ECOSYSTEM ECOLOGY - ORIGINAL PAPER

Dew water isotopic ratios and their relationships to ecosystem water pools and fluxes in a cropland and a grassland in China

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Received: 19 November 2010/Accepted: 18 July 2011/Published online: 6 August 2011 © Springer-Verlag 2011

Abstract Dew formation has the potential to modulate the spatial and temporal variations of isotopic contents of atmospheric water vapor, oxygen and carbon dioxide. The goal of this paper is to improve our understanding of the isotopic interactions between dew water and ecosystem water pools and fluxes through two field experiments in a wheat/maize cropland and in a short steppe grassland in China. Measurements were made during 94 dew events of the D and ¹⁸O compositions of dew, atmospheric vapor, leaf, xylem and soil water, and the whole ecosystem water flux. Our results demonstrate that the equilibrium fractionation played a dominant role over the kinetic fractionation in controlling the dew water isotopic compositions. A significant correlation between the isotopic compositions of leaf water and dew water suggests a large role of top-down exchange with atmospheric vapor

Communicated by Dan Yakir.

Electronic supplementary material The online version of this article (doi:10.1007/s00442-011-2091-0) contains supplementary material, which is available to authorized users.

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controlling the leaf water turnover at night. According to the isotopic labeling, dew water consisted of a downward flux of water vapor from above the canopy (98%) and upward fluxes originated from soil evaporation and transpiration of the leaves in the lower canopy (2%).

Keywords Stable isotope · Dew water · Water vapor · Leaf water · TDLAS · Flux partitioning

Introduction

Dew formation is a widespread meteorological and hydrologic phenomenon and is likely to intensify in future years because of worldwide increasing trends in atmospheric humidity (Willett et al. 2007; Dai 2006). It occurs in more than 50% of the night periods in the growing season of a temperate forest in Canada (Fuentes et al. 1992) and over 20% in the dry season in a tropical forest in Indonesia (Dietz et al. 2007). In the upper Midwest of the US, its frequency of occurrence is 84% during the peak growing season (Welp et al. 2008). Interest in the dew phenomenon is motivated by a number of considerations: the presence of dew on plant foliage alters the ozone deposition pathway (Fuentes et al. 1992); in some arid and semiarid ecosystems, dew is an important hydrological input (Malek et al. 1999); dew-covered plant leaves are more vulnerable to diseases than under dry conditions (Agama and Berlinera 2006); a recent study shows that dew water can alter the predawn leaf water potential (Kim and Lee 2011); and the presence of dew water on plant canopies also interferes with remote sensing of soil moisture (Cosh et al. 2009; Rosnay et al. 2006).

Three sources of water are involved in dew formation in an ecosystem. The dominant one is water vapor in the

lower atmosphere. The second one originates from the soil, which typically maintains a temperature higher than that of the foliage and dew point temperature during dew formation (Richards 2004; Garratt and Segal 1988; Monteith 1957). The last one is transpiration originating from the leaves in the lower canopy. Our experience has been that, in dew events, a portion of the foliage near the soil is free of dew water and can continue to lose water via transpiration (Welp et al. 2008). The first stream of water vapor exchange occurs in the opposite direction as the second and the third stream. Condensation removes water vapor from the atmosphere and results in a negative (downward) water vapor flux whereas soil evaporation and transpiration by the lower canopy result in a positive (upward) flux. The net water vapor flux observed above the canopy is a balance of these two opposite fluxes. These exchange pathways resemble those of CO_2 in the daylight hours which consist of foliage uptake and plant and soil respiration, also in opposite directions. Quantifying the contributions of these three water flux pathways should yield insights into the interaction of dew water with other ecosystem water pools and contribute to methodological development on ecosystem flux partitioning (Yepez et al. 2003; Yakir and Sternberg 2000).

The published research on the dew phenomenon is mostly devoted to quantifying dew intensity and duration (e.g., Agama and Berlinera 2006; Richards 2004). Few studies have been carried out on the isotopic compositions of dew water and their relationships to other ecosystem water pools and fluxes. Bariac et al. (1989) and Welp et al. (2008) examined the interaction between the isotopic compositions of dew water, atmospheric water vapor and leaf water for a small number of dew events. Kim and Lee (2011) investigated the dew effect on the leaf water isotopic compositions (δ_L) with a dark plant chamber in the laboratory. Dew formation can alter the isotopic interactions between the ecosystem and its environment. For example, Welp et al. (2008) found that the isotopic composition of water vapor (δ_{v}) above a soybean canopy is depleted during dew formation and enriched during the evaporation of dew in the morning.

The dew phenomenon provides an opportunity to study fractionation processes associated with phase changes of water. The isotopic composition of dew water is related to the mechanism of equilibrium with atmospheric vapor, similar to the liquid–vapor equilibrium state found in clouds (Stewart 1975; Jouzel 1986; Ingraham 1998). In the present study, oversaturation conditions often occur during dew events because the leaf surface, the location where condensation takes place, tends to be cooler than the dew point temperature of the surface air. The observations in this study show that relative humidity could be as high as 120%. Because there is a net diffusion of water vapor towards the surface, we hypothesize that the kinetic fractionation may play a role in the isotopic relation of dew water and atmospheric vapor. Evidence of a kinetic effect is also found for liquid–vapor interactions when raindrops descend into an unsaturated layer below the cloud (Stewart 1975; Wen et al. 2010). The question of interest is whether the leafscale or canopy-scale kinetic factor should be used to quantify the fractionation process. The leaf-scale kinetic fractionation factor is linked to diffusion through the stomatal opening and the leaf boundary layer (Farquhar et al. 1993). The canopy kinetic factor is more appropriate at the ecosystem scale in field conditions where diffusion consists of both turbulent and molecular contributions (Lee et al. 2009).

