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Sensitivity analysis of an ozone deposition model

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ABSTRACT

In this study, sophisticated sensitivity analyses of a detailed ozone dry deposition model were performed for five soil types (sand, sandy loam, loam, clay loam, clay) and four land use categories (agricultural land, grass, coniferous and deciduous forests). Deposition velocity and ozone flux depend on the weather situation, physiological state of the plants and numerous surface-, vegetation-, and soil-dependent parameters. The input data and the parameters of deposition-related calculations all have higher or lower spatial and temporal variability. We have investigated the effect of the variability of the meteorological data (cloudiness, relative humidity and air temperature), plant-dependent (leaf area index and maximum stomatal conductance) and soil-dependent (soil moisture) parameters on ozone deposition velocity. To evaluate this effect, two global methods, the Morris method and the Monte Carlo analysis with Latin hypercube sampling were applied. Additionally, local sensitivity analyses were performed to estimate the contribution of non-stomatal resistances to deposition velocity. Using the Monte Carlo simulations, the ensemble effect of several nonlinear processes can be recognised and described. Based on the results of the Morris method, the individual effects on deposition velocity are found to be significant in the case of soil moisture and maximum stomatal conductance. Temperature and leaf area index are also important factors; the former is primarily in the case of agricultural land, while the latter is for grass and coniferous forest. The results of local sensitivity analyses reveal the importance of non-stomatal resistances.

1. Introduction

Near-surface ozone plays an important role in the formation of photochemical air pollution (Krupa and Manning, 1988). During the last few years, in spite of the rigid emission reduction of ozone precursor compounds, ozone concentration still has high values in Europe (Jonson et al., 2006). Ozone and other compounds produced by photochemical cycles affect both vegetation and human health (Fiscus et al., 2005; Eller and Sparks, 2006; Black et al., 2007). In particular, elevated ozone concentrations can be potentially harmful to agricultural and natural vegetation. Occasional extreme concentrations may cause visible injury to the vegetation while the long-term, growing-season averaged exposure can result in decreased productivity and crop yield (Fuhrer et al., 1997). Recently it has also been shown that the indirect radiative forcing of climate change through ozone effects on the land carbon exchange could be an important factor and can induce a positive feedback for global warming (Ashmore, 2005; Stich et al., 2007).

From the biological aspect the response of vegetation to ozone is more closely related to the absorbed dose through the stomata than to external ozone exposure (Musselman et al., 2006; Paoletti and Manning, 2007). To characterize the vegetation damage caused by ozone, in the past decade, flux-based ozone exposure metrics have been favoured as opposed to concentration-based indices (Ashmore et al., 2004; Matyssek et al., 2007).

The ozone flux has been estimated by both more and less sophisticated deposition models for several types of vegetation and even for different climatic and geographic regions (in the last few years e.g. Emberson et al., 2000; Zhang et al., 2002; Nussbaum et al., 2003; Lagzi et al., 2004, 2006; Mészáros et al., 2006; Alonso et al., 2007; Ashmore et al., 2007; Keller et al., 2007; Pleijel et al., 2007; Schaub et al., 2007; Simpson et al., 2007; Tuovinen et al., 2007).

In such models, the ozone flux is controlled by ozone concentration and by deposition velocity via parameterization of the canopy and stomatal conductances. In general, in the models a multiplicative algorithm of stomatal conductance is applied. This method includes functions for the effects of photosynthetically active radiation, air temperature, soil water content and other parameters affecting stomatal conductance. Plant stomatal conductance and the calculation of deposition velocity play a key role in most deposition models applied to risk assessment and to estimation climatic effects of tropospheric ozone.

The main limitation of these deposition models lies in the uncertainty and variability of the model input data, such as the

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Table 1
Vegetation-dependent parameters used in the simulations.

Vegetation type	Albedo	Surface resistance R_s ($s\,m^{-1}$)	Cuticular resistance R_{cut} ($s\,m^{-1}$)	Radiation correction term b_{st} ($W\,m^{-2}$)	Optimal temperature t_{opt} (°C)	Minimum temperature t_{min} (°C)	Maximum temperature t_{max} (°C)	Vapour pressure deficit b_e (hPa)
Agricultural land	0.17	400	1500	60	25	5	45	0.02
Grass	0.19	300	2000	20	40	10	55	0.02
Coniferous forest	0.12	300	2000	44	15	−5	40	0.03
Deciduous forest	0.16	300	2000	43	27	0	45	0.04

Sources: Baldocchi et al. (1987), Hicks et al. (1987), Meyers et al. (1998), and Brook et al. (1999).

time- and species-dependent parameters. Therefore, these parameters may give rise to significant uncertainties in the simulation results, and it is very important to know the effect of the individual input parameters on model output. Nonlinear models, such as most of the deposition models, can magnify the uncertainties of some parameters and damp others. In many cases, the models may over- or underestimate the stomatal ozone fluxes through the calculation of deposition velocity. Sensitivity analysis is an effective tool for exploring the relation between the output of mathematical models and the input data which comprise the values of parameters as well as the initial conditions (Turányi et al., 2002; Zádor et al., 2005a,b; Zsély et al., 2005; Tomlin, 2006). To investigate the effects of six important model input parameters on total deposition and stomatal conductance of the ozone, the Monte Carlo and the Morris analyses (Saltelli et al., 2000) were performed for four vegetations and for five soil types. The following model input values were analyzed: air temperature and relative humidity at 2 m height, cloudiness, leaf area index, maximum stomatal conductance and root-zone soil water content. To explore the uncertainty of non-stomatal deposition, the effects of soil and cuticular resistance on deposition velocity were analysed in the frame of a local sensitivity analysis.

A main aim of this study is to reveal the variability of some environmental parameters and data on the estimation of ozone deposition velocity, which can also help to understand the controlling mechanisms of deposition processes. Detailed statistical analyses of a regional scale deposition model could draw a picture on the effects of input data: to which degree and how the meteorological variables and vegetation parameters influence the model results. With the application of the Monte Carlo method, the nature of the relationship between each model input and output can be described, while the Morris investigation presents their sensitivities.

In this paper we present the values of both the total and the stomatal part of deposition velocity along with the determination of the probability density functions of the model results.

2. Materials and methods

2.1. Description of the applied deposition model

For the purpose of estimating the environmental load caused by atmospheric pollutants, a high spatial resolution deposition model was developed and tested (Lagzi et al., 2004, 2006; Mészáros et al., 2006). Up to now, model applications have been carried out to simulate the turbulent fluxes of ozone from the atmosphere into the underlying surface. The total ozone flux (F_t) can be described as a product of the deposition velocity (v_d) and the concentration (c_r) of ozone at a reference height (within the surface layer of the model):

$$F_t = v_d c_r. \tag{1}$$

The concentration fields are obtained from a transport model (Lagzi et al., 2004). However, in this study we have focused only on the deposition velocity and its dependence on some input parameters. Deposition velocity of ozone was estimated using a simple resistance method. In this process the deposition velocity is defined as the inverse of the sum of the atmospheric and surface resistances:

$$v_d = \left(R_a + R_b + R_c\right)^{-1}, \tag{2}$$

where R_a, R_b, and R_c are the aerodynamic resistance, the quasi-laminar boundary layer resistance, and the canopy resistance, respectively.

