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Multilayered Modeling of Particulate Matter Removal by a Growing Forest over Time, From Plant Surface Deposition to Washoff via Rainfall

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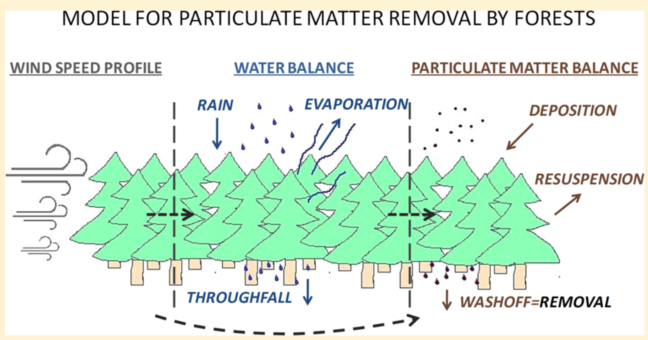
Supporting Information

ABSTRACT: Airborne fine particulate matter (PM) is responsible for the most severe health effects induced by air pollution in Europe. Vegetation, and forests in particular, can play a role in mitigating this pollution since they have a large surface area to filter PM out of the air. Many studies have solely focused on dry deposition of PM onto the tree surface, but deposited PM can be resuspended to the air or may be washed off by precipitation dripping from the plants to the soil. It is only the latter process that represents a net-removal from the atmosphere. To quantify this removal all these processes should be accounted for, which is the case in our modeling framework. Practically, a multilayered PM removal model for forest canopies is developed. In addition, the framework has been integrated into an existing forest growth model in order to account for changes in PM removal efficiency during forest growth. A case study was performed on a Scots pine stand in Belgium (Europe), resulting for 2010 in a dry deposition of 31 kg $PM_{2.5}$ (PM < 2.5 μm) ha^{-1} yr^{-1} from which 76% was resuspended and 24% washed off. For different future emission reduction scenarios from 2010 to 2030, with altering $PM_{2.5}$ air concentration, the avoided health costs due to $PM_{2.5}$ removal was estimated to range from 915 to 1075 euro ha^{-1} yr^{-1}. The presented model could even be used to predict nutrient input via particulate matter though further research is needed to improve and better validate the model.



INTRODUCTION

Airborne particulate matter (PM), occurring as solid or liquid matter, has a considerable damaging effect on human health by contributing to cardiovascular and cerebrovascular diseases.[1−3] According to the World Health Organization (WHO) PM air pollution contributes to approximately 800 000 premature deaths each year, ranking it as the 13th leading cause of mortality worldwide.[4] With regard to severity of human toxicity, an increase in damage has been associated with a decrease in particle size,[5,6] though Perronne et al.[7] argue this matter. Airborne particles are commonly subdivided according to their size via their (aerodynamic) diameter, for example, $PM_{2.5}$ denotes all particles with an (aerodynamic) diameter smaller than 2.5 μm. Important (emission) sources for PM, thoroughly discussed in the review by Belis et al.,[8] consist of traffic, crustal/mineral dust, sea/road salt, biomass and fossil fuel burning, (industrial) point sources and atmospheric formation of secondary aerosol.

Trees/forests can mitigate the damaging effect of PM through removal and subsequent lowering of its concentrations in the air.[9−11] This ecosystem process is being increasingly regarded as an important ecosystem service. Various experimental and modeling studies have by consequence been made to examine, measure or estimate PM removal by trees and/or forests.[12−22]

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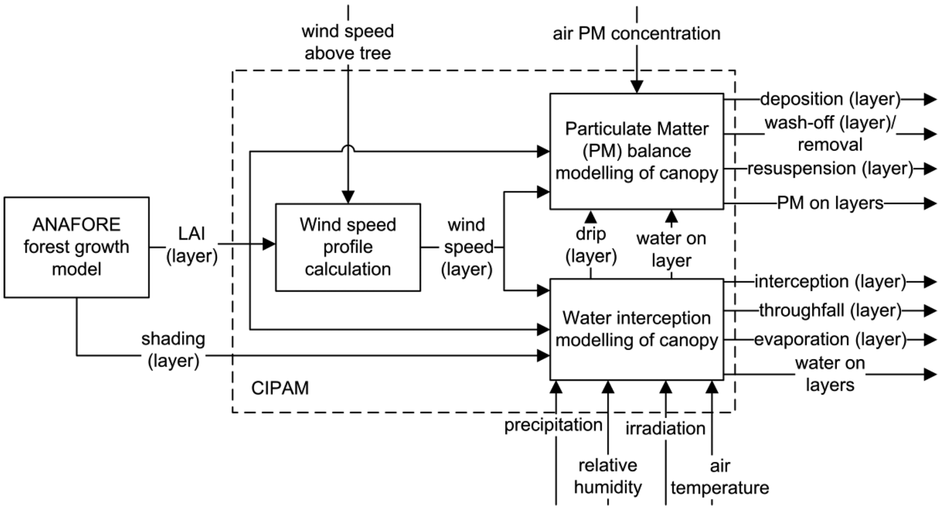

Figure 1. Introduced canopy interception and particulate matter removal model (CIPAM) and its integration with the analysis in forest ecosystems (ANAFORE) model. The leaf area index and shading per canopy layer is provided by ANAFORE as input for CIPAM. Model calculations are made at a certain time interval (e.g., 30 min) and per canopy layer with living foliage. Only variables with the labeling "(layer)", need to be known or are calculated per layer. The feedback loops within the dry matter balance and interception modeling are not depicted. PM: particulate matter; LAI: leaf area index.

To quantify the total removal by vegetation, all relevant underlying dynamic processes should be addressed. These are dry deposition (DD) on the vegetation surface, the subsequent (delayed) dry resuspension from the vegetation surface, washoff due to precipitation events,[9] and dissolution in water, plant uptake and/or encapsulation into the wax layer.[18,20,21] Removal of PM is defined here as the amount that cannot be resuspended again, thus the washed-off, taken-up, dissolved and encapsulated amounts, and not just the deposited share. No values are currently known for the rates at which dissolution, encapsulation and uptake of PM occur and they are therefore not considered further on. To our knowledge Nowak et al.[9] present the only framework which also covers washoff besides deposition and resuspension, and thus integrates PM and canopy interception modeling. However, considerable improvements can be made to their model. The first needed methodological improvement is the consideration of different vegetation layers, as the leaf area may vary considerably along a vertical gradient of a canopy,[23,24] with water and PM exchange between layers and a layer-specific characterization of wind speed, evaporation, dry deposition, etc. Nowak et al.[9] after all only perform calculations for a total tree canopy without subdivision in layers and considering a site average wind speed. Second, they did not consider dry deposition, resuspension and interception evaporation during precipitation events, while to the contrary PM concentrations do not drop to zero when it rains.[25,26] As a third need for improvement, in the study by Nowak et al.[9] was also assumed that the PM quantity that is washed off by precipitation is independent of the amount of water washed off, while this should be calculated otherwise, and they acknowledge this as a limitation. Lastly, a dynamic modeling of PM removal over time as the forest grows and alters under different management and weather/climate scenarios is lacking. In this study, a new modeling framework is therefore presented in order to estimate PM removal by trees and this by addressing the above-mentioned four required improvements. The model is applied to a case study of a Scots pine (*Pinus sylvestris* L.) stand in the Campine region of Flanders (northern Belgium) for the year 2010 using model runs with half-hourly calculations. To illustrate the potential importance of PM removal, Scots pine is a relevant example since studies have reported its good PM removal efficiency.[20,27] This is, among other features, caused by its evergreen and coniferous canopy.[28] Scots pine is also a major tree species in Flanders[30] and Europe.[29,30] Moreover, airborne PM is a major health concern in these highly populated and heavily industrialized areas. In the period 2009–2011 more than 90% of the European population was exposed to a yearly average $PM_{2.5}$ concentration that exceeds the current threshold value of the WHO (10 μg m^{-3}).[31] Also in Flanders this threshold value is exceeded since the average $PM_{2.5}$ concentration in 2011 was 17–24 μg m^{-3} at different sites.[32] In future, however, PM concentrations are predicted to decrease in Flanders in response to the implementation of emission legislation.[33] These concentration changes have been modeled for different scenarios until the year 2030.[33] The model introduced below will also run until 2030 for these emission reduction scenarios to examine the response to changes in PM concentrations and to predict the future PM amounts removed by the studied forest.