The presence of dew water on the leaf surface can affect $\delta_{\rm L}$ (Kim and Lee 2011; Welp et al. 2008). The temporal dynamics of $\delta_{\rm L}$ are relevant to several important problems in hydrological and ecological sciences. For example, $\delta_{\rm L}$ exerts direct influences on photosynthetic discrimination against ¹⁸O and therefore the budgets of ¹⁸O in atmospheric oxygen and carbon dioxide (Hoffmann et al. 2004; Farquhar et al. 1993). Its temporal variations cause the isotopic content of transpiration to deviate from that of xylem water, confounding the interpretation of flux partitioning and isotopic labeling of the transpiration water (Lee et al. 2007; Harwood et al. 1998). A recent laboratory study shows that stomata stay open in the presence of dew and that dew water serves as an intermediary that facilitates the exchange of the H₂¹⁸O and HDO molecules between the leaf water and atmospheric vapor (Kim and Lee 2011). Using isotopic labeling, Kim and Lee (2011) reported that at the end of dew exposure about 90% of the leaf water comes from atmospheric vapor via the stomatal pathway and only 10% comes from the xylem. One objective of this study is to quantify the relative roles of these leaf water sources in dew events in field conditions.

The data used for this study came from two field experiments consisting of 94 dew events in north China and a grassland in northwest China. During the experiments, measurements were made of the isotopic compositions of dew, atmospheric vapor, leaf water, xylem water and soil water, and the whole ecosystem water flux. Such a large dataset on dew water is the first of its kind, and along with concurrent supporting measurements. provides an opportunity to test the isotopic fractionation effects discussed above. Our specific objectives are: (1) to characterize the isotopic compositions of various ecosystem water pools and fluxes during the dew events, (2) to test the hypothesis that kinetic fractionation plays a role in the dew isotopic compositions, (3) to investigate the relative contributions of atmospheric vapor and xylem water to leaf water using isotopic labeling, and (4) to quantify the relationship of the dew flux to the whole ecosystem water vapor flux.

Materials and methods

Site description

The same measurement strategy was used in the two field experiments. Both sites had good fetch (>200 m). The reader is referred to the online supporting material for photographs of the sites (Figs. S1-S3 of Supplementary Material). The first experiment was conducted in a winter wheat and summer maize double-cropping system in north China at the Luancheng Agricultural Ecosystem Experimental Station (37°50'N, 114°40'E, elevation 50 m above sea level) of the Chinese Ecosystem Research Network (CERN), Chinese Academy of Sciences. Winter wheat (Triticum aestivum L.) was sown in early October 2007 and harvested in mid-June 2008. Summer maize (Zea mays L.) was planted inside the matured wheat crop at the beginning of June and harvested at the end of September 2008. The experiment was conducted between April 5 and September 13, 2008. The maximum LAI was 4.5 and 4.2 m² m⁻² and the maximum canopy height was 0.75 and 2.7 m for the winter wheat and summer maize, respectively.

The second experiment was conducted in a steppe ecosystem in northwest China at the Duolun Restoration Ecology Research Station ($42^{\circ}03'$ N, $116^{\circ}17'$ E, elevation 1,333 m above sea level), Institute of Botany, Chinese Academy of Sciences. The dominant species were *Stipa krylovii*, *Agropyron cristatum*, and *Artemisia frigida*. The experiment was conducted from June 2 to September 17, 2009. The maximum LAI was 0.5 m² m⁻² and the canopy height was 0.35 m.

In situ measurement of water vapor and water flux isotope ratios

The δ_v in surface air was measured using a tunable diode laser (TDL) trace gas analyzer (Model TGA100A; Campbell Scientific, Logan, UT, USA). The air samples and calibration gasses were pumped through the analyzer sequentially in 100- to 120-s cycles with 20 s spent on each measurement. The δ_v was calibrated in every cycle using a zero gas and two span gases (Wen et al. 2008; Lee et al. 2005). During the Luancheng experiment, δ_v was measured at two heights above the canopy. The heights of the two intakes increased from 0.6/1.6 m at the beginning to 1.1/ 2.1 m at the end of the wheat season and from 1.1/2.1 m at the beginning to 3.2/4.2 m by the end of the maize season to adjust for canopy growth. In the Duolun experiment, δ_v were measured at three heights (0.2, 0.6 and 1.6 m) above the ground.

The molar flux ratio of the whole ecosystem water vapor flux above the canopies (δ_n) was determined by the fluxgradient approach using the vertical gradients of water isotopologues at the two sampling heights above the canopy (Welp et al. 2008; Lee et al. 2007). The molar flux ratios were converted to the delta notation in reference to the VSMOW standard.

Measurement of isotopic compositions of ecosystem water pools

Dew water collection was carried out before dawn when condensation was still occurring. Dew water was wiped with clean cotton balls from the leaf surface and was squeezed into a sample vial. Simultaneously, leaf and stem samples were collected for analysis. In the Luancheng experiment, leaf samples from the upper and lower canopy were archived separately, with the main leaf vein removed. The maize leaf samples were a mixture of small leaf sections cut from the upper, middle and bottom positions of the leaf.

Soil samples were collected from depths of 0–5, 15–20 and 40–45 cm every 2–4 days in the Luangcheng experiment and from depths of 0–5, 10–15 and 20–25 cm every week in the Duolun experiment. Water in these solid samples was extracted cryogenically using a vacuum line. Precipitation water was collected for each rain event. All the liquid samples were analyzed for their isotope ratios on a liquid water isotope analyzer (Model DLT-100; Los Gatos Research, Mountain View, CA, USA). The precision of the liquid water isotope analyzer was typical better than 0.3% for D and 0.1% for ¹⁸O.