The aerodynamic resistance and the boundary layer resistance retard the turbulent gas-transport and molecular diffusion above the canopy and in a thin layer over surfaces, respectively. The aerodynamic resistance can be described by the Monin–Obukhov similarity theory taking into account the atmospheric stability (e.g. Lagzi et al., 2006), and it was parameterized iteratively from Monin–Obukhov length, friction velocity, sensible and latent heat fluxes. During the estimation of the energy budget components, a constant value for albedo was considered for each biome type (Table 1).

The boundary layer resistance is calculated by an empirical relationship after Hicks et al. (1987).

The canopy resistance depends on both meteorological data and the physiological soil and plant characteristics, and it is parameterized by the following equation:

$$R_c = \frac{1}{R_{st}^{-1} + R_s^{-1} + R_{cut}^{-1}}, \tag{3}$$

where R_{st}, R_s, and R_{cut} are the stomatal, the surface and the cuticular resistances, respectively. Surface dependent values of R_s and R_{cut} are presented in Table 1. The stomatal resistance can be obtained from the widely used, empirical formula of Jarvis (1976) referring to a vegetation canopy:

$$R_{st} = \frac{1}{G_{st}(\mathrm{PAR}) f_t(t) f_e(e) f_\theta(\theta) f_{D,i}}, \tag{4}$$

where $G_{st}(\mathrm{PAR})$ is the unstressed canopy stomatal conductance, a function of PAR (photosynthetically active radiation). In this parameterization, the canopy is divided into sunlit and shaded leaves, and G_{st} is calculated with the following form:

$$G_{st}(\mathrm{PAR}) = \frac{\mathrm{LAI_s}}{r_{st}(\mathrm{PAR_s})} + \frac{\mathrm{LAI_{sh}}}{r_{st}(\mathrm{PAR_{sh}})}, \tag{5}$$

$$r_{st}(\mathrm{PAR_s}) = r_{st,min}(1 + b_{st}/\mathrm{PAR_s}), \tag{6}$$

$$r_{st}(\mathrm{PAR_{sh}}) = r_{st,min}(1 + b_{st}/\mathrm{PAR_{sh}}), \tag{7}$$

where $\mathrm{LAI_s}$ and $\mathrm{LAI_{sh}}$ are the total sunlit and shaded leaf area indices, respectively, $\mathrm{PAR_s}$ and $\mathrm{PAR_{sh}}$ are PAR received by sunlit

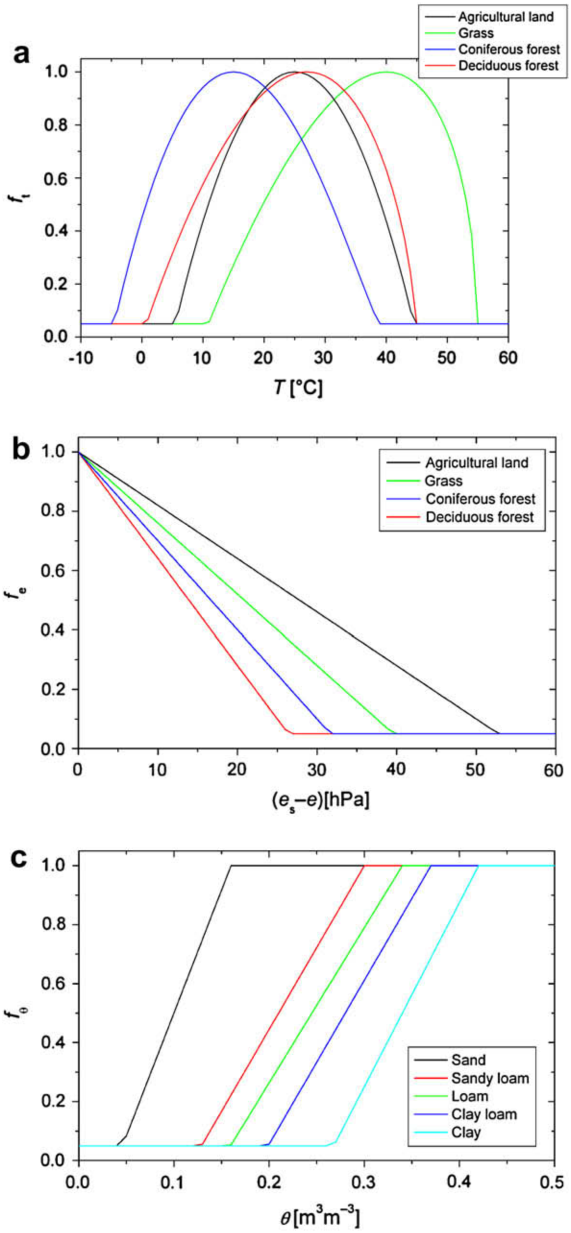

Fig. 1. Stress function for the estimation of stomatal resistance: temperature stress (a), water vapour stress (b) and soil moisture stress (c), respectively.

and shaded leaves, respectively. The term $r_{\mathrm{st,min}}$ is defined as a reciprocal value of the so-called maximum stomatal conductance ($g_{\max}$) and b_{st} is a plant species dependent constant. LAI$_\mathrm{s}$, LAI$_\mathrm{sh}$, PAR$_\mathrm{s}$ and PAR$_\mathrm{sh}$ terms are parameterized after Zhang et al. (2001).

The stress factors in the denominator in Eq. (4) range between 0 and 1 and modify the stomatal resistance: $f_\mathrm{t}(t)$, $f_\mathrm{e}(e)$ and $f_\theta(\theta)$ describe the effect of temperature, vapour pressure deficit and soil water stress on stomata, respectively (Fig. 1), while $f_{\mathrm{D},i}$ modifies the stomatal resistance for the pollutant gas of interest (for ozone, $f_{\mathrm{D},i} = 0.625$).

The temperature stress function is described by the following relation:

$$f_\mathrm{t} = \frac{t - t_{\min}}{t_{\mathrm{opt}} - t_{\min}}\left(\frac{t_{\max} - t}{t_{\max} - t_{\mathrm{opt}}}\right)^{b_\mathrm{t}}, \tag{8}$$

where

$$b_\mathrm{t} = \frac{t_{\max} - t_{\mathrm{opt}}}{t_{\max} - t_{\min}}. \tag{9}$$

Here $t_{\min}$, $t_{\max}$ and t_{opt} are the vegetation dependent minimum, maximum and the optimal temperature (Table 1), respectively.

The stress of the vapour pressure deficit can be parameterised by the following form:

$$f_\mathrm{e} = 1 - b_\mathrm{e}(e_\mathrm{s} - e), \tag{10}$$

where b_e is a vegetation dependent constant, e and e_s are the water vapour pressure and the saturated water vapour pressure, respectively.

The soil water stress function $f_\theta(\theta)$ is calculated with root-zone soil water content (θ):

$$f_\theta = \begin{cases} 1, & \text{if } \theta > \theta_\mathrm{f} \\ \max\left\{\dfrac{\theta - \theta_\mathrm{w}}{\theta_\mathrm{f} - \theta_\mathrm{w}}, 0.05\right\}, & \text{if } \theta_\mathrm{w} < \theta \le \theta_\mathrm{f} \\ 0.05, & \text{if } \theta \le \theta_\mathrm{w} \end{cases}, \tag{11}$$

where θ_w and θ_f are the soil moisture contents at wilting point and at field capacity, respectively. These terms depend on the soil texture. The following soil texture categories were used in the model: sand, sandy loam, loam, clay loam and clay. Table 2 contains θ_w and θ_f values for the soil textures used in this study. Root-zone soil water content, θ was modelled by a simple water-budget model.