■ MATERIALS AND METHODS

Modeling Framework and Integration into ANAFORE. A new modeling framework, called canopy interception and particulate matter removal model (CIPAM) is introduced. It encompasses three submodels that estimate: (1) the wind speed along the tree crowns: (2) the water interception; and (3) the particulate matter (PM) balance of the forest canopy (Figure 1).

The focus of this paper is on the overall framework, and less attention is paid to the separate submodels. It is integrated into a forest growth model (4). The selected model is the process-based analysis in forest ecosystems (ANAFORE) model.[34,35] Note that through integration, our framework also has improved the ANAFORE model. CIPAM may, however, be used on its own if the necessary inputs are provided. These four different aspects are explained separately further on. The ANAFORE model provides leaf area (index) values, which is an

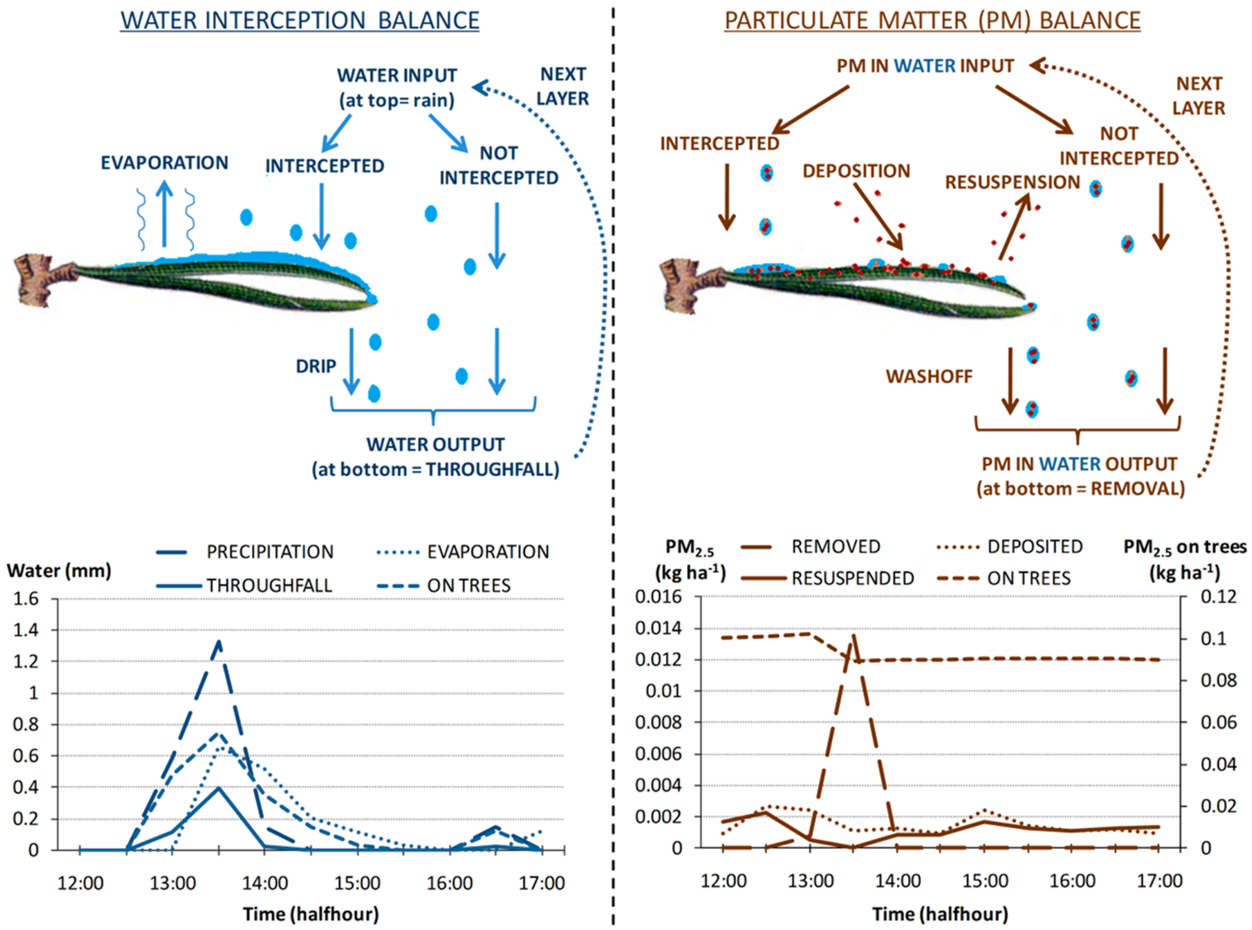

Figure 2. Considered fluxes per layer (drawing) and modeled results of these for the total tree over time (graphs), concerning the water and particulate matter (PM) canopy balances in the modeling framework. Washoff and drip occur when the water on the layer exceeds the storage capacity. The loop to the next tree layer is depicted using dotted arrows in the drawings. The graphs represent the case study results of the complete canopy for the Scots pine stand on the 1st of July 2010.

important input variable for all three submodels, and shading values, which influence interception evaporation in the canopy layers. Wind speed is an important driver for the other submodels since it affects canopy evaporation and dry deposition and resuspension of PM. The interception model yields the amount of water dripping to the lower layers per canopy layer, used to estimate the washoff of PM, and the interception water amount remaining per layer, which protects PM from being resuspended. Figure 2 gives an overview. These calculations are done per horizontal layer with living foliage and are thus restricted to the canopy part with living foliage. The thickness and amount of layers can be freely selected as long as leaf area index (LAI) and shading of all the layers are given as inputs. If foliage or whole trees die-off or are cut (due to thinning) the water and PM on the layers are considered as throughfall and removed PM, respectively. The calculations of CIPAM can be done for a given time interval, for example, half-hourly in the case study, and are performed per layer starting from the top layer and continue progressively toward the lower layers. Additionally, the ANAFORE model allows estimating the included processes while the forest is growing and is being managed. In the following text, subscript denotes a specific canopy layer with living foliage, where the layer counting starts from the top of the tree downward, unless mentioned otherwise. Note that in this framework no horizontal change of deposition across the forest is considered. The forest stand is considered to be surrounded by other stands of similar height, so that forest edge effects can be neglected.[36] The PM removal by understory vegetation can also be considered when including their LAI values and introducing respective model parameter values. We assume that water and PM are inert to other processes (aggregation, plant uptake, encapsulation,...) than the ones described below. Practically, the programming code is written in FORTRAN (with Intel Fortran compiler 14.02). Despite the presented improvements in the modeling framework, there are still considerable assumptions and shortcomings, which are presented throughout the model description and summarized in Table S1 of the Supporting Information (SI).

Wind Speed Calculations. Wind speed is a function of height in the canopy.[37] The ANAFORE model already provides a calculation of wind speed using a natural logarithm function,[38] which does not fit observed S-shaped profiles.[37] We will therefore adopt the equation of Yi,[39] which calculates wind speed at different heights through canopies with a uniform vertical distribution of the leaf area index (LAI; m^2 leaf area m^{-2} ground area) as

$$U(h) = \mathrm{Uh} \times \exp(-\frac{1}{2} \times \mathrm{LAI} \times (1 - h/Hc)) \tag{1}$$

In this formula, $U(h)$ is the wind speed ($m\ s^{-1}$) at the height h (m) within the canopy, Uh is the wind speed at the top of the canopy and Hc is the height of the canopy (m). This is done for each layer based on the wind speed of above layer and assuming a tree stand with similar configuration as the particular layer. The wind speed for each layer i, U_i (m s^{-1}), is considered as the average of the wind speed at the top and bottom of the layer.