Eddy covariance and micrometeorological measurements

Supporting measurement consisted of an eddy covariance system (Model CSAT-3, Campbell Scientific; Model LI-7500, Licor, Lincoln, NE, USA) and a suite of micrometeorological sensors mounted above the canopy and in the soil. They provided half-hourly measurement of momentum, sensible heat, latent heat and CO_2 fluxes, air temperature, relative humidity, wind speed, soil water content, soil temperature, leaf temperature, precipitation and leaf wetness.

Theoretical considerations

Isotopic composition of dew water

The dew phenomenon provides an opportunity to study fractionation processes associated with phase changes of water. The isotopic content of dew water (δ_d) is controlled by atmospheric humidity, the vapor isotope content in air, and the equilibrium and the kinetic fractionations. In the following, we present a derivation of the dew isotopic ratio model. Let ρ_v and $\rho_{v,i}$ denote the vapor density (in units of mol m⁻³) of the major species H₂¹⁶O and the minor species (either HDO or H₂¹⁸O), respectively, in the surface layer above the canopy, *r* and *r*_i their diffusion resistances (s/m), ρ_v^* and ρ_{vi}^* the saturation vapor densities at the dew water temperature which is identical to the leaf temperature. Let *R*_d be the molar ratio of dew water. Isotopic equilibrium requires that the molar ratio in the vapor phase at the surface of dew water be given by

$$\frac{\rho_{\rm vi}^*}{\rho_{\rm v}^*} = \frac{1}{\alpha_{\rm e}} R_{\rm d} \tag{1}$$

where α_e is the equilibrium fractionation factor (Majoube 1971).

Using the resistance analogy, we obtain an expression for the molar ratio of the dew flux which is identical to R_d

$$R_{\rm d} = \frac{\rho_{\rm v,i}^* - \rho_{\rm v,i} r}{\rho_{\rm v}^* - \rho_{\rm v}} \frac{r}{r_{\rm i}}$$
(2)

Combining Eqs. (1) and (2), solving for R_d and converting all the molar ratios to their respective counterparts in the delta notation, we obtain

$$\delta_{\rm d} = \frac{\delta_{\rm v} + \varepsilon_{\rm eq}/h + (1-h)\varepsilon_{\rm k}/h}{1 + \varepsilon_{\rm k}/1000 - (1/h)(\varepsilon_{\rm eq} + \varepsilon_{\rm k})/1000} \tag{3}$$

which for ¹⁸O can be linearized to a good approximation as

$$\delta_{\rm d} = \delta_{\rm v} + \frac{\varepsilon_{\rm eq}}{h} + \frac{1-h}{h} \varepsilon_{\rm k} \tag{4}$$

where *h* is relative humidity in reference to the dew water temperature $(h = \rho_v / \rho_v^*)$, $\varepsilon_{eq} = (1 - 1/\alpha_e) \times 1000$ is the equilibrium fractionation factor expressed in the unit of ‰, and $\varepsilon_k = (1/k - 1) \times 1000$ is the kinetic fractionation factor, also in the unit of ‰, with $k = r/r_i$.

Equation (3) raises several points in need of further comments. In the limit of saturation (h = 1), dew water is in isotopic equilibrium with atmospheric vapor. In supersaturation conditions (h > 1), δ_d should be lower than the equilibrium predictions due to the kinetic effect. The molecular values of ε_k are 28 and 25‰ for H₂¹⁸O and HDO, respectively (Merlivat 1978). However, in canopy-scale studies, the variables in Eqs. (3) and (4) are measured at some height above the canopy. The water vapor diffusion pathway consists of molecular (the leaf boundary layer) and turbulent part (atmospheric surface layer). According to Lee et al. (2009), ε_k should be calculated according to $19r_b/(r_a + r_b)$ and $17r_b/(r_a + r_b)$ for H₂¹⁸O and HDO, respectively. The aerodynamic (r_a) and leaf boundary-layer resistance (r_b) were calculated according to the methods of Lee et al. (2009) and Xiao et al. (2010).

Nighttime water vapor flux under saturation conditions

The eddy covariance water vapor flux was biased low in saturation conditions because of the poor frequency response of its open-path analyzer (Roode et al. 2010). To circumvent the problem, we used the gradient diffusion method to determine the water vapor flux above the canopy. In this method, the vapor mixing ratio gradient was measured with the TDL analyzer. The turbulent diffusion coefficient was determined with the methods of Arya (1988). The sign of the vapor gradient was also used to determine the onset and termination of each dew event.

Isotope end members of water vapor fluxes during dew events

The total water vapor flux (F_n) during a dew event consists the dew flux $(F_d$, directed downward) and the combined flux of soil evaporation and leaf transpiration $(F_2$, directed upward). Conservation principles require

$$F_{\rm n} = F_{\rm d} + F_2 \tag{5}$$

$$\delta_{\rm n}F_{\rm n} = \delta_{\rm d}F_{\rm d} + \delta_2F_2 \tag{6}$$

where δ_n , δ_d and δ_2 are the isotopic compositions of F_n , F_d , and F_2 , respectively. Here, δ_n was measured with the gradient diffusion method, δ_d is the isotopic composition of the dew flux according to Eqs. (3) and (4), and δ_2 is not known.

