Biogeosciences Discuss., 5, S1558–S1569, 2008
www.biogeosciences-discuss.net/5/S1558/2008/

Biogeosciences Discussions

Interactive comment on "Plant physiological and environmental controls over the exchange of acetaldehyde between forest canopies and the atmosphere" *by* K. Jardine et al.

K. Jardine et al.

Received and published: 30 August 2008

We are very thankful for the thorough review which should help start a public discussion and improve our manuscript if accepted. Our point by point responses are below:

Reviewer comment: According to the model by Niinemets and Reichstein (2003) the exchange is dependent on the source (production) term, the water solubility (Henry's constant), the stomatal conductance, and the (fast and slow) aqueous storage capacity. The idea that the production may also be compensated by physiological consumption within the plant, preventing further plant internal accumulation, is indeed a critical detail that extends the more physicochemical view of the aforementioned model. However, the impact of the stomata on the emission rate (and delta c, respectively) is also de-

pendent on the size of the aqueous storage pool, the pH and the temperature; all influencing the Henry's law concept (see also Gabriel et al. 1999).

Response: We agree and propose to insert the following passage: Page 2662, line 17. Recently, a physicochemical model has emerged which estimates VOC emission rates from leaves as a function of a source (production) term, the VOC water solubility (Henry's constant), the stomatal conductance, and the (fast and slow) aqueous storage capacity (Niinemets and Reichstein, 2003). Here, we extend this more physicochemical view of the aforementioned model by suggesting that production may also be compensated by physiological consumption within the plant, preventing further plant internal accumulation.

Reviewer comment: I actually like having put together canopy flux and the lab exchange data. However, from my point of view, I am not as positive on the general agreement between both data sets as the authors tend to declare. In the lab mainly emissions (and very high compensation points) were observed, and in the field mainly deposition. In Fig. 8 the calculated canopy fluxes mainly revealed deposition for Michigan (MI), and North Carolina (NC). In North Carolina the peak in LAI rather corresponds with the strongest deposition flux (substantiating the emission scenario stated on page 2660, line 8 ff). In the Michigan case the peak in LAI (0.7 at 20m) actually corresponds to a mix of the strongest emission (calculated for 22m) and the strongest deposition (calculated for 17m), both of similar magnitude. The observed deposition fluxes are similar to those reported in Karl et al. (2005). According to the high compensation point concentrations found by the enclosure measurements, a strong emission would have to be assumed at the field sites with ambient concentrations below those of the compensation points, even as measured under absolutely dark conditions in the lab. Highlighting and discussing the discrepancies of the different approaches (enclosures versus the Lagrangian approach) could be one focus of the paper. For example, Karl et al. (2005, ACP) reported that ambient temperature lead to higher compensation points. How did the temperatures applied in the lab compare to those in the field flux sites?

BGD

5, S1558–S1569, 2008

Interactive Comment

The temperatures in the lab should have been higher than at the field sites to help to explain the discrepancies.

Response: While laboratory measurements of compensation point behavior are not expected to quantitatively match the behavior of field plants for a variety of reasons, the experiments do reveal important information on processes that likely occur in field plants. Our focus is to present novel quantitative laboratory and field data that help identify the key plant physiological and environmental processes that influence the exchange of acetaldehyde between plants and the atmosphere. We only have light/temperature profile measurements for the CHATS canopy and assume that during the day PAR and temperature decrease similarly from the top to the bottom in all canopies investigated here. In the lab, emissions predominated in the light (compensation points $>$12 ppbv) and uptake predominated in the dark (compensation points 1-3 ppbv). This suggests than sunlit leaves mainly emit acetaldehyde, while shade leaves have the potential to behave as sinks. This is consistent with what was observed at all three field sites where during the day net emissions occurred from the upper canopy while at lower heights, reduced emission rates or net uptake were observed. In the CHATS canopy during the day, the ambient concentration where net emissions rates were zero was 3.4 pbbv (at the bottom of the canopy). This is consistent with compensation point measurements on poplar branches made in the dark (1-3 pbbv). However during the day, strong uptake of acetaldehyde occurred within the lower canopies of Michigan and North Carolina with ambient concentrations as low as 0.74-1.0 ppbv and 0.59-0.62 ppbv respectively. This can be explained if compensation points for shade leaves in the field were lower than laboratory compensation point measurements on poplar in the dark (1-3 ppbv). Such low compensation points have been measured for two drought deciduous Amazonian tree species in the field (0.56 ppbv, Hymenaea courbaril and 0.32 ppbv, Apeiba tibourbou) (Rottenberger et al., 2004). Dr. Kuhn is correct in pointing out that the net emissions at the top of the canopies during the day do not necessarily correspond to the first peak in leaf area index, which could have been partly caused by photochemical production of acetaldehyde. However, it is not

BGD

5, S1558–S1569, 2008

the case that field measurements revealed mainly deposition. In California for example, net emissions occurred throughout the entire canopy. We attribute the lack of net uptake in California to the relatively open nature of the canopy which necessarily increases the proportion of leaves that are sunlit.