Interception Modeling. Interception modeling is well reviewed by Muzylo et al.[40] Many studies focus only on water interception and storage by the leaf surface area. Llorens and Gallart,[41] however, point out the importance of including the wood area as well, particularly for Scots pine, which was done accordingly in the present study. Note that we did not account for stemflow. However, stemflow is generally a minor flow and not always accounted for in interception modeling.[40] Based on the review and results of Crockford and Richardson[42] we concluded that stemflow is rarely higher than 10% for tree species, and only 2% is reported for Scots pine by Llorens et al.[43] The calculation of the water mass balance per canopy layer constitutes the basis of this submodel:[44]

$$\Delta W_i = f_i \times I_i - E_i - D_i \tag{2}$$

where W_i (mm) is the water amount of layer i, I_i (mm) the water input, f_i (−) the fraction of intercepted water, E_i (mm) the evaporation rate and D_i (mm) the drip rate to the next layer, per layer i and time interval.

The interception fraction f_i, as calculated by Deckmyn et al.,[35] is based on Van Dijk and Bruijnzeel:[45]

$$f_i = 1 - \exp(-k \times \mathrm{LAI}_i) \tag{3}$$

Factor k is here called the interception coefficient. This constant is considered equal to 0.7 for forest.[35,44]

The water input I_i is the sum of the drip and not-yet intercepted, free throughfall, amount of water input received from the above layer:

$$I_i = D_{i-1} + (1 - f_i) \times I_{i\text{-}1} \tag{4}$$

For the topmost layer, this input, I_1, is the precipitation (mm) over the given time interval. A crucial parameter for calculating evaporation and drip is the storage capacity S_i (mm), which is the amount of water which can be stored/retained/accumulated by a layer on its foliage and wood (stem and branches). Specific storage capacity amounts can be measured for both tree parts as well as for layers.[41,46] The following formula for storage capacity was derived by Llorens and Gallart:[41]

$$S_i = \mathrm{LAI}_i \times 2 \times \mathrm{SL} + \mathrm{SW} \times \mathrm{WAI} \tag{5}$$

where SL (mm) and SW (mm) are the specific storage capacities per LAI and wood area index (WAI; m^2 wood area m^{-2} ground area), respectively. The wood area can be related on an empirical basis to the average leaf area of a certain time interval t by R, the ratio of LAI per WAI. This results in[41]

$$S_i = \mathrm{LAI}_i \times 2 \times \mathrm{SL} + \mathrm{SW}/R \times \pi \times \mathrm{LAI}_i(t) \tag{6}$$

Prior to calculation of the actual evaporation rate per layer E_i, the potential evaporation rate (Ep_i) needs to be calculated per time interval. This potential evaporation rate is the rate of actual evaporation if the considered canopy surface would be fully covered by water. It is here calculated using the widely applied Penmann[47]−Monteith[48] equation as done in the ANAFORE model, but without stomatal resistance. This rate is based on meteorological conditions: wind speed (varying for each layer), solar radiation, humidity and temperature.[35] As solar radiation has a considerable influence on evaporation rates, we took into account the influence of shading. For each layer, separate potential evaporation rates are calculated for the shaded (Eps_i) and sunlit (Epl_i) canopy parts using their respective different irradiation inputs. An overall potential evaporation rate is then estimated by the weighted average of the separate ones, as represented in the next equation:

$$\mathrm{Ep}_i(U_i) = \mathrm{SF}_i \times \mathrm{Eps}_i(U_i) + \mathrm{LF}_i \times \mathrm{Epl}_i(U_i) \tag{7}$$

SF_i and LF_i are the fractions of the layer which are shaded and lit, respectively, computed by ANAFORE. Having calculated the potential evaporation rate, the actual evaporation rate can be calculated via the following equation:[44]

$$E_i = (W_i/S_i)^{2/3} \times \mathrm{Ep}_i(U_i) \tag{8}$$

The values W_i and S_i represent the values at the beginning of the considered time interval. No actual evaporation rate is computed separately for the shaded and sunlit part as the specific water amounts on these parts are not known and the sunlit parts of the tree change during daytime as the sun position alters. A complex geometrical model is needed to address this matter. Indirectly we thus assume that the water per surface area is equal for the sunlit and shaded parts of each layer.

Drip D_i (mm) from a layer to the next layer below occurs if the water input W_i (mm) exceeds the storage capacity S_i (mm) of a layer at the end of a time interval:

$$D_i = W_i\text{-}S_i \tag{9}$$

The W_i (mm) is in that case set equal to S_i at the end of an interval.

The forest throughfall over a certain time interval, T (mm), is then the water leaving the lowest layer s with living foliage:

$$T = D_s + (1 - f_s) \times I_{S-1} \tag{10}$$

The total canopy evaporation rate, CE (mm), is the sum of the evaporation from all layers per time interval:

$$\mathrm{CE} = \sum_{i=1}^{S} E_i \tag{11}$$

This multilayered interception model, with evaporation based on Penman-Monteith for each layer and inclusion of wood area and shading, appears to be conceptually a high-end model among the ones mentioned by Muzylo et al.[40] Our submodel is a considerable improvement compared to the original approach in the ANAFORE model, in which canopy evaporation and drip were considered very simple using constant fractions (0.5) of the intercepted rain amount, based on Sampson et al.[49]

Particulate Matter Modeling. The particulate matter (PM) amount on a tree layer changes over time. The basic mass balance is the following:

$$\Delta P_i = \mathrm{DD}_i - \mathrm{RS}_i - \mathrm{WO}_i + \mathrm{PI}_i \times f_i \tag{12}$$

where P_i (μg) is the PM amount on the surface of foliage and wood of the layer, DD_i (μg) is the dry deposition, RS_i (μg) the resuspension, and WO_i (μg) the washoff amounts per layer and time interval. The f_i term is the interception fraction as explained in the above section. The last term of this equation denotes the input, besides through deposition, of PM, PI_i, over layer i and the given time interval. This is the sum of washoff from and nonintercepted input of the above layer:

$$\mathrm{PI}_i = \mathrm{WO}_{i-1} + (1\text{-}f_i) \times \mathrm{PI}_{i-1} \tag{13}$$

Dry deposition is the combined removal of particles from the atmosphere by sedimentation, Brownian motion, impaction, and direct interception.[17] Sedimentation can be neglected for smaller-size particles belonging to class $PM_{2.5}$.[50] Different research with associated approaches exists to address dry deposition on vegetation surfaces (reviewed by Petroff et al.[17]). The direct dry deposition rate or flux of a pollutant, here PM, per leaf area, without considering resuspension, DD_i (μg m^{-2} time interval^{-1}) can be estimated as

$$\mathrm{DD}_i = V_i(U_i) \times C \tag{14}$$

where V_i is the dry deposition velocity of the pollutant, here PM, per surface area (m time interval^{-1}) and C is the concentration of the pollutant, here PM (μg m^{-3}).[9,51] Deposition is usually expressed per ground surface area instead of per plant surface area, but here we refer to the one per plant area unless mentioned otherwise. To obtain the deposition rate per layer, the deposition velocity is multiplied with the surface area of the layer. This deposition velocity per plant surface area depends on the wind speed, particle size and tree configuration, defined, among others, by the tree species.[9,17] For example, pine needles are highly dissected and have a high surface area compared to flat broadleaves, per length of primary branch, and have been found to have 10 times higher deposition velocities than broadleaves.[28] These species-specific deposition velocities, related to wind speed (or friction velocity) and PM size, need to be derived from experiments (empirically), via wind tunnel or field measurements, or calculated (mechanistically). Although the latter approach has been widely used,[16,17,52,53] we here consider an empirical approach, similar to Nowak et al.[9] This approach was selected for its simplicity, linkage with measured results and inclusion of rebound, that is, the direct removal of particles during impaction.[54]