Four different vegetation types (agricultural land, grass, coniferous forest and deciduous forest) were distinguished in this study. The vegetation-dependent parameters are presented in Table 1.

The stomatal conductance or in other words, the stomatal deposition velocity means the reciprocal value of the stomatal resistance (R_{st}), which characterizes the flux through the stomata, similar to total deposition velocity (v_d) in Eq. (2), which describes the total flux in the near surface layer.

2.2. Data sources

The effects of the six model inputs were investigated by the analyses; two plant parameters (leaf area index, maximum stomatal conductance), three atmospheric variables (cloudiness, relative humidity, temperature) and the root-zone soil moisture content, which expresses the effect of soil type on dry deposition velocities.

All the plant parameter values (average, minimum, maximum and standard deviation) were taken from a significant work of Breuer et al. (2003), which contains plant-specific parameter values for four main land cover types: crops, pasture (herbs, forbs, grasses), coniferous and deciduous trees both in global and European temperate ecosystems. The plant parameters (maximum stomatal conductance and leaf area index) concerning the European vegetation summarised in this overview were used as data for the sensitivity analysis (Table 3a).

The meteorological data were taken from the ALADIN mesoscale limited area numerical weather prediction model used by the

Table 2
A summary of the soil moisture contents used in this study (based on Ács, 2003).

Soil type	Soil moisture at wilting point θ_w (m^3 m^{-3})	Soil moisture at field capacity θ_f (m^3 m^{-3})	Saturated soil moisture θ_s (m^3 m^{-3})
Sand	0.03	0.15	0.40
Sandy loam	0.11	0.29	0.45
Loam	0.14	0.33	0.50
Clay loam	0.18	0.36	0.53
Clay	0.25	0.41	0.55

Table 3a
A summary of the statistics of model input data – plant parameters (source: Breuer et al., 2003).

Variables		Vegetation	Input data for the probability density function			
Vegetation parameters			Mean	Min	Max	SD
LAI	Leaf area index	Agricultural land	3.7	1.8	10.0	1.5
		Grass	7.2	0.5	16.2	3.8
		Coniferous forest	6.2	1.1	14.0	3.3
		Deciduous forest	5.8	2.5	10.0	1.7
g_{max} ($mm\,s^{-1}$)	Maximum stomatal conductance	Agricultural land	5.7	2.9	10.0	2.6
		Grass	5.4	1.2	12.5	2.7
		Coniferous forest	1.8	0.5	4.0	0.9
		Deciduous forest	4.2	1.6	8.5	1.8

Hungarian Meteorological Service (Horányi et al., 1996). In this case, 12 UTC analysis fields for July 1998 were used (Table 3b). For this period, the statistical values (average, minimum, maximum and standard deviation) of the variables (temperature, relative humidity and cloudiness) were calculated from grid data over a region that covers Hungary (φ: 45.7°N–48.6°N, λ: 16.1°E–23.0°E, with resolution: 0.1° × 0.15°).

The input value of daily root-zone soil moisture was calculated by a simple bucket model on a rectangular grid with a 0.1° × 0.15° resolution over Hungary for July 1998. The soil texture data were obtained using a Hungarian soil-map (Várallyay et al., 1980). The grid cell soil texture was represented by the dominant soil texture. The meteorological data (mean daily temperature and relative humidity, as well as precipitation amount) utilised in root-zone soil moisture calculation were generated by the ALADIN model. The upper limit of soil moisture was the saturated soil moisture (θ_s) applied for each soil type (Table 2). Based on the estimation of the bucket model, the statistical parameters of soil moisture were determined for five soil categories using the spatial average of the results for each soil type over the whole period (Table 3c). The investigated parameters, meteorological and soil statistical data are shown in Tables 3a–c.

Though the above presented statistical datasets are for Hungary and its surrounding area, our results are characteristic for the behaviour of the deposition models used for the temperate region. Moreover, meteorological data for a typical summer month were used in this study.

2.3. Global sensitivity analysis

In this investigation two different methods were applied. Both of them are global techniques (i.e. they explore the whole parameter space, the parameters are not fixed at their mean values). The first method is the Monte Carlo Analysis with Latin Hypercube Sampling (LHS-MC) (Saltelli et al., 2000; Moore and Londergan, 2001; Zádor et al., 2005a,b; Zsély et al., 2005, 2008). For this method, the probability density functions of the input data (see Section 2.2) were assumed to have a normal distribution truncated at the minimum and maximum values.

According to these functions a large number (10000) of parameter sets were generated and the model was run with each of these parameter sets. Model calculations were carried out for an arbitrarily chosen geographical point ($\varphi = 46.97°$, $\lambda = 19.55°$) for July 1998 at 12 UTC for each day. All these 31 daytime deposition velocities were averaged and used as the representative deposition velocity for the given dataset. Simulations with the same parameter set were performed for the 20 combinations of the five soil and four vegetation types. Additionally, both total and stomatal deposition velocities were calculated. This means 40 (20 for total and 20 for stomatal velocities) output datasets for the six examined model parameters.

This method provides a good estimation of the attainable minimum and maximum values of the calculated results (Zádor et al., 2005b; Zsély et al., 2005, 2008), while the parameters change in their possible intervals. The Latin hypercube sampling ensures that the parameter space is represented with a good approximation of full coverage. The LHS-MC analysis provides accurate and unbiased (McKay et al., 1979) information about the sensitivity of models, while it does not reveal the individual contributions.

The second method was the Morris one-at-a-time method (Morris, 1991; Saltelli et al., 2000, 2004; Zádor et al., 2005b; Campolongo et al., 2007). The estimation of probability density functions of the input values is not required, only their possible intervals are used (see Section 2.2.). In this method $N+1$ parameter sets are generated (where N is the number of parameters) using the algorithm of Morris, so that a given parameter takes precisely two values throughout the sets: in every run, just one parameter is changed randomly compared to the previous run, and every parameter is changed precisely once during the $N+1$ runs. The values of the parameters are selected from the whole range of the parameter values by setting out a small number of equidistant points. The procedure was repeated 10 times, so new $N+1$ parameter sets were designed in the same way. The elementary effect of changing a parameter can be calculated as the difference between the calculated results using different values of the parameter, while the other parameters remain unchanged (but not at their mean values). The means and the standard deviations of these effects are plotted against each other. Parameters with a high mean effect are influential, whereas a low mean effect shows that variability in that parameter does not affect the given output variable significantly. Low standard deviation represents the parameter has an approximately linear effect; whereas a high value means that the effect of that parameter is nonlinear or depends to a large extent on the actual values of the other parameters (interaction).

2.4. Sensitivity for non-stomatal resistances

The deposition process depends on the local weather conditions, surface and soil type as well as plant physiological state. Here

Table 3b
A summary of the statistics of model input data – meteorological data (sources: Aladin numerical mesoscale model).

