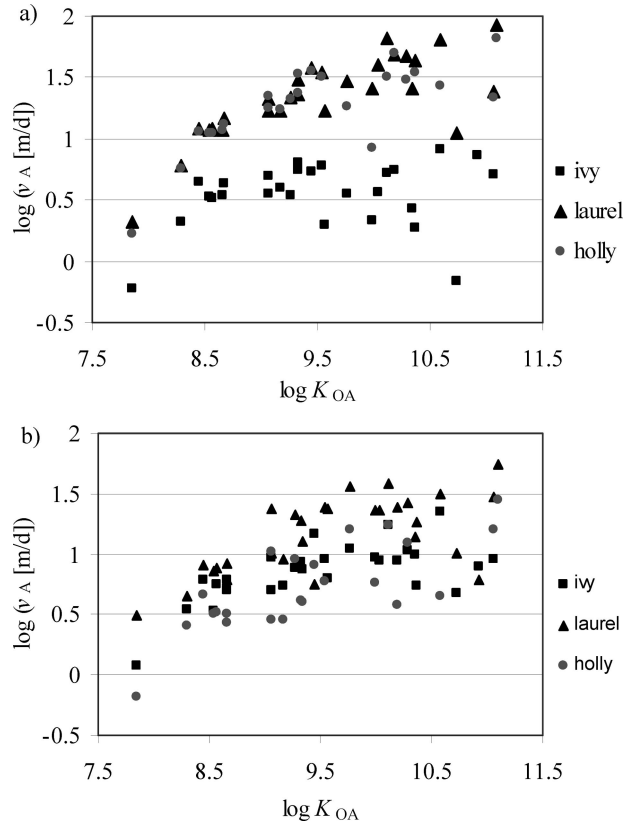

FIGURE 4. Log (υ_A [m/d]) calculated for the period day1-day2 against log K_{OA} in (a) cuticles and (b) waxes.

Comments on Applicability of the Results to Real Environmental Conditions. This study allows comparison of the uptake of PCBs into whole cuticles and extracted waxes from the same and different species using a study design that excluded the major sources of field variation (e.g., caused by variations in leaf surface area and shape, canopy density, and wind speed). The boundary layers around cuticle and wax samples in the chambers were believed to be uniform, but greater than those that have been estimated for single leaves in natural environments where they are assumed to be only a fraction of a millimeter deep (*33*). However, experimental results showed that effective boundary layer thicknesses of a few centimeters are possible, probably caused by canopy effects (*10*). The present overall MTCs are within (or exceed) the range observed in other studies on complete leaves (*12, 15*). Therefore, we believe it is acceptable to apply the conclusions made from these data to field situations. The kinetically limited uptake, as it could be observed for PCBs with log K_{OA} higher than ca. 9.5 or 8.5 (depending on the plant species) suggests that the "air cleaning capacity" of vegetation systems in the field will be leaf surface area

controlled for many PCB congeners (and other compounds with similar properties).

Acknowledgments

We are grateful to the EU AQUATERRA project for financial support.

Supporting Information Available

Additional information in one figure and four tables. This material is available free of charge via the Internet at http: pubs.acs.org.

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