Resuspension, more precisely delayed resuspension, is the resuspension of material, such as PM, from surfaces, strictly speaking only the quantity which was deposited via atmospheric pathways, through wind shear or mechanical actions.[19,55] Though it is shown to be an important process,[27,55,56] it is rarely addressed in studies on PM removal by dry deposition onto vegetation. Sometimes a fixed constant for resuspended fraction per deposited amount is considered, such as 50% for PM_{10}.[13,57] However, resuspension depends on the accumulated PM amount on the tree (layer) and the wind speed.[19,27,55] The more particles accumulate on the foliage, the more particles can be removed. In addition, we consider the prevention of resuspension due to the water present on the canopy. Though, not the complete surface of the canopy (layer) is wet, only a part. Here, we estimate this fraction by the ratio of W_i on S_i. Resuspension is then calculated using the following formula:

$$\mathrm{RS}_i = \mathrm{RSf}_i(U_i) \times P_i \times (1 - W_i/S_i) \tag{15}$$

In this equation RSf_i (−) is the fraction of resuspensed PM per PM present on the layer per time interval of layer i. The values of W_i, S_i, and P_i are those at the beginning of the time interval. Note that W_i can be maximally equal to S_i at the beginning of a time interval (see section interception modeling). RSf_i is influenced by the wind speed.[27,55] To our knowledge, no mechanistic approach to calculate these values has been reported yet. Empirical values should therefore be used. The washoff of PM due to drip is calculated as

$$\mathrm{WO}_i = P_i \times D_i/(S_i + D_i) \tag{16}$$

In contrast to the approach of Nowak et al.,[9] not all PM is considered to wash off during canopy drip, which implies an important difference. The total PM removed by a forest, PR, (μg) over a certain time span is (with s the lowest canopy layer with living foliage):

$$\mathrm{PR} = \mathrm{WO}_s + (1 - f_s) \times \mathrm{WO}_{s-1} \tag{17}$$

The total resuspension, TRS, is the sum of the resuspension of all layers with living foliage:

$$\mathrm{TRS} = \sum_{i=1}^{S} \mathrm{RS}_i \tag{18}$$

Integration into the ANAFORE Model. The process-based ANAFORE model was developed by Deckmyn et al.[35] and later on improved with a new soil submodel.[34] It has already been applied to and validated for the Scots pine stand considered here.[34,35] For more information, see SI section B.

Because of the high variance in time of wind speed, PM concentrations, weather conditions and rainfall, it is crucial that the calculations are done using appropriate small time intervals. Our submodels were therefore integrated at the lowest, half-hourly, time step of ANAFORE. The inputs for the submodels are the leaf area (index) of the different canopy layers and the shading. The leaf area and LAI are recalculated on a daily basis, while the share of sunlit and shaded leaf area is determined on a half-hourly basis. The layer height is variable and is here set at 0.6 m, the smallest that can be used in the model, as LAI may vary considerably along a tree stem.

Case Study. The model is tested for $PM_{2.5}$ exchange between the atmosphere and a Scots pine stand for the year 2010 and also ran for different future scenarios for the period 2010−2030 while the forest grows.

Site Description. The specific forest ecosystem is a managed Scots pine forest stand located in Belgium (51°18′33” N, 4°31′14” E), the same stand as described and researched by Schaubroeck et al.[58] but now for the year 2010. Stand characteristics are discussed in the below section. A map is given in SI section C.

Model Input Data for the Specific Scots Pine Stand. The main input variables concerning the Scots pine stand for the ANAFORE model are derived from Gielen et al.[59] and Neirynck et al.,[60] and are mentioned in the SI section D. The modeled forest consists of trees which are assumed to be identical and no understory vegetation was considered to be present. This latter consideration is reasonable as on average the deposition velocity below the tree is only 15% of that at the canopy top due to a drop in wind speed and understory vegetation only represented 8% of the net primary production from 2001 to 2010 on average, reflecting a low yearly average LAI.[59] A yearly value of nitrogen deposition to the soil is considered of 40 kg N ha^{-1} yr^{-1} with a share of 0.21 NO_y-N and 0.79 NH_x-N,[60] and 390 ppmv CO_2. Half-hourly values for wind speed above the tree tops, air temperature, precipitation, relative humidity and radiation are obtained specifically for the Scots pine stand for the year 2010 from the Research Institute of Nature and Forest[61] and were measured as described in Neirynck et al.[50] These meteorological values are considered to

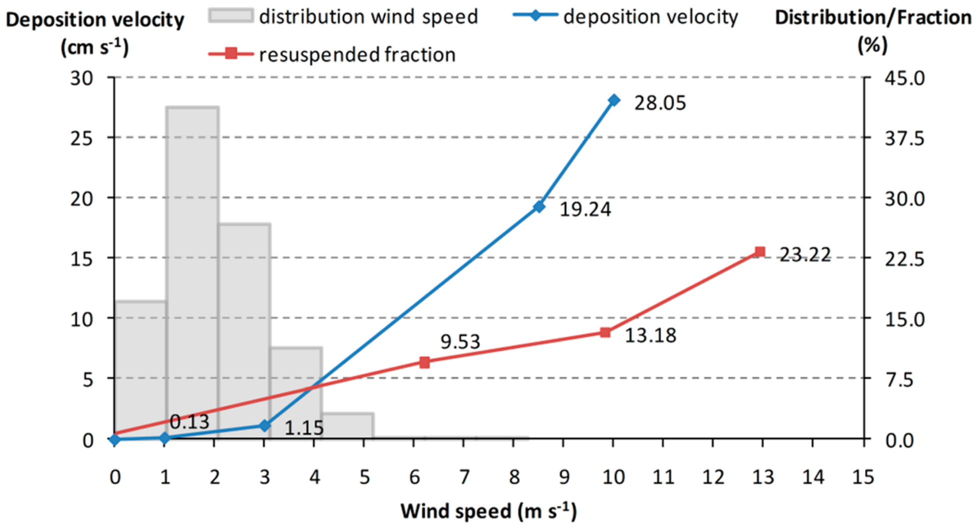

Figure 3. Distribution (%) of measured wind speed values (m s^{-1}) above the tree top at the Scots pine stand, considered deposition velocities (cm s^{-1}) per leaf area and resuspended fraction (%) as a function of wind speed.[9,27,28] Wind speed was measured on a half-hourly basis as described by Neirynck et al.[50] All discrete values (labeled points on the graph) of the deposition velocity and resuspended fraction, except the (0,0) points, which are set by default, are retrieved from Beckett et al.[28] and Pullman,[27] respectively. Linear interpolation between these discrete values, represented by the straight lines, is used to obtain values for other wind speeds.

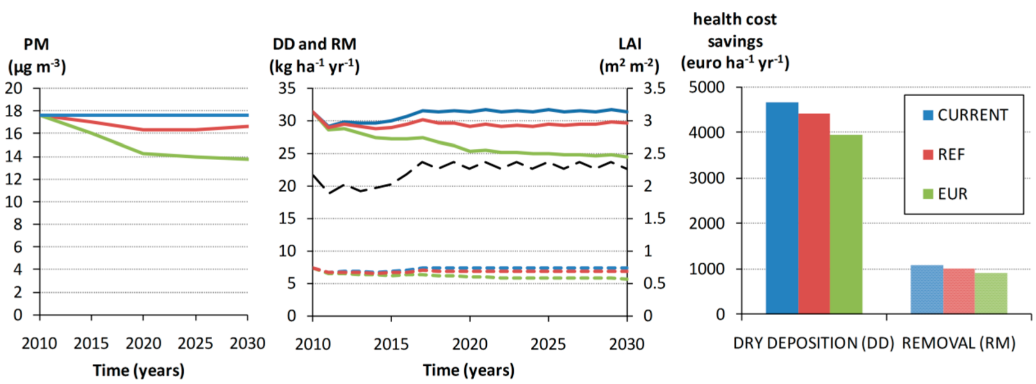

Figure 4. Change of airborne $PM_{2.5}$ concentrations (left graph), the associated dry deposition (DD, full lines) and removal (RM, dotted lines) of PM and the leaf are index (LAI, black dotted line) as the forest grows over time (middle graph). This all is shown for the "CURRENT" (blue) scenario (PM concentration unchanged since year 2010) and for the two future scenarios "REF" (red), a business-as-usual scenario, and "EUR" (green), a scenario where environmental European guidelines are followed. In the last graph DD and RM are presented in a monetary unit (based on the value of 150 euro kg^{-1} $PM_{2.5}$), depicted for the three scenarios.

be the same for all other years in all scenarios, e.g. windspeed on a specific time in 2030 is equal to that on the same time in 2010. A distribution of these yearly wind speed values is depicted in Figure 3. Less than 1% of the time points had no value and were given the average wind speed value of 2010, namely 1.931 m s^{-1}.