Variable		Input data for the probability density function				Period	Resolution	Area	Source
Meteorological data		Mean	Min	Max	SD				
N (%)	Cloudiness	12.70	0.00	100.00	14.26	1998 July	0.1° × 0.15°	45.7°N–48.6°N, 16.1°E–23.0°E	ALADIN numerical meso-scale model 12UTC
RH (%)	Relative humidity at 2 m	69.37	35.00	100.00	10.88				
T (K)	Air temperature at 2 m	297.52	277.55	309.65	5.00				

Table 3c
A summary of the statistics of model input data – soil data (calculated by a bucket model).

Variable			Input data for the probability density function				Period	Resolution	Area	Source
Soil data			Mean	Min	Max	SD				
θ ($m^3\ m^{-3}$)	Soil moisture	Sand	0.111	0.037	0.236	0.037	1998 July	0.1° × 0.15°	45.7°N–48.6°N, 16.1°E–23.0°E	Calculated daily values by a bucket-model
		Sandy loam	0.215	0.124	0.355	0.038				
		Loam	0.259	0.136	0.500	0.044				
		Clay loam	0.296	0.209	0.420	0.036				
		Clay	0.369	0.230	0.550	0.071				

the effects of the variation of non-stomatal deposition pathways (cuticular and surface resistances) were also analysed using the local sensitivity technique. For this purpose, the deposition model runs were performed with appropriate fixed (mean) values of plant, meteorological and soil data (Tables 3a–c). The effects of the changes of non-stomatal resistances on the deposition velocity of ozone were calculated separately. The cuticular and surface resistances – which are dominantly constant in deposition models – were considered. The cuticular resistance was modified individually from 1000 up to 10000 s m^{-1}. The surface resistance (which represents the soil pathways) was varied between 100 and 1500 s m^{-1}. These are usual ranges for both resistances obtained from the literature (e.g. Massman, 2004).

3. Results and discussion

3.1. Monte Carlo analysis

The main advantage of these statistical simulations is the comprehensive approach: with a large number of parameter sets, the ensemble effect of several nonlinear processes can be recognised and described. The only weakness is that this method treats the parameters as independent variables, even though some of them related to others. It is well known that meteorological variables are not always independent of each other. For example, in general there is a correlation between temperature and relative humidity. However, a wide range of temperature values can occur in the case of a given relative humidity and vice versa. During the analysis, the whole range of realistic values of meteorological elements was covered, with respect to the specified area and period. Nevertheless, the application of the Monte Carlo analysis is a useful tool to investigate the behaviour of the applied model.

The application of sensitivity analysis often reveals errors in the model or its unexpected behaviour. Usually in the deposition models LAI is below 10. However, the achievable maximum value of this index is larger in case of some vegetation (see Table 3a). The Monte Carlo calculations showed that the model does not give an adequate response when LAI is larger than a threshold value. This value depends on some model parameters and the day of the year. The reason for this behaviour is due to the insufficient parameterization of photosynthetically active radiation (Zhang et al., 2001). As it can be seen in Fig. 2a, PAR_{sh}, that is PAR received by shaded leaves (see Eq. (9) in Zhang et al., 2001), decreases as LAI increases. In the function of incoming solar radiation, PAR_{sh} could become lower than zero. The higher the solar radiation is, the lower the value of LAI when PAR_{sh} reaches zero. In our investigations, for July 1998, the threshold LAI was found to be around 14.5. Therefore, above this value of LAI the deposition velocity was not estimated. The characteristic shape of total deposition velocity as a function of LAI can be seen in Fig. 2b.

Fig. 3 presents the distribution of the total and the stomatal deposition velocities as the function of the given parameter. All diagrams in the figure refer to loam soil and agricultural land. This combination of soil and vegetation types was chosen arbitrarily and similar distribution patterns were obtained in the case of the other 19 pairs of soil/vegetation. Based on the distributions, soil moisture and maximum stomatal conductance have a near-linear relationship with deposition velocity in both total and stomatal cases. The relative humidity has a small linear effect. The actual value of the total deposition velocity is primarily affected by both meteorological data (through R_a, R_b and R_{st}) and plant physiological parameters. However, the distribution of the deposition velocity is mainly governed by the variability of temperature via temperature stress function Eq. (8), which has a local maximum as can be shown in Fig. 1a. In this case the deposition velocity has an optimal shape distribution, where for optimal temperature (when the stomatal conductance is not limited) the highest deposition velocities can be found (Fig. 3).

In the case of LAI, the distribution of deposition velocity shows a similar pattern. The higher the LAI is, the higher the v_d is until a maximum value (this is around LAI = 6 in Fig. 2). A further increase of LAI causes a decrease of deposition velocity due to stomatal conductance. G_{st} (5) also decreases with higher LAI through the parameterization of photosynthetically active radiation, PAR received by sunlit and shaded leaves (PAR_s and PAR_{sh}). As

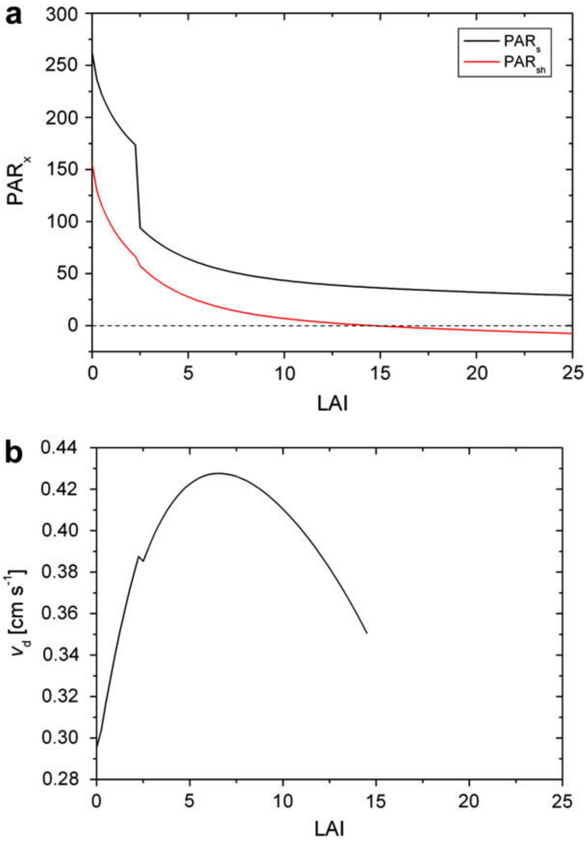

Fig. 2. Parameterization of PAR and PAR_{sh} functions (a) and v_d (b) as a function of LAI using the mean values for the input parameters (Tables 3a–c). The discontinuities at LAI = 2.5 are due to the different parameterization of these functions in the Zhang model (Zhang et al., 2001).