The isotopic composition of the soil component δ_e was calculated using the Craig–Gordon model, which does not approach the delta value of the ascending liquid water in the source or that soil evaporation is not at steady state (Yepez et al. 2003, 2011; Williams et al. 2004; Yakir and Sternberg 2000; Craig and Gordon 1965),

$$\delta_{\rm e} = \frac{\delta_{\rm s}/a_{\rm e} - h\delta_{\rm v} - \varepsilon_{\rm eq} - (1-h)\varepsilon_{\rm k}}{(1-h) + (1-h)\varepsilon_{\rm k}/1000} \tag{7}$$

where δ_s represents the isotopic composition of liquid water at the evaporating front, approximated here by the isotopic composition of soil water at the 0–5 cm depth, and *h* is relative humidity normalized to the soil temperature at the same depth. In Eq. (7), atmospheric humidity and the vapor isotopic ratio were measured at the upper intake of the TDL analyzer. The kinetic factors for soil evaporation are 28 and 25‰ for H₂¹⁸O and HDO, respectively.

Equations (5) and (6) form the basis for understanding the relationship of the dew flux to the net flux. If the isotopic end members are known precisely, the fractional contributions of dew and evapotranspiration flux to the total water vapor flux are given by

$$F_{\rm d}/F_{\rm n} = (\delta_{\rm n} - \delta_2)/(\delta_{\rm d} - \delta_2) \tag{8}$$

and

$$F_2/F_n = (\delta_d - \delta_n)/(\delta_d - \delta_2).$$
(9)

Results

Seasonal variability of isotopic compositions of water pools

We consider that dew formation was occurring when the vapor mixing ratio of the upper TDL intake exceeded that of the lower intake by 100 ppm or more. Based on this detection criterion, the dew frequencies were 65, 56, and 51% of the night periods for the wheat, maize and grassland growing seasons, respectively. The cumulative water vapor flux during the dew events amounted to 10.1, 6.5 and 5.5 mm on the basis of the flux-gradient method for the three seasons, respectively. The vapor flux intensities were on average 0.21, 0.13 and 0.10 mm per night, respectively. The actual dew amounts were 17% greater than these values (see "Partitioning of the ecosystem water vapor flux"). Owing to its dependence on radiation balance, dew amount can reach a theoretical maximum of about 0.8 mm per night, but measured values rarely exceed 0.5 mm (Garratt and Segal 1988). For comparison, the total precipitation was 170, 320 and 137 mm, respectively, during the three seasons. So dew input was negligible in the water budget of these ecosystems.

To provide the context for interpreting the nearly daily measurements of δ_d , we first present the measurements of the isotopic compositions of all the water pools during dew events in Luancheng (Fig. 1). They included dew water (δ_d), water vapor (δ_v) and water in the upper canopy leaves (δ_L) at the time of dew formation, xylem water (δ_x) , soil water at the 0–5 cm depth (δ_s) , and precipitation $(\delta_{\rm p})$. Table S1 gives the mean values of these quantities for the three seasons along with the mean values of water vapor mixing ratio, canopy temperature and relative humidity. Table S2 lists their values for the individual dew events. The isotopic compositions of these water pools were more variable in the wheat season than in the maize season. The switching between the two distinct groups coincided with the onset of the summer monsoon (Wen et al. 2010). The mean (standard deviation) δD and δ^{18} O of dew water were $-13.4 \pm 16.7\%$ (range -63.1 to 10.3‰) and $-1.2 \pm 2.4\%$ (range -8.6 to 2.8‰), respectively, in the wheat season. In comparison, the mean δD and $\delta^{18}O$ of dew water were $-44.1 \pm 10.4\%$



Fig. 1 Time series of the isotopic composition of dew (δ_d , *open circle*), atmospheric water vapor (δ_v , *filled circle*), leaf water (δ_L , *filled triangle*), xylem water (δ_x , *filled square*), and soil water (δ_s , *open square*) at 0–5 cm depth for **a** δD and **b** $\delta^{18}O$ in Luancheng during dew events. For comparison, the isotopic compositions of precipitation (δ_p , *open triangle*) event are also shown. Leaf water was sampled in the upper canopy

(range -72.8 to -23.4%) and $-4.9 \pm 1.5\%$ (range of -9.4 to -2.3%), respectively, in the maize season. The isotopic compositions of other water pools were also more enriched in the wheat season than in the maize season (Table S2 of Supplementary Material). The difference in the observed δ_d among the three growth periods was driven by differences in the background hydrological conditions rather than by differences in vegetation morphology.

Variations in the isotopic compositions of both dew water and the bulk leaf water were synchronous with those of atmospheric water vapor. There were significant linear correlations between dew water and atmospheric water vapor. The linear relationship was quite robust for δD $[\delta_{\rm d} = 0.96 \ (\pm 0.08) \ \delta_{\rm v} + 78.7 \ (\pm 9.0), \ R^2 = 0.88, \ p < 0.000 \ r^2$ 0.001; parameter in the parentheses given for the 95% confidence level] and δ^{18} O [$\delta_{d} = 0.99 \ (\pm 0.09) \ \delta_{v} + 10.72$ $(\pm 1.33), R^2 = 0.85, p < 0.001]$. Linear correlation also existed between dew water and the leaf water in the upper canopy with the regression equations $\delta_{I} = 0.79$ $(\pm 0.13) \delta_{\rm d} - 7.2 (\pm 2.5) (R^2 = 0.92, p < 0.001)$ for δD and $\delta_{\rm L} = 0.72$ (±0.21) $\delta_{\rm d} - 1.77$ (± 0.85) ($R^2 = 0.76$, p < 0.001) for δ^{18} O (see Fig. 3, below). The correlations between the dew water δD and $\delta^{18}O$ with those of the xylem water and the soil water were not significant.