Hourly $PM_{2.5}$ concentrations above the Scots pine stand for the year 2010 are obtained from the Belgian Interregional Environment Agency (IRCEL),[62] which uses interpolation techniques to derive the concentration at other locations than those measured in discrete points by the Flemish Environment Agency (VMM).[63] For these data the more accurate RIO model was used with a resolution of 4 × 4 km.[64] In 2010 the modeled average $PM_{2.5}$ concentration above the Scots pine stand amounted to 17.65 μg m^{-3} (71% of PM_{10}), which was due to vehicle emission from a nearby highway, surrounding suburban traffic and particle/soot emissions from petrochemical refinery/power plants situated at the left bank of Antwerp port (see SI section C). For the predictions until 2030 only the PM concentrations were assumed to alter. Every five year (2015, 2020, 2025, 2030) PM concentrations were predicted for 3 × 3 km grids in Flanders for two alternative scenarios as was done in Van steertegem.[33] This was done based on the integrated approach of Deutsch et al.[65] in which the outcomes of the BelEUROS model, the integrated Eulerian air quality modeling system for European Operational Smog adapted to model PM in Belgium, was interpolated with RIO, Residual Interpolation Optimized for ozone and extended to other pollutants,[65,66] for the year 2007. These were renormalized to the measured value of 2010. The values for the years within the five-year intervals were determined using interpolation. The two alternative environmental policy scenarios are specific for Flanders and are those presented by a Flemish report of the VMM:[33] the Reference scenario (REF), representing future conditions under an unaltered Flemish environmental policy of the year 2008, and the Europe scenario (EUR), in which stricter policy regarding emission of PM and its precursors of the European Union is fulfilled.[67] The hourly PM concentrations are divided by the yearly 2010 average and multiplied with the predicted value. These values are shown in Figure 4.

Model Parameter Values for Scots Pine. The parameter values are given in Figure 3 and as in Table S3 of SI.

Regarding the leaf and woody storage capacity, specific values for Scots pine were adopted from the study of Llorens and Gallart.[41] The leaf storage capacity value is less than half of the value used by Nowak et al.[9] for all their considered tree species.

An important parameter in interception modeling is the R-ratio (LAI/WAI), though this ratio is variable. Deblonde et al.[74] denote an R-ratio of 3.0−11.6 for different red and jack pine stands. This R-ratio depends on different stand characteristics. Therefore, in our study we have selected the R-ratio value of 11.6 (i.e., the value of a stand most similar to ours). See SI, section F. A variable R-ratio in function of (these) stand characteristics or a direct calculation of WAI is needed to better address this matter.

For the deposition velocity per foliar surface area as a function of wind speed, we used values for black pine (*Pinus nigra*) reported by Becket et al.[28] based on wind tunnel tests with pot-grown small trees using particles of 1.28 (±0.07) μm diameter. Since *Pinus sylvestris* and *Pinus nigra* belong to the same genus, their branching (amount, structure and orientation) and needle structure is rather similar, justifying the use of black pine values for Scots pine. However, the deposition velocity also depends on the particle size.[12,17] Since the particles used by Beckett et al.[28] were smaller than 2.5 μm, applying their values is a reasonable choice, though it might be a crude estimation. Deposition velocities and resuspension fractions are only given for discrete values of wind speed (Figure 4), so that functions are needed to determine these values as a function of wind speed. Similar to Nowak et al.,[9] for 0 m s^{-1} the deposition velocity was set to 0 cm s^{-1} and the resuspended fraction to 0, by default, and linear interpolation was used to derive estimated values between the discrete values.

Pullman[27] studied the resuspension of $PM_{3.0}$ (with a mass-based average of 2.5 μm) from tree branches of three coniferous species in wind tunnel tests during 5, 10, and 20 min. We used the data from this study as reinterpreted by Nowak et al.[9] to address resuspension fractions. Note that latter authors used these values for all types of different tree species over an hour. Since Scots pine is a conifer, as are the tested species of Pullman,[27] it is appropriate to apply her values. Also here the values are used for a half-hourly interval, which is closer to the original intervals reported by Pullman.[27] However, since the values are for $PM_{3.0}$, an overestimation of $PM_{2.5}$ resuspension is probable.

RESULTS AND DISCUSSION

Case Study Results for 2010, Validation and Interpretation. Figure 2 shows half-hourly example results of the water and particulate matter (PM) balances of the Scots pine stand at the smallest time interval. The total measured rainfall of 2010 was 842 mm of which, according to two measurement campaigns, 678 and 720 mm were measured in two gutter-like throughfall collectors.[50] Our modeling framework, using a half-hourly time step, estimated a throughfall amount of 697 mm, which is very close to the measured amounts. The associated canopy evaporation was 145 mm. For validation of throughfall results on smaller time scales, see SI section G.1. The ANAFORE model as presented in Deckmyn et al.,[35] unadjusted, would have obtained a throughfall of 518 mm. Hence, according to these first results, our modified ANAFORE model leads to more accurate results in terms of canopy interception modeling.

Concerning the PM balance, our modeling framework, CIPAM with ANAFORE, calculated for 2010 a total dry deposition of 31.43 kg ha^{-1} yr^{-1} $PM_{2.5}$, from which 23.93 kg was resuspended, 7.38 kg was considered as definitely removed (dripping of the canopy to the forest floor) and 0.11 kg was still present on the tree canopy at the end of the year. Data validation of removal on a monthly time scale is presented in SI section G.2. The contribution of resuspension is 76%, which is rather high, but not unrealistic as Hirabayashi et al.[13] assumed a resuspension fraction of 50%, based on the work of Zinke et al.,[57] and Nowak et al.[9] obtained an average of 34% with a range of 27−43%. However, one needs to keep into account the differences, discussed in this manuscript, between our model and that of Nowak et al.[9] On the other hand, the applied parameter values need to be defined more precisely. Hence, it is clear that further research is required to improve the model parameters. Regarding dry deposition, most of the concerned studies have reported deposition velocities per ground area of forest. For our study we obtained a yearly value for $PM_{2.5}$ (based on the yearly total deposition and average $PM_{2.5}$ concentration) of 0.56 cm s^{-1} and a yearly average (of half-hourly deposition velocities) of 0.71 cm s^{-1} with a standard deviation of 0.83 cm s^{-1}. This is within the normal range of 0.1−1 cm s^{-1} reported by Belot et al.[68] and Pryor et al.[19] Specifically for this Scots pine stand Neirynck et al.[50] calculated a deposition velocity for particulate NH_4^+ as fraction of $PM_{2.5}$ of 1.2 cm s^{-1} from September 1999 to October 2000 and of 1.5 cm s^{-1} from January until March 2001. These values are about double as high as ours, though a different approach was used to obtain their values and they were only for the NH_4^+ fraction of $PM_{2.5}$. Deposition velocity values for Scots pine mentioned in the review by Petroff et al.[17] range from 0.15 to 4 cm s^{-1}, although this is for different particle sizes. There is thus still large variation in reported deposition values. Additionally, an accurate size distribution of the considered PM needs to be known to calculate and use more precise deposition velocities as a function of particle diameter and wind speed. Regarding model uncertainty, the exact size of uncertainty is impossible to define as no uncertainty intervals are known for all input and parameter values. It will however for sure be considerable with a roughly estimated deviation of 15−50% for the final $PM_{2.5}$ removal. For a better understanding of CIPAM, its assets and limitations, the influence of parameters wind speed, precipitation, $PM_{2.5}$ concentration and LAI was assessed by altering these parameter values for the Scots pine stand in 2010. This sensitivity analysis is given in SI section H.