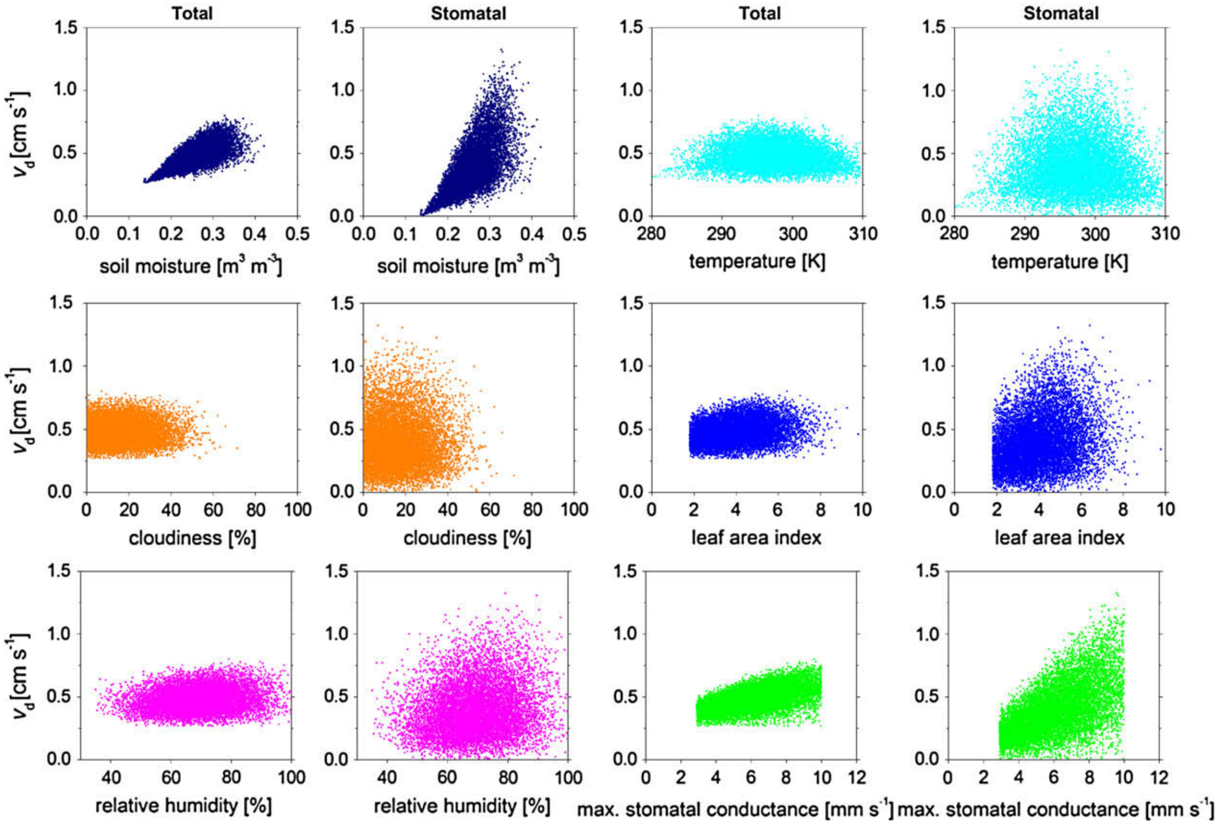

Fig. 3. Distribution of the total and the stomatal deposition velocities over loam soil and agricultural land. Results obtained from Monte Carlo analysis.

it can be seen in the graphs, cloudiness, which affects the incoming solar radiation and the net radiation, has no significant coherence with the deposition velocities.

The distributions of total and stomatal deposition velocity in the case of the same parameters show some similarities, but the ranges of attainable values are different. Minimum values of stomatal deposition velocities can approach zero when some effects block the uptake through the stomata. Stomatal deposition velocity (stomatal conductance) has greater variability than total deposition velocity. Under some conditions, when one or more environmental stresses hit the vegetation, the stomatal uptake is nearly zero, and when almost no environmental stress appears the stomatal deposition velocity approaches its vegetation dependent maximum.

Fig. 4 shows the summarized results of the Monte Carlo analysis together with the average and statistical parameters of both the total and the stomatal deposition velocities. The results characterize the whole range of parameter values. For a given spatial and temporal situation, the calculated values related to given vegetation and soil, as well as the differences among these values could be very different. Even so, based on Fig. 4, some similar properties of

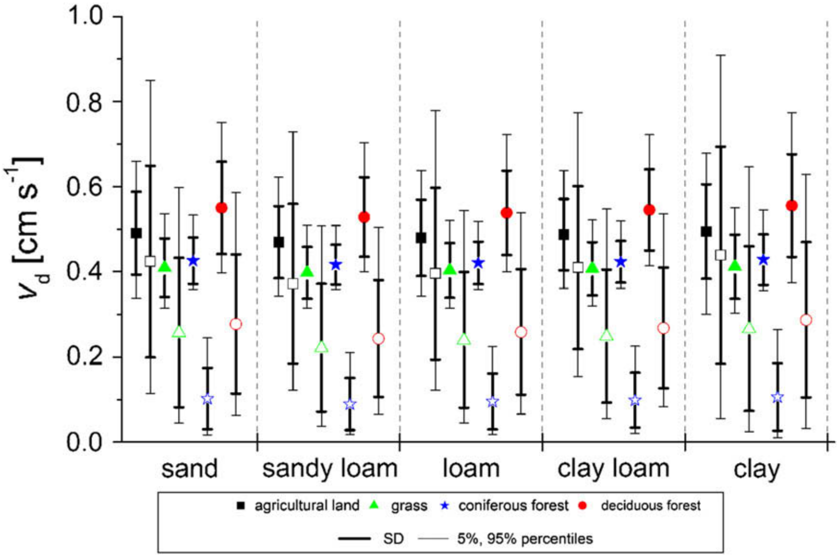

Fig. 4. Average, standard deviation and percentiles of the total and the stomatal deposition velocities over the various soil and surface types. The stomatal deposition velocities are presented by empty symbols. Results obtained from Monte Carlo analysis.