Relationships between δD and $\delta^{18}O$ of water pools

The measured δD and $\delta^{18}O$ of individual water pools were highly correlated as expected (Figure S4 and Table S3). They follow the GMWL line very closely except for the leaf water whose deuterium excess (-27.1 ± 7.4) deviated from the GMWL standard value of 10‰. The regression fit to the leaf water data yields an equation with a slope of 7.4 (± 1.9) and an intercept of -27.5 (± 3.9). The regression fit to the xylem water data yields an equation with a slope of 5.1 (± 1.8) and an intercept of -21.5 (± 10.0). For comparison, the regression fit to the dew water data yields an equation with a slope of 7.3 (± 0.5) and an intercept of -6.5 (± 1.9). That the leaf water slope was much closer to the dew slope than the xylem water slope suggests that dew exerted a stronger influence on the leaf water isotopic compositions.

Relationships between dew water and water vapor isotopic ratios

To understand the relationships between the isotopic compositions of dew water and environmental factors, we calculated δ_d using three methods. In method 1, δ_d was assumed to be in equilibrium with atmospheric water vapor measured at the upper air intake at the canopy temperature. The equilibrium value was computed according to Eq. (3)with h = 1. In method 2, δ_d was calculated with Eq. (3) with the molecular kinetic fractionation factor. In method 3, δ_d was again calculated with Eq. (3) but using the canopy kinetic fractionation factor as described in "Isotopic composition of dew water". Figure 2 shows the deviation of the calculated from the measured δ_d as a function of relative humidity in fraction referenced to the canopy temperature during all dew water events in Luancheng and Duolun. Over-saturation (h > 1) occurred in roughly 90% of the dew events. The relative humility had a mean value of 1.06 ± 0.05 and varied in the range of 0.88-1.17.

Here, we use the root mean square difference (RMSD) to measure the prediction performance of the three methods. The RMSDs were 6.9, 9.2 and 7.8% for δ D, 1.3, 3.3 and 1.8% for ¹⁸O and 8, 19 and 10% for d-excess, using methods 1, 2 and 3, respectively. Overall, the equilibrium prediction had the lowest RMSD despite deviations from the saturation conditions. Incorporating the molecular kinetic effect deteriorated the quality of the prediction. Use of the canopy kinetic effect produced smaller RMSD than the prediction with the molecular kinetic effect.

Dependence of the isotopic ratios of leaf water on dew and xylem water

The leaf water during a dew event is a mixture of dew water, xylem water and the initial water left in the leaf



Fig. 2 Residual errors of the dew water isotopic compositions calculated with three methods for **a** δD , **b** $\delta^{18}O$ and **c** d-excess $(\delta D - 8 \times \delta^{18}O)$: equilibrium prediction $(\delta_{v,e}-\delta_d, open \ circle)$ and predictions that incorporate the molecular kinetic factor $(\delta_{v,m}-\delta_d, open \ square)$ and the canopy kinetic factor $(\delta_{v,c}-\delta_d, filled \ triangle)$. Relative humidity (*h*) is in fraction referenced to the canopy temperature. The data from all three growth seasons are included in this analysis

from the previous day. Figure 3 shows the linear dependence of $\delta_{\rm L}$ on $\delta_{\rm x}$ (xylem water isotopic composition) and $\delta_{\rm d}$ in Luancheng. (There were too few leaf data samples from Duolun for a similar analysis.) The correlation of $\delta_{\rm L}$ with $\delta_{\rm d}$ was much stronger than with $\delta_{\rm x}$ for both ¹⁸O and D. The mean δ D values of leaf water in the upper canopy leaves, dew water and xylem water were -31.2, -28.6 and -47.7%, respectively. The corresponding δ^{18} O values were -0.5, -3.0 and -5.2%. That $\delta_{\rm L}$ was closer to and better correlated with $\delta_{\rm d}$ than $\delta_{\rm x}$ indicates that $\delta_{\rm d}$ was a more importance water source for the leaves than the xylem water during the dew events.



Fig. 3 Relationships between the isotopic compositions of three water pools (δ_x , *open square* and δ_d , *filled square*) for **a** δD and **b** $\delta^{18}O$ in Luancheng. Regression parameters are given with 95% confidence intervals

Isotopic ratios of ecosystem water vapor fluxes during dew events

The isotopic labeling method can also be used to understand the relationship of the dew flux to the total ecosystem water vapor flux during the dew events (Eqs. 8 and 9). Similar to Fig. 3, in Fig. 4 we show the linear dependence of δ_n on δ_d of the dew water samples and δ_e in Luancheng. Each data point represents the average value of one dew event whose duration varied between 0.8 and 10.5 h. The slope of the regression of δ_n versus δ_d was 3.82 (±1.41, 95% confidence interval) and 3.30 (\pm 1.12) for D and ¹⁸O, respectively. The regression of δ_d versus δ_e had a slope that was smaller in magnitude, at a value of $-0.24 (\pm 0.20)$ for D and -0.03 (± 0.17) for ¹⁸O, and showed much more scatter than the δ_n versus δ_d regression. Averaged over the two crop seasons, the mean values of δ_n , δ_d and δ_e were -62, -28.6, and -191.0% for D and -16, -3.0 and -42% for ¹⁸O, respectively. These results indicate that the dew flux was the dominant component of the net ecosystem water vapor flux.