Predictions for Future Scenarios Until 2030. First we discuss the results of the current scenario (no change in PM concentration), in order to define the influence of the change in forest growth. The most important variable of the forest in this context is LAI, its change over time is depicted in Figure 4. Note that the number of trees is assumed to stay the same (no management or dieback). The average LAI of 2010 was calculated as 2.17. LAI dropped slightly at the beginning, then increased and further on remained quasi constant at 2.3. Its increase might be attributed to canopy closure as there was still a gap fraction of 43% in the period 2007−2008.[69] Dry deposition (DD) and removal (RM) of $PM_{2.5}$ follow the same pattern as LAI, although the relative increase in DD and RM is less pronounced compared to the LAI increase. This is mainly due to the fact that increasing LAI reduces the wind speed within the canopy, which is a negative feedback on deposition and removal. For more information see section H.4.

For the two future scenarios, REF and EUR, the $PM_{2.5}$ concentration declines over time (Figure 4), which is due to a decrease in secondary PM formation because of a reduction in emission of precursors such as NO_x (transport sector), NH_3 (cattle) and SO_2 (energy and household sectors). This decline is, as such, not caused by a decrease of (primary) PM emission, which only decreases until 2015 but then starts to increase again until 2030 because of a rise in emissions from the industry and energy (coal burning) sectors due to economic growth.[33] This drop in $PM_{2.5}$ concentration is logically more profound for the EUR than the REF scenario.

In the first years, DD and RM decrease for both the REF and EUR scenario mainly in response to the LAI decrease, along with the decrease in $PM_{2.5}$ concentration. After that, DD and RM in the EUR and REF scenarios follow the same pattern as the current scenario but lower values are reached. The decrease in PM concentration outweighs the effect of an increased LAI and subsequently DD and RM decrease. After 20 years, the relative decrease in DD and RM is quasi identical to the relative decrease in airborne $PM_{2.5}$ concentration. Overall, change in land characteristics and PM concentrations need both to be predicted in order to estimate future PM removal.

Associated Health/Economic Benefit. Specifically for Flanders, based on hospital stay, work absence and willingness-to-pay costs induced by health damage, the health benefit of $PM_{2.5}$ removal can be converted to an estimated average monetary value of 150 euro kg^{-1} $PM_{2.5}$ removed, while this is only 25 euro kg^{-1} in case of $PM_{2.5-10}$, often called coarse PM.[5,70] The derivation of this value in literature is summarized in SI section I. As the site is situated close to populated areas (see SI section C) and the region Flanders, for which the number is valid, is a densely populated area, this validates to a certain extent the use of a single estimated value as an approximation. We applied the value to our case study results (see Figure 4). For the year 2010 this results in a benefit of 1073 euro ha^{-1} yr^{-1} for removed $PM_{2.5}$, compared to 4763 euro ha^{-1} yr^{-1} if only deposition without resuspension would be considered. Over the period 2010−2030, an average range of 915−1075 euro ha^{-1} yr^{-1} is obtained for $PM_{2.5}$ removal for the different future scenarios; the lowering in $PM_{2.5}$ concentration due to emission legislation, decreases its removal by the Scots pine stand. In 2030 a larger difference is obtained: 853 euro ha^{-1} yr^{-1} for the EUR scenario compared to 1093 euro ha^{-1} yr^{-1} for the current scenario. Comparing these values with an estimated rental price of 143.6 euro ha^{-1} yr^{-1} (based on the sale price for the Scots pine stand of 16000 euro ha^{-1}, obtained from the current public owner Agency of Nature and Forest, and on a local land buy to rent price ratio) illustrates for all scenarios that this ecosystem service, removal of $PM_{2.5}$ out of the air, is currently underrated.

Future Perspectives. First, besides the perspectives mentioned here, the limitations and assumptions (see SI Table S1) can be elucidated through additional research. Second, CIPAM results should be validated with more experimental results. Third, the model can be adapted to other tree species for further improvement and validation. Fourth, the model can be modified to calculate removal of other (gaseous) pollutants besides PM, such as nitrogen dioxide, sulfur dioxide, etc.[13] In addition, dry deposition of atmospheric particles is, besides wet deposition via rainfall, an important pathway for relevant chemical compounds (e.g., nitrogen compounds), which do not only affect forest growth but also alter global biogeochemical cycling, water and soil pollution.[12] Concerning nitrogen deposition for the Scots pine stand, studied in this study, Neirynck et al.[50] calculated that dry deposition of the particulate NH_4^+ and NO_3^- comprised in $PM_{2.5}$ was already responsible for 20% of the total, showcasing the importance of this pathway for nitrogen input. In that field of science so-called canopy budget models are mostly applied to derive removal (in that context called deposition) and canopy exchange of different compounds from measured data of throughfall and wet deposition, but they are inapt for predictive purposes.[71−73] CIPAM can in fact be seen as a predictive canopy budget model which is only suited for PM. It does not account for gaseous compounds and does not allow for canopy exchange, although the model might be extended for these purposes.

Of the studied Scots pine stand, at maximum only 15% of the wet and dry nitrogen deposition (also including deposition of gases) was estimated to be taken up by the canopy.[50] Nonetheless, not considering interactions on the vegetation surface between water, PM, and the vegetation itself, is an important limitation of the proposed model, which should be kept in mind. If rates of these processes are known, they should be integrated into the modeling framework. Considering these interactions, resuspension and removal could change considerably. CIPAM may, however, be further used as a tool to study these interactions as it generates half-hourly water and PM amounts on plant surfaces per canopy layer.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information gives additional information on limitations and assumptions of the presented modeling framework (section A), additional information on ANAFORE (section B), geographical location of the Scots pine stand (section C), Scots pine stand input data (section D), model parameter values (section E), the R-ratio (section F), data validation for 2010 (section G), sensitivity analysis (section H) and explanation of health cost derivation (section I). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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REFERENCES

(1) Anderson, J. O.; Thundiyil, J. G.; Stolbach, A. Clearing the air: A review of the effects of particulate matter air pollution on human health. *J. Med. Toxicol.* **2012**, *8*, 166−175.

(2) Nelin, T. D.; Joseph, A. M.; Gorr, M. W.; Wold, L. E. Direct and indirect effects of particulate matter on the cardiovascular system. *Toxicol. Lett.* **2012**, *208*, 293−299.

(3) Wu, S.; Deng, F.; Wei, H.; Huang, J.; Wang, X.; Hao, Y.; Zheng, C.; Qin, Y.; Lv, H.; Shima, M.; et al. Association of cardiopulmonary health effects with source-appointed ambient fine particulate in Beijing, China: A combined analysis from the healthy volunteer natural relocation (HVNR) study. *Environ. Sci. Technol.* **2014**, *48*, 3438−3448.

(4) WHO. *World Health Report 2002*; World Health Organization (WHO): Geneva, 2002.

(5) De Nocker, L.; Michiels, H.; Deutsch, F.; Lefebvre, W.; Buekers, J.; Torfs, R. *Actualisering van de Externe Milieuschadekosten (algemeen Voor Vlaanderen) Met Betrekking Tot Luchtverontreiniging En Klimaatverandering, Studie Uitgevoerd in Opdracht van de Vlaamse Milieumaatschappij, MIRA, MIRA/2010/03*; VITO, 2010.

(6) Mirowsky, J.; Hickey, C.; Horton, L.; Blaustein, M.; Galdanes, K.; Peltier, R. E.; Chillrud, S.; Chen, L. C.; Ross, J.; Nadas, A.; et al. The effect of particle size, location and season on the toxicity of urban and rural particulate matter. *Inhal. Toxicol.* **2013**, *25*, 747−757.

(7) Perrone, M. G.; Gualtieri, M.; Consonni, V.; Ferrero, L.; Sangiorgi, G.; Longhin, E.; Ballabio, D.; Bolzacchini, E.; Camatini, M. Particle size, chemical composition, seasons of the year and urban, rural or remote site origins as determinants of biological effects of particulate matter on pulmonary cells. *Environ. Pollut.* **2013**, *176*, 215−227.

(8) Belis, C. A.; Karagulian, F.; Larsen, B. R.; Hopke, P. K. Critical review and meta-analysis of ambient particulate matter source apportionment using receptor models in Europe. *Atmos. Environ.* **2013**, *69*, 94−108.