Reviewer comment: With compensation points under irradiation far exceeding any previous published values (page 2661, line 2), I wonder whether secondary production of acetaldehyde might have mimicked acetaldehyde emissions within the enclosure due to strong accumulation and degradation of primarily emitted reactive VOC precursor compounds (by O3 at the enclosure inlet or OH produced by the 1000 Watt high intensity discharge lamp)? For highly reactive VOC emitted like e.g. beta-Caryophyllene or alpha-Terinene estimated atmospheric lifetimes are in the order of seconds to minutes, and gas phase oxidation could play a role. See Neeb et al. 1997 for details on the potential role of secondary production of carbonyls in enclosure studies. The secondary production of primarily emitted VOC is assumed to also play a major role in determining the profiles of oxygenated VOC within and above the canopy (Karl et al., 2005; Rottenberger et al. 2004; Holzinger et al. 2004), and we very recently learned that high isoprene mixing ratios do not necessarily deplete OH at least over forest canopies (Lelieveld et al. 2008, Nature).

Response: We propose to insert the following two passages to clarify this issue:

Page 2658, Line 12: Secondary photochemical production of acetaldehyde in the enclosure is unlikely because the inlet of the enclosure was supplied with hydrocarbon free air produced by passing room air through a catalytic converter heated to 400 oC. As such, the OH and ozone concentrations were likely to be very low due to a lack of NOx chemistry. While some secondary photochemical production from terpene oxidation can produce acetaldehyde, the yields are quite low. For example, Lee et al. (2006b) investigated the products of photooxidation of 16 different terpenes including isoprene, 8 monoterpenes, 3 oxygenated terpenes, and 4 sesquiterpenes including beta-Caryophyllene. The measured acetaldehyde yields ranged between 0.2 % and

BGD

5, S1558–S1569, 2008

Interactive Comment

2.9 % with beta-Caryophyllene having an intermediate value of 1.6 %. When similar experiments were carried out to specifically investigate the ozonolysis of gas phase terpenes, acetaldehyde yields ranged from 0.9 % to 15 % with beta-Caryophyllene having a low value of 0.9 % (Lee et al., 2006a). Therefore, the high compensation points measured in the light are likely due to higher plant production rates in the light than in the dark.

Page 2660, Line 16: In our field experiments, we do not see evidence of significant photochemical production of acetaldehyde above the canopies, but we acknowledge that some photochemical production via long-lived precursors transported to the site could be possible. Within the canopies, the secondary photochemical production of acetaldehyde from reactive terpene species does not appear to be a significant source of acetaldehyde. For example in North Carolina during the same experiment reported in this paper (CELTIC), Stroud et al. (2005) used a one-dimensional canopy model to quantify the impact of photochemistry in modifying biosphere-atmosphere exchange of trace gases. The estimated loss rates of beta-Caryophyllene due to ozonolysis throughout the canopy during the day ranged between 10 and 140 pptv min-1. Using an ozonolysis rate of 140 pptv min-1 for the layer between 15 m and 20 m and assuming a 2 % acetaldehyde yield, the maximum secondary acetaldehyde production rate within the canopy was 1.7 x 10-3 mg m-2 hr-1. Using the inverse Lagrangian model, we estimate that this layer (15 m to 20 m) corresponds to a strong net source of acetaldehyde of 8.0 x 10-1 mg m-2 hr-1, over one order of magnitude larger than the estimated rate of acetaldehyde production from beta-Caryophyllene ozonolysis. Therefore, the secondary production of acetaldehyde within the canopy from the gas phase oxidation of reactive terpenes appears to have only a small impact on the estimated canopy scale fluxes.

Reviewer comment: With a residence time of 5min, could the plants have suffered from CO2 depletion within the enclosure?