The role of the dew flux in the whole ecosystem water vapor flux can also be examined with the diurnal variations in δ_n . Figure 5 illustrates the ensemble mean diurnal cycles of the isotopic ratios of the net water vapor flux. The data were grouped into two categories filtered by the presence or absence of dew for both Luancheng and Duolun. In

Luancheng, the 24-h mean values of δD and $\delta^{18}O$ of the whole ecosystem water vapor flux were -64.0 and -7.5%, respectively, on the days of dew formation, and increased to -53.9 and -2.9% with no dew. In Duolun, these mean values were, respectively, -73.2% (δD) and -9.9% $(\delta^{18}O)$ on the days with dew and -27.3% (δD) and -1.1% $(\delta^{18}O)$ on the days without dew events. On the days without dew formation, δ_n shows a diurnal pattern predicted by the non-steady state model of evapotranspiration (Xiao et al. 2010; Farquhar and Cernusak 2005): it had the lowest values in mid-morning, enriched progressively through the afternoon and into the night, and reached the highest values at midnight. This pattern changed on the days with dew formation. The onset of dew formation caused abrupt switches in δ_n from large positive values to large negative values. The timing of the switches, approximately 2100-2200 hours LST, coincided with the time when the water vapor gradient switched from being negative to being positive. Similar diurnal patterns have been observed by Welp et al. (2008).

Discussion

Equilibrium and kinetic fractionations during dew events

Our results show that, even though air humidity did deviate from saturation conditions, the equilibrium fractionation still played a dominant role over the kinetic fractionation in controlling the dew water isotopic compositions. Use of the canopy kinetic factor gave slightly better prediction of δ_d than if the molecular factor was used. However, the dew observations were not sensitive enough to the kinetic fractionation to permit a rigorous evaluation of different kinetic fractionation formulations. Towards that goal, future work should focus on daytime low humidity conditions when the kinetic fractionation exerts a much stronger effect on the isotopic exchange process. Our original hypothesis, that the kinetic fractionation plays a role in the isotopic relation of dew water and atmospheric vapor, has no significant consequence for practical purposes. The theoretically correct formulation for δ_d (Eqs. 3 and 4) can be approximated with the equilibrium relation to an accuracy of 1.6% for D and 0.5% for 18 O.

The dominant role of the equilibrium fractionation is further supported by the excellent correlation between δ_d and δ_v (Fig. 1). We propose that, in situations where δ_v observations are not available, δ_d of the collected dew water can be used to infer δ_v from the equilibrium relationship. Similarly, Helliker and Griffiths (2007) used the δ_L signal reserved as cellulose of ¹⁸O in the tropical CAM epiphyte *Tillandsia usneoides* to approximate δ_v of the **Fig. 4** Relationships between three isotopic end members of water vapor flux (δ_d , δ_n , and δ_e) were δD (**a**, **c**) and for $\delta^{18}O$ (**b**, **d**) during dew events in Luancheng. Regression parameters are given with 95% confidence intervals



Fig. 5 Ensemble mean diurnal cycles of the isotopic flux ratios of the net ecosystem water vapor flux filtered by the presence (*filled square*) or absence (*open square*) of dew in the wheat/maize field in Luancheng (**a**, **b**) and in the grassland in Duolun (**c**, **d**)

atmosphere. In comparison with the observed δ_d , the equilibrium prediction gives δ_d that is biased low by 3.1% for D and 0.9% for ¹⁸O. Welp et al. (2008) reported low ¹⁸O biases by 0.1–0.9% during three dew events, and Bariac et al. (1989) showed more variable biases in the ranges of -5.6 and 0.7% for ¹⁸O and of -10.6 and -1.4% for D at different sampling times during one dew event.

There are two sources of biases. First, the dew water found on the leaf surface might have been contaminated by the water exchanged through the stomatal pathway with the heavier leaf water. On average, the leaf water had slightly higher D (2.6‰) and ¹⁸O (2.5‰) compositions than dew water (Table S1; Fig. 1). Second, some of the dew water formed on the leaf may have been supplied by the vapor Fig. 6 Diurnal cycles of the isotopic compositions of soil (δ_{s} 5, open square, δ_{s} 20, open circle and δ_{s_45} , filled triangle, subscript denoting soil depth in cm) and xylem (δ_x , filled circle) water pools during two intensive campaigns in **a**, **b** the wheat (May 21-23) and c, d the maize (August 31-September 2) season. Error bars are standard deviations of four replicate plots. For comparison, the isotopic compositions of dew $(\delta_d, filled \ square)$ are also shown. Dew water was observed on May 21, 23 and August 31 but was not collected for lack of sufficient quantity



transpired from the lower canopy which had more enriched isotopic compositions. Strictly, the delta values of the dew water samples should therefore be viewed as an approximate to the isotopic composition of the downward dew flux occurring above the canopy.

The role of dew in ecosystem water budget

Even though dewfall was a negligible hydrological input in these ecosystems, its role in the leaf water turnover cannot be ignored. That the leaf continued to exchange HDO and $H_2^{18}O$ molecules with dew water suggests that the stomatal pathway was partially open during the dew events. The mass balance of the leaf water is regulated by two processes, a "top-down" exchange with atmospheric vapor with dew water serving as an intermediary and a "bottomup" diffusional exchange with xylem water (Kim and Lee 2011). Our results show that the top-down diffusion (the exchange with atmospheric vapor) played a more important role than the bottom-up diffusion (the exchange with xylem water) during the dew events. According to the Craig-Gordon model (Yakir and Sternberg 2000; Craig and Gordon 1965), the equilibrium state reached by the leaf water with the ambient moisture does not necessarily require dew when the humidity approached 100%. However, the existence on the leaf surface of dew water, which is also in equilibrium with the ambient moisture, may have enhanced the leaf water turnover. In a laboratory dew simulation experiment, Kim and Lee (2011) showed that the fractional contribution of the leaf water from dew/ atmospheric vapor is 0.78–0.87 according to ¹⁸O labeling and 0.90-0.98 according to D labeling after prolonged (48 h) dew exposures. Their results include species of both netted and parallel vein structures. In the field conditions, dew exposure (0.8–10.5 h vs. their 48 h) was too short to achieve steady state. In other words, the $\delta_{\rm L}$ value at the time of the dew sampling was still influenced by the conditions of the previous day. For this reason, we cannot use the method of Kim and Lee (2011) to partition the leaf water into the dew/atmospheric vapor and the xylem contributions. Nevertheless, the much tighter correlation of $\delta_{\rm L}$ with δ_d than with δ_x (Fig. 3) suggests that the exchange of leaf water with atmospheric water was more efficient than the exchange with the xylem water. Farquhar and Cernusak (2005) pointed out that incomplete stomatal closure permits diffusion exchange of the H₂¹⁸O and HDO molecules in the leaf water with atmospheric vapor when there is no net water flux.