(9) Nowak, D. J.; Hirabayashi, S.; Bodine, A.; Hoehn, R. Modeled $PM_{2.5}$ removal by trees in ten U.S. cities and associated health effects. *Environ. Pollut.* **2013**, *178*, 395−402.

(10) Schaubroeck, T.; Alvarenga, R. A. F.; Verheyen, K.; Muys, B.; Dewulf, J. Quantifying the environmental impact of an integrated human/industrial-natural system using life cycle assessment; A case study on a forest and wood processing chain. *Environ. Sci. Technol.* **2013**, *47*, 13578−13586.

(11) Tiwary, A.; Sinnett, D.; Peachey, C.; Chalabi, Z.; Vardoulakis, S.; Fletcher, T.; Leonardi, G.; Grundy, C.; Azapagic, A.; Hutchings, T. R. An integrated tool to assess the role of new planting in PM_{10} capture and the human health benefits: A case study in London. *Environ. Pollut.* **2009**, *157*, 2645−2653.

(12) Fowler, D.; Pilegaard, K.; Sutton, M. A.; Ambus, P.; Raivonen, M.; Duyzer, J.; Simpson, D.; Fagerli, H.; Fuzzi, S.; Schjoerring, J. K.; et al. Atmospheric composition change: Ecosystems−Atmosphere interactions. *Atmos. Environ.* **2009**, *43*, 5193−5267.

(13) Hirabayashi, S.; Kroll, C. N.; Nowak, D. J. Development of a distributed air pollutant dry deposition modeling framework. *Environ. Pollut.* **2012**, *171*, 9−17.

(14) Katul, G. G.; Grönholm, T.; Launiainen, S.; Vesala, T. The effects of the canopy medium on dry deposition velocities of aerosol particles in the canopy sub-layer above forested ecosystems. *Atmos. Environ.* **2011**, *45*, 1203−1212.

(15) Lin, M.-Y.; Khlystov, A. Investigation of ultrafine particle deposition to vegetation branches in a wind tunnel. *Aerosol Sci. Technol.* **2012**, *46*, 465−472.

(16) Petroff, A.; Zhang, L.; Pryor, S. C.; Belot, Y. An extended dry deposition model for aerosols onto broadleaf canopies. *J. Aerosol Sci.* **2009**, *40*, 218−240.

(17) Petroff, A.; Mailliat, A.; Amielh, M.; Anselmet, F. Aerosol dry deposition on vegetative canopies. Part I: Review of present knowledge. *Atmos. Environ.* **2008**, *42*, 3625−3653.

(18) Popek, R.; Gawrońska, H.; Wrochna, M.; Gawroński, S. W.; Sæbø, A. Particulate matter on foliage of 13 woody species: Deposition on surfaces and phytostabilisation in waxes—A 3-year study. *Int. J. Phytorem.* **2013**, *15*, 245−256.

(19) Pryor, S. C.; Gallagher, M.; Sievering, H.; Larsen, S. E.; Barthelmie, R. J.; Birsan, F.; Nemitz, E.; Rinne, J.; Kulmala, M.; Grönholm, T.; et al. A review of measurement and modelling results of particle atmosphere−Surface exchange. *Tellus B* **2008**, *60*, 42−75.

(20) Sæbø, A.; Popek, R.; Nawrot, B.; Hanslin, H. M.; Gawronska, H.; Gawronski, S. W. Plant species differences in particulate matter accumulation on leaf surfaces. *Sci. Total Environ.* **2012**, *427*−*428*, 347−354.

(21) Terzaghi, E.; Wild, E.; Zacchello, G.; Cerabolini, B. E. L.; Jones, K. C.; Di Guardo, A. Forest filter effect: Role of leaves in capturing/releasing air particulate matter and its associated PAHs. *Atmos. Environ.* **2013**, *74*, 378−384.

(22) Wang, L.; Liu, L.; Gao, S.; Hasi, E.; Wang, Z. Physicochemical characteristics of ambient particles settling upon leaf surfaces of urban plants in Beijing. *J. Environ. Sci.* **2006**, *18*, 921−926.

(23) Aber, J. D. Foliage-height profiles and succession in northern hardwood forests. *Ecology* **1979**, *60*, 18−23.

(24) Van der Zande, D.; Mereu, S.; Nadezhdina, N.; Cermak, J.; Muys, B.; Coppin, P.; Manes, F. 3D upscaling of transpiration from leaf to tree using ground-based LiDAR: Application on a mediterranean holm oak (*Quercus Ilex* L.) Tree. *Agric. For. Meteorol.* **2009**, *149*, 1573−1583.

(25) Feng, X.; Wang, S. Influence of different weather events on concentrations of particulate matter with different sizes in Lanzhou, China. *J. Environ. Sci.* **2012**, *24*, 665−674.

(26) Gonçalves, F. L. T.; Beheng, K. D.; Massambani, O.; Vautz, W.; Klockow, D. Scavenging processes of atmospheric particulate matter: A numerical modeling of case studies. *Rev. Bras. Meteorol.* **2010**, *25*, 437−447.

(27) Pullman, M. R. *Conifer $PM_{2.5}$ Deposition and Resuspension in Wind and Rain Events*; Cornell University, 2009.

(28) Beckett, K. P.; Freer-Smith, P. H.; Taylor, G. Particulate pollution capture by urban trees: Effect of species and windspeed. *Glob. Change Biol.* **2000**, *6*, 995−1003.

(29) Skjøth, C. A.; Geels, C.; Hvidberg, M.; Hertel, O.; Brandt, J.; Frohn, L. M.; Hansen, K. M.; Hedegaard, G. B.; Christensen, J. H.; Moseholm, L. An inventory of tree species in Europe—An essential data input for air pollution modelling. *Ecol. Model.* **2008**, *217*, 292−304.

(30) Tröltzsch, K.; Van Brusselen, J.; Schuck, A. Spatial occurrence of major tree species groups in Europe derived from multiple data sources. *For. Ecol. Manag.* **2009**, *257*, 294−302.

(31) European Environment Agency. *Air Quality in Europe - 2013 Report*, 2013.

(32) Vlaamse milieumaatschappij. *Luchtkwaliteit in Het Vlaamse Gewest Jaarverslag; Immissiemeetnetten 2011*; Flanders, Belgium, 2011.

(33) Van Steertegem, M. *Milieuverkenning 2030. Mileurapport Vlaanderen*; Vlaamse Milieumaatschappij: Aalst, 2009.

(34) Deckmyn, G.; Campioli, M.; Muys, B.; Kraigher, H. Simulating C cycles in forest soils: Including the active role of micro-organisms in the ANAFORE forest model. *Ecol. Model.* **2011**, *222*, 1972−1985.

(35) Deckmyn, G.; Verbeeck, H.; Op de Beeck, M.; Vansteenkiste, D.; Steppe, K.; Ceulemans, R. ANAFORE: A stand-scale process-based forest model that includes wood tissue development and labile carbon storage in trees. *Ecol. Model.* **2008**, *215*, 345−368.

(36) Wuyts, K.; Verheyen, K.; De Schrijver, A.; Cornelis, W. M.; Gabriels, D. The impact of forest edge structure on longitudinal patterns of deposition, wind speed, and turbulence. *Atmos. Environ.* **2008**, *42*, 8651−8660.