Response: While we did not measure photosynthesis, we acknowledge that a res-

BGD

5, S1558–S1569, 2008

idence time of 5 minutes could have caused a significant draw down of the room air CO2. However, leaf shading effects probably resulted in reasonable mixing ratios (200-300 ppmv) although there is no way of knowing. While we are unaware of any studies of acetaldehyde emissions from leaves exposed to low ambient CO2 concentrations, several studies using branch enclosures have demonstrated that acetaldehyde emissions are positively correlated with net photosynthetic uptake of CO2. For example, Kesselmeier et al. (2002) found that acetaldehyde emissions can be up to 0.049% of net photosynthetic uptake rates and that the emissions are light and temperature dependent. Supporting this idea, acetaldehyde emissions were unchanged or enhanced under elevated CO2 (Kreuzwieser et al., 2002). Therefore, a depletion of CO2 in our branch enclosure studies should tend to decrease, not increase acetaldehyde production rates. This is consistent with the idea that acetaldehyde is produced during ethanolic fermentation within leaves where the carbon source is derived in-part from the export of triosephosphates from chloroplasts (Jardine, 2008). However, acetaldehyde production may also be derived from the transport of ethanol to leaves from other tissues via the transpiration stream (Kreuzwieser et al., 1999). Because the export of triosephosphates and the delivery of ethanol in the transpiration stream should increase during photosynthesis, so should the production of acetaldehyde in leaves. Nevertheless, we cannot rule out the possibility that low CO2 concentrations may lead to higher acetaldehyde production rates within leaves as has been observed for isoprene (Rosenstiel et al., 2003). New studies are therefore needed to clarify the role of ambient CO2 concentrations on the compensation point of acetaldehyde.

Reviewer comment: The discrimination rate of 13C acetaldehyde by stomatal uptake (or respective enrichment in the enclosure air) was used as an additional indication of the preference by stomatal uptake of acetaldehyde versus the uptake by the leaf surface. Fractionation factors reflect both physiological (e.g. discrimination of the enzyme Rubico in the case of CO2) and internal constraints of stomatal conductance and diffusion across cell walls. Indeed I found it an interesting approach to show the discrimination of acetaldehyde by observing the isotope ratios in the enclosure headspace

BGD

5, S1558–S1569, 2008

air. If a dry dead leaf is put in the enclosure and no acetaldehyde uptake is observed (while the live leaf does take up), then deposition to this dry surface can be neglected. This is quite an important finding (and I would also be curious whether a humidified leaf surfaces would do the same). But I do not comprehend which additional information in this context the 13C discrimination does tell us (page 2661, line 19). As mentioned by the authors, the deposition to the surface of the live leaf surface would be prone to the 13C discrimination as well (via diffusion through the molecular-turbulent leaf layer, referring to Rb). The arguing is based on the assumption that the dead leaf surface can only be a temporary sink; but even then the diffusion through the molecular-turbulent layer at the leaf surface should not lead to a change in 13C discrimination, as the same rules of fractionation apply to diffusion to the surface (Rb) and through the stomata (Rs). May be I just missed the point, please clarify. Moreover, a dry surface of dead leaves might not resemble the physicochemical properties of a live (humid) leaf. To inspire the discussion on the role of leaf surface, I might refer to measurements carried out in our lab (mentioned in Rottenberger et al. 2008): data provided experimental evidence that (passive) cuticular uptake can play a substantial role in the exchange process. Acetaldehyde uptake remained high when fumigating with mixing ratios of 15-25 ppb acetaldehyde even when stomatal closure of Quercus ilex leaves was artificially induced by treatment with abscisic acid. Also the exchange of organic acids of dead leaf litter was found to be strongly dependent on the water content of the dead leaves, with strong uptake on humid surfaces, which only ceased (and changed to emissions from a certain threshold level on) when leaves were dried. However, differentiation between the different impacts of pure physicochemical deposition onto the hydrophobic cuticle or onto humid leaf surface components and/or the involvement of active uptake by surface biological consumers could not be provided. I also have to acknowledge that live leaves with very low transpiration rate during dark conditions investigated in the manuscript discussed inhere did not act as a significant sink, though (page 2661, line 15).

Response: As discussed on page 2661, Line 14, we have three lines of evidence that

BGD

5, S1558–S1569, 2008

Interactive Comment

stomatal exchange dominates the exchange of acetaldehyde with the live branches studied here.