The isotope labeling method of Kim and Lee (2011)assumes that δ_x remains constant over the duration of a dew event. Our data collected during several intensive campaigns show that δ_x sampled near the soil surface was actually variable through the course of a day, with the highest values at the time of dew formation (Fig. 6). In a tropical savanna site, δ_x (¹⁸O) of several grass and shrub species was $\sim 1\%$ higher at sunrise than at midday (Le Roux et al. 1995). In a maize field in Minnesota (Griffis et al. 2010), δ_x was highest (-4.4‰, ¹⁸O) at 0900 hours LST when dew water was still present on the foliage and lowest (-5.9%) at 1800 hours LST on a mid-August day (T Griffis, personal communication, 2010). In an earlier isotope experiment during soybean cultivation in the same field (Welp et al. 2008), δ_x was -6.8% on the morning of July 29, 2005, which is 1.9% higher than the value of -8.7% observed at 1700 hours on July 29 (X Lee, unpublished data).

The causes of the diurnal variability are not well understood. In the present study, that δ_x approached δ_s at the 5 cm depth seems to suggest that the plants had switched its water source from the deeper soil layers to this depth in the early morning hours (Fig. 6). This scenario is, however, unlikely because the soil had a much lower water content at this depth than deeper layers. For example, on the morning of day 143 (May 15), soil water content was 34, 41 and 60% by volume at the depths of 5, 20 and 50 cm, respectively. An alternative hypothesis is that some enriched leaf water moved down the xylem during the dew event, causing δ_x to rise. In a dew exclusion experiment, Kim and Lee (2011) showed that leaves covered with dew had higher pre-dawn water potential than dry leaves. We suggest that the exchange with dew water created a downward water potential gradient between the leaves and the soil and caused a reversed xylem flow. Reversal of stem flow within the root system redistributes water in forest soils (Dawson 1993; Sakuratani et al. 1999; Oliveira et al. 2005). Higuchi and Sakuratani (2006) observed that mango fruits lose water via a reversed xylem flow when they have higher water potential than the soil. Although in the present study flow reversal did not have a measurable impact on the soil water status, it may have brought temporary relief to the plants in physiological drought stress. In desert plants, Gat et al. (2007) showed that large differences in the $\delta_{\rm I}$ relative to local precipitation are caused by differences in the depth of water uptake and the timing of stomatal openings.

The dew effects have some implications for the atmospheric budgets of ¹⁸O in oxygen and carbon dioxide. The direct impact of dew water on the daytime isotopic exchange is limited because dew water usually disappears 1-2 h after sunrise. But because of the slow turnover of leaf water, dew can have an indirect effect on the photosynthetic discrimination in mid-morning hours. The global $^{18}\text{O-CO}_2$ and $^{18}\text{O-O}_2$ budgets are sensitive to the leaf water ¹⁸O isotope content (δ_L) and the extent of ¹⁸O equilibrium (Gillon and Yakir 2001). For example, the equilibrium solution of δ_{I} suggests that a change of 2‰ in $\delta_{\rm L}$ can change atmospheric ¹⁸O–CO₂ by 1.2‰ (Cuntz et al. 2003). Currently, the estimate of global mean $\delta_{\rm L}$ is uncertain, varying from 0.4 to 6‰ (Hoffmann et al. 2004; Ciais et al. 1997; Farquhar et al. 1993). This contributes to the inability of global circulation models to close the budgets of ¹⁸O in O₂ and CO₂, which are roughly 2‰ out of balance (Cuntz et al. 2003; Bender et al. 1994). Welp et al. (2008) found that in a soybean field the leaves covered with dew are 3% more enriched in ¹⁸O than dry leaves. In a modeling study using an isotopic land surface scheme, Xiao et al. (2010) showed that accounting for dewfall and the subsequent evaporation of dew water improves the predicted temporal dynamics of $\delta_{\rm L}$ of a soybean ecosystem in Minnesota. The isotopic LSM developed by Xiao et al. (2010) has recently been extended to our crop systems (Xiao et al. 2011). Consistent with the results of Xiao et al. (2010, 2011), we found that accounting for dew formation and re-evaporation improves the LSM prediction of $\delta_{\rm L}$ in morning transitions.