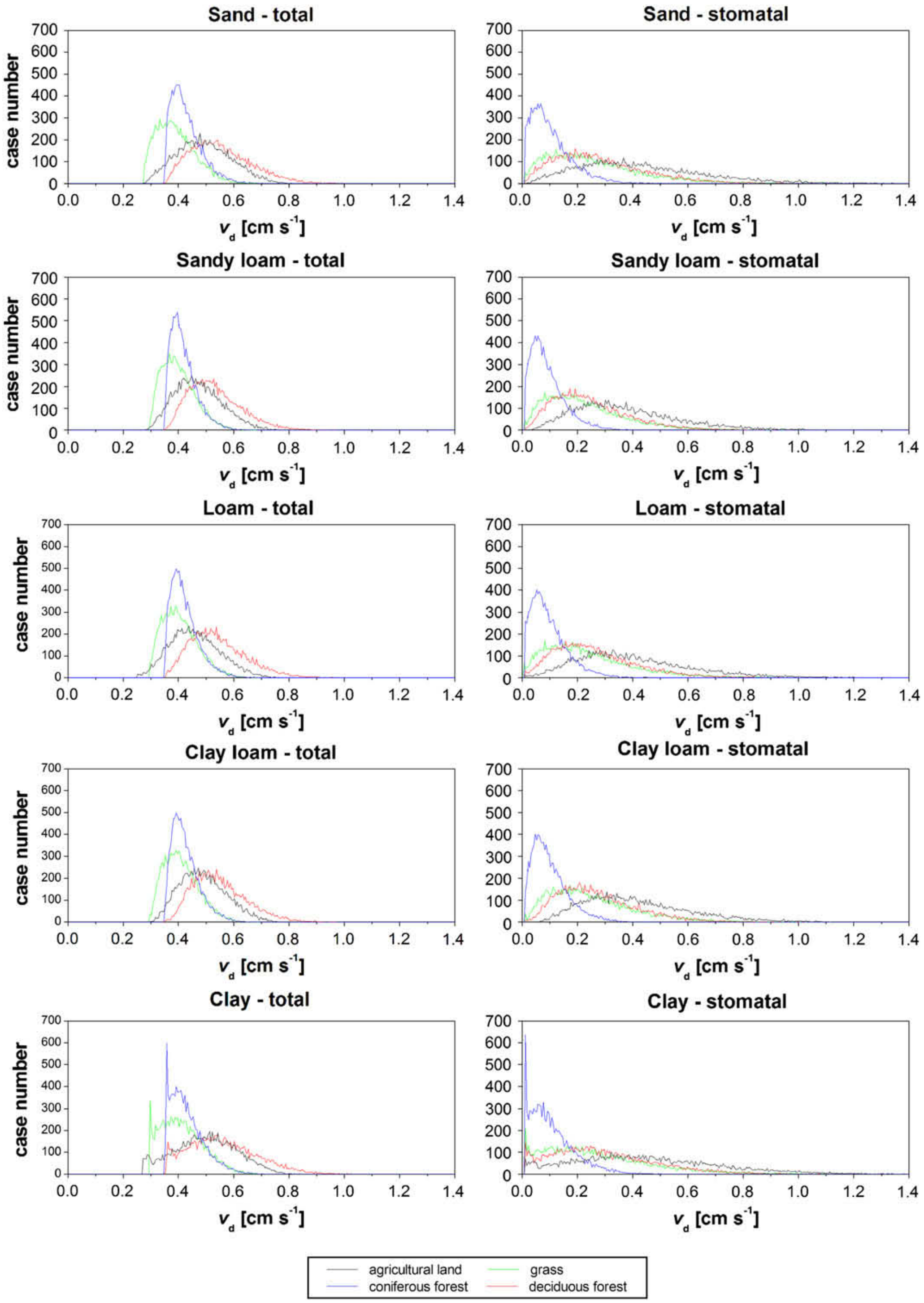

Fig. 5. Frequency histograms of the total and the stomatal depositions over five soil and four vegetation types. Results obtained from Monte Carlo analysis.

the deposition processes can be recognised. First of all, the averages of both total and stomatal deposition velocities are quite similar over each soil type, and they depend more on vegetation. Very different ratios between total and stomatal deposition velocity were found for each vegetation type; the greatest for coniferous forest, while the lowest was in the case of agricultural land.

Low stomatal deposition velocity of coniferous forest is due to its physiological properties (e.g. high temperature stress for summer, low maximum stomatal conductance). The highest stomatal values can be observed for agricultural land due to the highest value for maximum stomatal conductance and the given temperature range is the most favourable (no temperature stress) for this vegetation in this period. In the case of grass the high temperature stress caused by high optimal temperature can compensate the effects of the high maximum stomatal conductance and high LAI values. At the same time, lower G_{st} and LAI are balanced by lower temperature stress for deciduous forest (see Table 3a). Therefore, the stomatal deposition velocities for the latter forms of vegetation are quite similar.

The distribution of deposition values is plotted by frequency histogram (Fig. 5). All curves illustrate a similar pattern: after a quick growth a slow falloff can be seen, particularly in the stomatal cases.

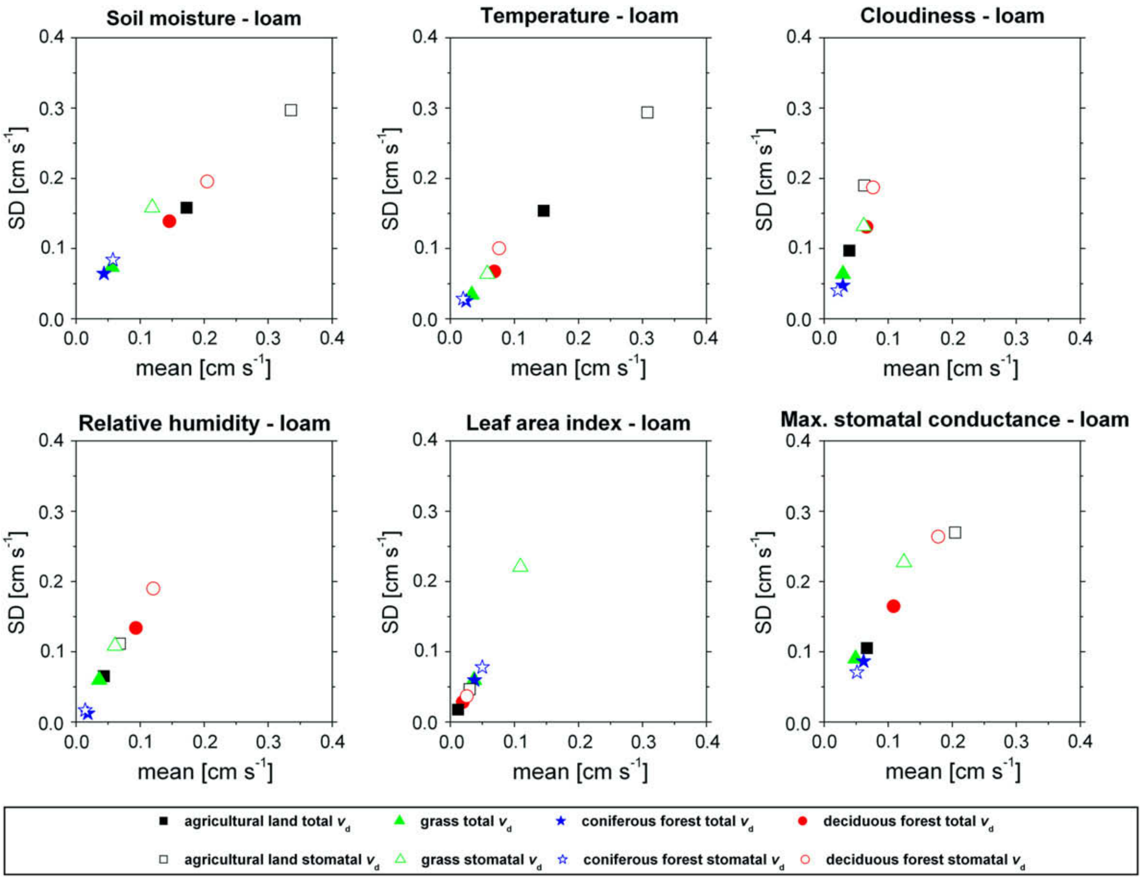

Fig. 6. Mean and standard deviation of the total and the stomatal deposition velocities over loam soil and four surface types obtained from the Morris method. The stomatal deposition velocities are indicated by empty symbols.

3.2. Morris method

While the Monte Carlo method presents accurate and unbiased information about the sensitivity of model results, it does not reveal the individual contributions. The Morris method can trace back the semi-quantitative individual effects of the parameters on deposition velocity and the inefficient parameters can be separated from the effective. However, in this case – in contrast to the Monte Carlo method – the probability density functions of the parameters are not used, so the calculated individual contributions are not unbiased.

Since there are no significant differences among the results of the Morris method for any of the soil types, we have arbitrarily chosen one of them (loam) for the presentation. Fig. 6 contains six graphs, the standard deviation of the elementary effects are plotted against the mean of the elementary effects. The points situated in the bottom left corner of each graph (low means together with low standard deviations) represent vegetation in which cases the given parameter is less important and the effect is linear between input and output. A higher value of mean denotes a greater effect of the input value on the results. High standard deviation refers to a nonlinear or interaction effect.