(37) Sypka, P.; Starzak, R. Simplified, empirical model of wind speed profile under canopy of istebna spruce stand in mountain valley. *Agric. For. Meteorol.* **2013**, *171*−*172*, 220−233.
(38) Raupach, M. R. Simplified expressions for vegetation roughness length and zero-plane displacement as functions of canopy height and area index. *Bound. Layer Meteorol.* **1994**, *71*, 211−216.
(39) Yi, C. Momentum transfer within canopies. *J. Appl. Meteorol. Climatol.* **2008**, *47*, 262−275.
(40) Muzylo, A.; Llorens, P.; Valente, F.; Keizer, J. J.; Domingo, F.; Gash, J. H. C. A review of rainfall interception modelling. *J. Hydrol.* **2009**, *370*, 191−206.
(41) Llorens, P.; Gallart, F. A simplified method for forest water storage capacity measurement. *J. Hydrol.* **2000**, *240*, 131−144.
(42) Crockford, R. H.; Richardson, D. P. Partitioning of rainfall into throughfall, stemflow and interception: Effect of forest type, ground cover and climate. *Hydrol. Process.* **2000**, *14*, 2903−2920.
(43) Llorens, P. Rainfall interception by a pinus sylvestris forest patch overgrown in a Mediterranean mountainous abandoned area II. Assessment of the applicability of Gash's analytical model. *J. Hydrol.* **1997**, *199*, 346−359.
(44) Wang, J.; Endreny, T. A.; Nowak, D. J. Mechanistic simulation of tree effects in an urban water balance model. *J. Am. Water Resour. Assoc* **2008**, *44*, 75−85.
(45) Van Dijk, A. I. J.; Bruijnzeel, L. Modelling rainfall interception by vegetation of variable density using an adapted analytical model. Part 2. Model validation for a tropical upland mixed cropping system. *J. Hydrol.* **2001**, *247*, 239−262.
(46) Liu, S. Estimation of rainfall storage capacity in the canopies in north-central Florida. 1998, *207*,32−41.
(47) Penman, H. L. Natural evaporation from open water, bare soil and grass. *Proc. R. Soc. London, Ser. A* **1948**, *193*, 120−145.
(48) Monteith, J. L. Evaporation and environment. In *The State and Movement of Water in Living Organisms*; Cambridge University Press: Londen, 1965; pp 205−234.
(49) Sampson, D. A.; Janssens, I. A.; Ceulemans, R. Simulated soil CO efflux and net ecosystem exchange in a 70-year-old Belgian scots pine stand using the process model SECRETS. *Ann. For. Sci.* **2001**, *58*, 31−46.
(50) Neirynck, J.; Kowalski, A. S.; Carrara, A.; Genouw, G.; Berghmans, P.; Ceulemans, R. Fluxes of oxidised and reduced nitrogen above a mixed coniferous forest exposed to various nitrogen emission sources. *Environ. Pollut.* **2007**, *149*, 31−43.
(51) Hicks, B. B.; Matt, D. R.; McMillen, R. T. A micro-meteorological investigation of surface exchange of O_3, SO_2, and NO_2: A case study. *Bound.-Layer Meteorol.* **1989**, *47*, 321−336.
(52) Kouznetsov, R.; Sofiev, M. A methodology for evaluation of vertical dispersion and dry deposition of atmospheric aerosols. *J. Geophys. Res., Atmos.* **2012**, *117*.
(53) Piskunov, V. N. Parameterization of aerosol dry deposition velocities onto smooth and rough surfaces. *J. Aerosol Sci.* **2009**, *40*, 664−679.
(54) Paw, U. K. T.; Braaten, D. A. Experimental evidence of the importance of rebound in net deposition of particles. *Aerosol Sci. Technol.* **1992**, *17*, 278−288.
(55) Nicholson, K. W. Wind tunnel experiments on the resuspension of particulate material. *Atmos. Environ., Part A* **1993**, *27*, 181−188.
(56) Gillette, D. A.; Lawson, R. E., Jr.; Thompson, R. S. A "test of concept" comparison of aerodynamic and mechanical resuspension mechanisms for particles deposited on field rye grass (*Secale cercele*). Part 1. Relative particle flux rates. *Atmos. Environ.* **2004**, *38*, 4789−4797.
(57) Zinke, P. J.; Sopper, W. E.; Lull, H. W. *Forest Interception Studies in the United States. In; Forest Hydrology. Proceedings of National Foundation advanced science seminar*; Pergamon Press: Oxford, 1967; pp 137−161.
(58) Schaubroeck, T.; Staelens, J.; Verheyen, K.; Muys, B.; Dewulf, J. Improved ecological network analysis for environmental sustainability assessment; A case study on a forest ecosystem. *Ecol. Model.* **2012**, *247*, 144−156.
(59) Gielen, B.; De Vos, B.; Campioli, M.; Neirynck, J.; Papale, D.; Verstraeten, A.; Ceulemans, R.; Janssens, I. A. Biometric and eddy covariance-based assessment of decadal carbon sequestration of a temperate scots pine forest. *Agric. For. Meteorol.* **2013**, *174*−*175*, 135−143.
(60) Neirynck, J.; Janssens, I. A.; Roskams, P.; Quataert, P.; Verschelde, P.; Ceulemans, R. Nitrogen biogeochemistry of a mature scots pine forest subjected to high nitrogen loads. *Biogeochemistry* **2008**, *91*, 201−222.
(61) Instituut voor Natuur- en Bosonderzoek. http://www.inbo.be/content/homepage_nl.asp (accessed December 11, 2013).
(62) IRCEL - CELINE Belgium. http://www.irceline.be/ (accessed March 19, 2014).
(63) Vlaamse Milieumaatschappij. http://www.vmm.be/ (accessed December 12, 2013).
(64) Janssen, S.; Dumont, G.; Fierens, F.; Mensink, C. Spatial interpolation of air pollution measurements using CORINE land cover data. *Atmos. Environ.* **2008**, *42*, 4884−4903.
(65) Deutsch, F.; Vankerkom, J.; Janssen, L.; Janssen, S.; Bencs, L.; Van Grieken, R.; Fierens, F.; Dumont, G.; Mensink, C. Modelling concentrations of airborne primary and secondary PM_{10} and $PM_{2.5}$ with the BelEUROS-model in Belgium. *Ecol. Model.* **2008**, *217*, 230−239.
(66) Hooyberghs, J.; Mensink, C.; Dumont, G.; Fierens, F. Spatial interpolation of ambient ozone concentrations from sparse monitoring points in Belgium. *J. Environ. Monit.* **2006**, *8*, 1129−1135.
(67) Amann, M.; Bertok, I.; Cofala, J.; Heyes, C.; Klimont, Z.; Rafaj, P.; Schöpp, W.; Wagner, F. *NEC Scenario Analysis Report Nr. 6 National Emission Ceilings for 2020*; International Institute for Applied Systems Analysis (IIASA), 2008.
(68) Belot, Y.; Camus, H.; Gauthier, D.; Caput, C. Uptake of small particles by tree canopies. *Sci. Total Environ.* **1994**, *157*, 1−6.
(69) Op de Beeck, M.; Gielen, B.; Jonckheere, I.; Samson, R.; Janssens, I. A.; Ceulemans, R. Needle age-related and seasonal photosynthetic capacity variation is negligible for modelling yearly gas exchange of a sparse temperate Scots pine forest. *Biogeosciences* **2010**, *7*, 199−215.
(70) Liekens, I.; Van der Biest, K.; Staes, J.; De Nocker, L.; Aertsens, J.; Broekx, S. *Waardering van Ecosysteemdiensten, Een Handleiding. Studie in Opdracht van LNE Afdeling Milieu-, Natuur- En Energiebeleid*; VITO, 2013.
(71) Adriaenssens, S.; Staelens, J.; Baeten, L.; Verstraeten, A.; Boeckx, P.; Samson, R.; Verheyen, K. Influence of canopy budget model approaches on atmospheric deposition estimates to forests. *Biogeochemistry* **2013**, *116*, 215−229.
(72) Hansen, K.; Thimonier, A.; Clarke, N.; Staelens, J.; Žlindra, D.; Waldner, P.; Marchetto, A. Atmospheric deposition to forest ecosystems. In *Developments in Environmental Science*; Elsevier, 2013; Vol. *12*, pp 337−374.
(73) Staelens, J.; Houle, D.; Schrijver, A. D.; Neirynck, J.; Verheyen, K. Calculating dry deposition and canopy exchange with the canopy budget model: Review of assumptions and application to two deciduous forests. *Water. Air. Soil Pollut.* **2008**, *191*, 149−169.
(74) Deblonde, G.; Penner, M.; Royer, A. Measuring Leaf Area Index with the LI-COR LAI-2000 in Pine Stands. *Ecology* **1994**, *75*, 1507−1511.