1) The lack of net uptake or isotope fractionation by dry dead leaves indicates isotopic thermodynamic equilibrium with respect to adsorption/desorption which did not influence the isotopic composition of the gas phase acetaldehyde. In contrast, the live leaves consumed and fractionated the acetaldehyde in the head space. Without the presence of a net sink, wet deposition to leaf surfaces will also not influence the isotopic composition of the gas phase acetaldehyde once isotopic equilibrium is established. We assume that carbon isotope fractionation during the partitioning of acetaldehyde into condensed water on leaf surfaces is insignificant, by analogy with the results of Johnson and Dawson (1993) who found that the equilibrium carbon fractionation associated with the partitioning of gaseous formic acid into an aqueous phase is negligible. They concluded that the carbon isotope signature of oxygenated organics is not affected by wet deposition. Therefore, our results from live leaves can only be explained if a continuous net sink for acetaldehyde exists. However, it is possible that significant surface sinks may exist on live leaves in the field such as leaf surface water runoff, microbial consumption, or unidentified chemical sinks.

2) We observed a strong correlation between acetaldehyde exchange velocities and transpiration rates for poplar and holly oak branches. If surface deposition dominated the uptake mechanism, this relationship would not be expected to hold.

3) Our result that the uptake of acetaldehyde by live Holly Oak leaves in the dark with very low transpiration rates was not significant is consistent with similar results obtained with several tree species using extremely high concentrations of acetaldehyde (95-105 ppbv) (Kondo et al., 1998). From these experiments, we can conclude that the deposition of acetaldehyde to the live leaf surfaces measured in these studies is not significant.

Reviewer comment: The authors state (page 2654, line 14) that they used the mixing

BGD

5, S1558–S1569, 2008

ratios at the enclosure inlet to calculate the acetaldehyde exchange velocities (g gdw-1 ppbv-1 h-1), as was actually also the case in Rottenberger et al. (2008). However, in a very similar study of part of the same group (Karl et al. 2005), the mixing ratios at the enclosure outlet was used. Is there any reasoning for the change? This is a general problem in literature, as the slopes are of course different with the two approaches and the absolute numbers therefore not really comparable (as e.g., is also the case in Fig. 5). I have to admit, though, that I do not have a proper solution for this problem, but it might be a good start to bring this issue up in a discussion forum like BGD.

Response: Dr. Kuhn is correct in pointing out that Karl et al. (2005) used the mixing ratios at the enclosure outlet. While compensation point estimates will not be affected, exchange velocity estimates will be higher when the outlet mixing ratio is used than when the inlet concentration is used. While convincing arguments can be made for both cases, the main reason for choosing acetaldehyde mixing ratios at the enclosure inlet to calculate the acetaldehyde exchange velocities (g gdw-1 ppbv-1 h-1) is to be consistent with previously published values (Rottenberger et al., 2004, 2005, 2008). Therefore, because Karl et al. (2005) used the mixing ratios at the enclosure outlet, we propose to remove this data from the acetaldehyde exchange velocity comparison in Fig. 5.

All technical corrections will be completed with responses where relevant below:

Reviewer comment: Page 2665, line 15: "... the driving force for acetaldehyde exchange with plants (deltaC) is relatively independent of stomatal resistance allowing stomatal behavior to strongly influence exchange rates." sounds contradictory to me.

Response: This is a very important point and is the reason (we propose) for the strong stomatal control over acetaldehyde exchange rates observed in this study. The idea is that the concentration gradient cannot be a strong function of stomatal resistance if stomatal resistance is to control long-term exchange rates.

Reviewer comment: Fig. 6: as the long-term measurement was carried out throughout

BGD

5, S1558–S1569, 2008

nighttime on April 24th, 2007: it would be interesting to note whether the (none excised, unlike in Jardine 2008, I assume) branch was under light conditions or dark conditions, or whether a change in light conditions occurred without any change in the carbon isotope fractionation pattern.

Response: For carbon isotope experiments, excised branches in tap water (as in Jardine 2008) were exposed to low intensity room lighting conditions that did not change during the course of the experiments. For compensation point measurements, intact branches were used.

References

Jardine, K.: The exchange of acetaldehyde between plants and the atmosphere: Stable carbon isotope and flux measurments, PhD, School of Marine and Atmospheric Science, Stony Brook University, Stony Brook, NY, 169 pp., 2008.