Similar results for each soil types were evaluated. The mean effects over the soil types were averaged and the parameters were classified using these values (Table 4). The numerical limits used for the classification are in the table caption. Leaf area index has a weak effect irrespective of the vegetation. Cloudiness and relative humidity have medium effects only in case of coniferous forest.

Table 4
Classification of the parameters based on the average effect of parameters to the deposition velocities. The results corresponding to the total and stomatal deposition velocities were classified separately. All cases were handled together (results of Morris method).

Land use categories	Agricultural land		Grass		Coniferous forest		Deciduous forest	
Input variable	Total	Stomatal	Total	Stomatal	Total	Stomatal	Total	Stomatal
Cloudiness	+	+	·	+	·	·	++	+
Relative Humidity	+	+	+	+	·	·	++	+
Leaf Area Index	·	·	+	+	+	+	·	·
Temperature	++	+++	·	+	·	·	+	+
Maximum stomatal conductance	+	++	+	++	+	+	++	++
Soil moisture	+++	+++	+	++	+	+	++	++

·, Very weak effect; $\text{mean}_{\text{total}} \leq 0.04$ cm s^{-1}; $\text{mean}_{\text{stomatal}} \leq 0.05$ cm s^{-1}.
+, Weak effect; 0.04 cm s^{-1} $< \text{mean}_{\text{total}} \leq$ 0.07 cm s^{-1}; 0.05 cm s^{-1} $< \text{mean}_{\text{stomatal}} \leq$ 0.13 cm s^{-1}.
++, Medium effect; 0.07 cm s^{-1} $< \text{mean}_{\text{total}} \leq$ 0.15 cm s^{-1}; 0.13 cm s^{-1} $< \text{mean}_{\text{stomatal}} \leq$ 0.25 cm s^{-1}.
+++, Strong effect; $\text{mean}_{\text{total}} > 0.15$ cm s^{-1}; $\text{mean}_{\text{stomatal}} > 0.25$ cm s^{-1}.

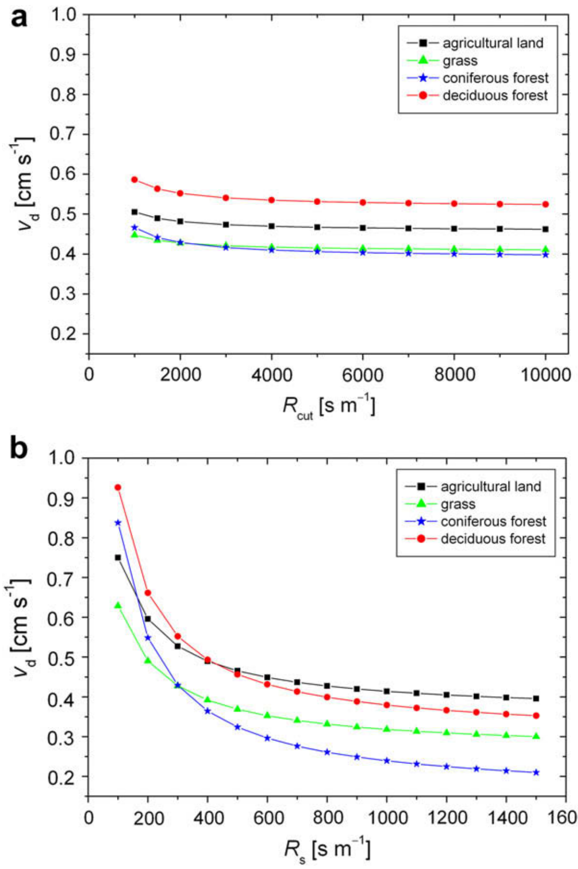

Fig. 7. Results of the local sensitivity analysis for loam soil: effect of cuticular resistance on total deposition velocity (a), and the effect of surface resistance on total deposition velocity (b) using the mean values for the input parameters (Tables 3a–c).

Temperature has a significant effect only in agricultural land for both total and stomatal deposition velocities. Maximum stomatal conductance has medium effect in most cases. However, soil moisture is the most significant parameter for both the total and stomatal deposition velocities for each vegetation type. These results of the Morris method can be summarized in that leaf area index is a less important parameter. Cloudiness, relative humidity and temperature are important parameters in some cases, and maximum stomatal conductance and soil moisture are influential parameters in all cases.

3.3. *Local sensitivity analysis*

In the former analyses the sensitivity of total and stomatal deposition velocity was investigated with global methods. However, the variability of the non-stomatal deposition pathways in contrast to stomatal uptake could also significantly affect ozone deposition. Therefore, to explore the effect of cuticular (leaf surface) and surface (soil) resistances on total deposition velocities a local sensitivity analysis was carried out. Fig. 7 presents the effect of the variability of non-stomatal resistances on deposition velocity. Results show that an increase in both resistances involves a decrease of total deposition velocity. It can also be recognised that the effect of surface resistance is more pronounced, because the range of realistic values of this resistance is lower than in the case of cuticular resistance. The variation of cuticular resistance from 1000 to 10000 s m^{-1} causes only less than 10% variability in the total deposition velocity. However, variation of surface resistance from 100 to 1500 s m^{-1} produces a two- or three-times variation in deposition velocity. In several models, the surface resistance is parameterized with a constant value. However, it has large degree of uncertainty because of its dependence on soil moisture, soil nitric oxide emission, surface roughness as well as the structure of the vegetation (Massman, 2004). Therefore, the importance of surface resistance in modelling deposition velocity plays a crucial role and further investigation is required.

4. Summary

The behaviour of a deposition model in a temperate climate in the Central European region and the effects of input parameters on the calculated total and stomatal depositions are investigated in this paper. Two global statistical methods, the Monte Carlo and the Morris analyses were used. With the Monte Carlo method it was possible to characterize the probability distribution of the total and stomatal depositions. The Morris method provided individual contributions of the investigated input variables to the daytime total and stomatal deposition velocity (or in other words the stomatal conductance) of ozone. Additionally, a local sensitivity analysis was carried out to reveal the contribution of non-stomatal pathways. The results correspond to Central Europe for July 1998, which represents a hot, summer period. Based on our sensitivity analyses, important and unimportant input data were defined. This information is very useful when creating an input database for deposition as well as dispersion models. For the estimation of the effective load caused by near surface ozone or to determine its projected effect for the future, these analyses tell which input values of the models need to be determined with high accuracy or need further refinement and in which cases the variability of the parameters is negligible. These results can be helpful for both actual environmental and climate-change studies. Since long-term prediction of atmospheric variables and feedbacks are very difficult to determine precisely, the sensitivity analyses can be effective tools to decrease the uncertainty of estimations.

The main results of this investigation are summarized in the following:

1. In former qualitative investigations (e.g. Mészáros et al., 2006) only local sensitivity analyses were carried out, and linear perturbations were applied on chosen model values. Results of these earlier investigations showed that the temperature is the most effective input parameter of the model. This linear approach cannot explore, on the one part, the whole parameter space, and, on the other part, the possible interactions between the parameters and does not provide quantitative information about the probability distribution functions of the model results. Instead of these former analyses, in this investigation two different methods were applied. The combined application of the Monte Carlo and the Morris methods is an appropriate tool to describe the sensitivity of a deposition model, and so general and specific properties of the deposition process can be recognized.
2. The results emphasize the importance of the deposition velocity estimation. Although average values of the deposition velocities (total and stomatal, respectively) over different vegetations are quite similar, very different ranges around the averages were found for each surface type. The large variability of the deposition velocities is due to the change of meteorological conditions, vegetation and surface dependent parameters.
3. The stomatal deposition velocity (stomatal conductance) has a larger variability than the total deposition velocity. Under some conditions, when environmental stresses hit the vegetation, stomatal uptake is nearly zero, while under optimum circumstances the stomatal deposition approaches its vegetation dependent maximum.