Partitioning of the ecosystem water vapor flux

Our results show that the nighttime whole ecosystem water vapor flux was dominated by the dew flux. During a dew event, the whole ecosystem water vapor flux consists of soil evaporation/plant transpiration and the dew flux occurring in opposite directions. Soil evaporation and transpiration of the foliage in the lower canopy release water vapor into the atmosphere, and dew formation draws water vapor from the air layer above the canopy. Although no measurements of the two upward fluxes were available, indirect evidence supports their existence. The soil temperature at 5 cm was 2.8 ± 1.8 °C warmer than the air temperature above the canopy. Visual inspection during dew sampling indicated that the leaves in the lower canopy were usually free of dew water. Measurement with a handheld infrared thermometer (model COMPAC3, Advanced Test Equipment, USA) in 5 dew events showed that the foliage temperature of the lower canopy was $1.6 \pm 1.0^{\circ}$ C higher than that of the upper canopy. It is known that plant stomata have the tendency to remain partially open at night (e.g., Caird et al. 2007; Snyder et al. 2003). This temperature difference means that a positive vapor pressure gradient existed between the stomatal cavity and the ambient air which would maintain an upward transpiration flux.

The isotopic data can be used to constrain the component fluxes. For the sake of brevity, we will restrict this discussion to the ¹⁸O tracer. The mean δ_n and δ_d and δ_e were -16, -4.4 and -42%, respectively, during the Luancheng experiment. To avoid the contamination errors described above, this δ_d value was based on the model calculation (Eq. 3) using the canopy kinetic factor. Another end member, that of the transpiration flux ($\delta_{\rm T}$), obtained with the Craig–Gordon Eq. (7) by replacing h and δ_s with the measured *h* (=0.97 \pm 0.035, *n* = 5) and $\delta_{\rm L}$ (=-0.2‰, n = 19) in the lower canopy, was approximately 90%. The $\delta_{\rm T}$ was very sensitive to h, changing to 38‰ at h = 0.95and 152‰ at h = 0.98. (The partitioned dew flux fraction was less sensitive to h, changing by less than 0.08.) Similarly large transpiration isotopic signals have been reported by Lee et al. (2007), Welp et al. (2008) and Griffis et al. (2010) for night periods. Because F_d and F_2 are in opposite signs in Eq. (6), mathematically δ_n must fall outside the range bounded by the two end members, δ_d (the dew flux



Fig. 7 Average isotopic signals (¹⁸O) of ecosystem water pools and fluxes during dew formation in Luancheng. Numbers in parentheses indicate total fluxes in mm

isotopic signal) and δ_2 (the isotopic signal of the combined soil evaporation and transpiration fluxes). This seemingly abnormal result was a consequence of mass balance of two opposing fluxes. Similar results are suggested for the isotopic end member signals of CO₂ in the daylight hours which consist of foliage uptake and plant and soil respiration in opposite directions (Griffis et al. 2008; Ogée et al. 2004). The observed inequality relationship $\delta_{\rm e} < \delta_{\rm n} < \delta_{\rm d}$ indicates that soil evaporation cannot be the dominant component of F_2 . According to the automatic soil chamber measurement in a corn field (Griffis et al. 2010), soil evaporation is about 20% of the nighttime foliage transpiration. Using this flux ratio, the isotopic signal of the combined upward flux F_2 was $\delta_2 = 62\%$. It follows from Eq. (8) that the ratio of the dew flux to the net flux was 1.17. The contributions to the dew water formed on the foliage in the upper canopy can also be constrained in a similar fashion as shown in Fig. 7. The flux ratio F_d/F_n is moderately sensitive to the assumption of the soil evaporation contribution, increasing to 1.40 if the soil contribution to F_2 is increased to 0.5. Replacing δ_d with the equilibrium value has little impact on this flux ratio estimate.

Conclusions

In this study, the relations of dew water isotopic ratio to ecosystem water recycling during dew events were investigated using the data obtained in a cropland and a grassland in China. The main findings are summarized as follows:

1. The isotopic ratio of dew water could be approximated to an accuracy of 3.1‰ for D and 0.9‰ for ¹⁸O with the

equilibrium fractionation calculation despite the fact that humidity deviated from the saturation conditions. Some of the biases may have been caused by the water exchanged through the stomatal pathway with the heavier leaf water and by the vapor transpired from the lower canopy which had more enriched isotopic compositions.

- 2. A significant correlation existed in the isotopic compositions of leaf water and dew water during the dew events. This correlation was much stronger than with xylem water, suggesting that the top-down diffusion (exchange with atmospheric vapor) played a more important role than the bottom-up diffusion (exchange with xylem water) in controlling the leaf water turnover. We hypothesize that the leaf exchange with dew water drove a downward xylem flow, causing higher delta values of xylem water during dew formation than in midday hours.
- 3. Three sources of water were involved in dew formation, including a downward flux of water vapor from above the canopy and upward fluxes originated from soil evaporation and transpiration of the leaves in the lower canopy. The isotopic composition of the net ecosystem flux was positively correlated with that of dew water (p < 0.001), indicating the dominant role of the dew flux in the nighttime water vapor exchange. Our best estimate of the ratio of the dew flux to the net flux was 1.2 for the cropland according to the isotopic labeling method.

Acknowledgments This study was supported by the Ministry of Science and Technology of China (grant 2010CB833501), the National Natural Science Foundation of China (grants 30970517 and 31070408), the Strategic Program of Knowledge Innovation of the Chinese Academy of Sciences (grant KZCX2-EW-QN305), the Hundred Talents Program of the Chinese Academy of Sciences, the U. S. National Science Foundation (grant ATM-0914473) and a Rice Family Foundation grant. We thank the Luancheng Agricultural Station of Chinese Ecosystem Research Network (CERN) and Duolun Grassland Station of Institute of Botany for providing the necessary infrastructure. The first author gratefully acknowledges the support of the K.C. Wong Education Foundation, Hong Kong that supported his visit to Yale University. Thanks also go to Prof. S.P. Chen, Institute of Botany, for sharing her flux data for Duolun.

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