Johnson, B. J., and Dawson, G. A.: A Preliminary-Study of the Carbon-Isotopic Content of Ambient Formic-Acid and 2 Selected Sources - Automobile Exhaust and Formicine Ants, Journal of Atmospheric Chemistry, 17, 123-140, 1993.

Karl, T., Harley, P., Guenther, A., Rasmussen, R., Baker, B., Jardine, K., and Nemitz, E.: The bi-directional exchange of oxygenated VOCs between a loblolly pine (Pinus taeda) plantation and the atmosphere, Atmospheric Chemistry and Physics, 5, 3015-3031, 2005.

Kesselmeier, J., Ciccioli, P., Kuhn, U., Stefani, P., Biesenthal, T., Rottenberger, S., Wolf, A., Vitullo, M., Valentini, R., Nobre, A., Kabat, P., and Andreae, M. O.: Volatile organic compound emissions in relation to plant carbon fixation and the terrestrial carbon budget, Glob. Biogeochem. Cycle, 16, 9, 1126 10.1029/2001gb001813, 2002.

Kondo, T., Hasegawa, K., Uchida, R., and Onishi, M.: Absorption of atmospheric C-2-C-5 aldehydes by various tree species and their tolerance to C-2-C-5 aldehydes, Science of the Total Environment, 224, 121-132, 1998.

BGD

5, S1558–S1569, 2008

Kreuzwieser, J., Scheerer, U., and Rennenberg, H.: Metabolic origin of acetaldehyde emitted by poplar (Populus tremula x P-alba) trees, Journal of Experimental Botany, 50, 757-765, 1999. Kreuzwieser, J., Cojocariu, C., Jussen, V., and Rennenberg, H.: Elevated atmospheric CO2 causes seasonal changes in carbonyl emissions from Quercus ilex, New Phytol., 154, 327-333, 2002.

Lee, A., Goldstein, A. H., Keywood, M. D., Gao, S., Varutbangkul, V., Bahreini, R., Ng, N. L., Flagan, R. C., and Seinfeld, J. H.: Gas-phase products and secondary aerosol yields from the ozonolysis of ten different terpenes, J. Geophys. Res.-Atmos., 111, 2006a.

Lee, A., Goldstein, A. H., Kroll, J. H., Ng, N. L., Varutbangkul, V., Flagan, R. C., and Seinfeld, J. H.: Gas-phase products and secondary aerosol yields from the photooxidation of 16 different terpenes, J. Geophys. Res.-Atmos., 111, 2006b.

Niinemets, U., and Reichstein, M.: Controls on the emission of plant volatiles through stomata: Differential sensitivity of emission rates to stomatal closure explained, J. Geophys. Res.-Atmos., 108, 2003.

Rosenstiel, T. N., Potosnak, M. J., Griffin, K. L., Fall, R., and Monson, R. K.: Increased CO2 uncouples growth from isoprene emission in an agriforest ecosystem, Nature, 421, 256-259, 10.1038/nature01312, 2003.

Rottenberger, S., Kuhn, U., Wolf, A., Schebeske, G., Oliva, S. T., Tavares, T. M., and Kesselmeier, J.: Exchange of short-chain aldehydes between Amazonian vegetation and the atmosphere, Ecological Applications, 14, S247-S262, 2004.

Rottenberger, S., Kuhn, U., Wolf, A., Schebeske, G., Oliva, S. T., Tavares, T. M., and Kesselmeier, J.: Formaldehyde and acetaldehyde exchange during leaf development of the Amazonian deciduous tree species Hymenaea courbaril, Atmos. Environ., 39, 2275-2279, 2005.

Rottenberger, S., Kleiss, B., Kuhn, U., Wolf, A., Piedade, M. T. F., Junk, W., and

BGD

5, S1558–S1569, 2008

Kesselmeier, J.: The effect of flooding on the exchange of the volatile C2-compounds ethanol, acetaldehyde and acetic acid between leaves of Amazonian floodplain tree species and the atmosphere, Biogeosciences Discussions, 5, 463-499, 2008.

Stroud, C., Makar, P., Karl, T., Guenther, A., Geron, C., Turnipseed, A., Nemitz, E., Baker, B., Potosnak, M., and Fuentes, J. D.: Role of canopy-scale photochemistry in modifying biogenic-atmosphere exchange of reactive terpene species: Results from the CELTIC field study, J. Geophys. Res.-Atmos., 110, 2005.

Interactive comment on Biogeosciences Discuss., 5, 2645, 2008.