4. The type of the soil slightly affects the deposition velocity; however, root-zone soil moisture is one of the most crucial factors of deposition in the continental climate region.
5. Based on the results of the Morris method, the individual effects on deposition velocity are precisely determined and found to be significant in the case of soil moisture and maximum stomatal conductance.
6. The local sensitivity analysis pointed out that variation of surface resistance can involve differences in variability of total deposition velocity of up to two or three times. Therefore, more sophisticated parameterization of surface resistance is required in deposition models.

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References

Ács, F., 2003. On the relationship between the spatial variability of soil properties and transpiration. Időjárás 107, 257–272.

Alonso, R., Bermejo, V., Sanz, J., Valls, B., Elvira, S., Gimeno, B.S., 2007. Stomatal conductance of semi-natural Mediterranean grasslands: implications for the development of ozone critical levels. Environmental Pollution 146, 692–698.

Ashmore, M.R., 2005. Assessing the future global impacts of ozone on vegetation. Plant, Cell and Environment 28, 949–964.

Ashmore, M.R., Emberson, L., Karlsson, P.-E., Pleijel, H., 2004. New direction: a new generation of ozone critical levels for the protection of vegetation in Europe. Atmospheric Environment 38, 2213–2214.

Ashmore, M.R., Büker, P., Emberson, L.D., Terry, A.C., Toet, S., 2007. Modelling stomatal ozone flux and deposition to grassland communities across Europe. Environmental Pollution 146, 659–670.

Baldocchi, D.D., Hicks, B.B., Camara, P., 1987. A canopy stomatal resistance model for gaseous deposition to vegetated canopies. Atmospheric Environment 21, 91–101.

Black, V.J., Stewart, C.A., Roberts, J.A., Black, C.R., 2007. Ozone affects gas exchange, growth and reproductive development in *Brassica campestris* (Wisconsin Fast Plants). New Phytologist 176, 150–163.

Breuer, L., Eckhardt, K., Frede, H., 2003. Plant parameter values for models in temperate climates. Ecological Modelling 169, 237–293.

Brook, J.R., Zhang, L., Di-Giovanni, F., Padro, J., 1999. Description and evaluation of a model of deposition velocities for routine estimates of air pollutant dry deposition over North America. Part I: model development. Atmospheric Environment 33, 5037–5051.

Campolongo, F., Cariboni, J., Saltelli, A., 2007. An effective screening design for sensitivity analysis of large models. Environmental Modelling and Software 22, 1509–1518.

Eller, A.S.D., Sparks, J.P., 2006. Predicting leaf-level fluxes of O_3 and NO_2: the relative roles of diffusion and biochemical processes. Plant, Cell and Environment 29, 1742–1750.

Emberson, L.D., Ashmore, M.R., Cambridge, H., Simpson, D., Tuovinen, J.-P., 2000. Modelling ozone flux across Europe. Environmental Pollution 109, 403–412.

Fiscus, E.L., Booker, F.L., Burkey, K.O., 2005. Crop responses to ozone: uptake, modes of action, carbon assimilation and partitioning. Plant, Cell and Environment 28, 997–1011.

Fuhrer, J., Skärby, L., Ashmore, M.R., 1997. Critical levels for ozone effects on vegetation in Europe. Environmental Pollution 97, 91–106.

Hicks, B.B., Baldocchi, D.D., Meyers, T.P., Hosker, R.P., Matt, D.R., 1987. A preliminary multiple resistance routine for deriving dry deposition velocities from measured quantities. Water, Air and Soil Pollution 36, 311–330.

Horányi, A., Ihász, I., Radnóti, G., 1996. ARPEGE/ALADIN: a numerical weather prediction model for Central-Europe with the participation of the Hungarian meteorological service. Időjárás (Journal of the Hungarian Meteorological Service) 100, 277–301.

Jarvis, P.G., 1976. The interpretation of the variations in leaf water potential and stomatal conductance found in canopies in the field. Philosophical Transactions of the Royal Society of London, Series B 273, 593–610.

Jonson, J.E., Simpson, D., Fagerli, H., Solberg, S., 2006. Can we explain the trends in European ozone levels? Atmospheric Chemistry and Physics 6, 51–66.

Keller, F., Bassin, S., Ammann, C., Fuhrer, J., 2007. High-resolution modelling of AOT40 and stomatal ozone uptake in wheat and grassland: A comparison between 2000 and the hot summer of 2003 in Switzerland. Environmental Pollution 146, 671–677.

Krupa, S.V., Manning, W.J., 1988. Atmospheric ozone: formation and effects on vegetation. Environmental Pollution 50, 101–137.

Lagzi, I., Mészáros, R., Horváth, L., Tomlin, A., Weidinger, T., Turányi, T., Ács, F., Haszpra, L., 2004. Modelling ozone fluxes over Hungary. Atmospheric Environment 38, 6211–6222.

Lagzi, I., Mészáros, R., Ács, F., Tomlin, A.S., Haszpra, L., Turányi, T., 2006. Description and evaluation of a coupled Eulerian transport-exchange model. Part I: model development. Időjárás (Journal of the Hungarian Meteorological Service) 110, 349–363.

Matyssek, R., Bytnerowicz, A., Karlsson, P.-E., Paoletti, E., Sanz, M., Schaub, M., Wieser, G., 2007. Promoting the O_3 flux concept for European forest trees. Environmental Pollution 146, 587–607.

Massman, W.J., 2004. Toward an ozone standard to protect vegetation based on effective dose: a review of deposition resistances and a possible metric. Atmospheric Environment 38, 2323–2337.

McKay, M.D., Conover, W.J., Beckman, R.J., 1979. A comparison of three methods for selecting values of input variables in the analysis of output from a computer code. Technometrics 21, 239–245.

Mészáros, R., Lagzi, I., Juhász, Á., Szinyei, D., Vincze, Cs., Horányi, A., Kullmann, L., Tomlin, A.S., 2006. Description and evaluation of a coupled Eulerian transport-exchange model. Part II: sensitivity analysis and application. Időjárás (Journal of the Hungarian Meteorological Service) 110, 365–377.

Meyers, T.P., Finkelstein, P., Clarke, J., Ellestad, T.G., Sims, P.F., 1998. A multilayer model for inferring dry deposition using standard meteorological measurements. Journal of Geophysical Research 103, 22,645–22,661.

Moore, G.E., Londergan, R.J., 2001. Sampled Monte Carlo uncertainty analysis for photochemical grid models. Atmospheric Environment 35, 4863–4876.

Morris, M.D., 1991. Factorial sampling plans for preliminary computational experiments. Technometrics 33, 161–174.

Musselman, R.C., Lefohn, A.S., Massman, W.J., Heath, R.L., 2006. A critical review and analysis of the use of exposure- and flux-based ozone indices for predicting vegetation effects. Atmospheric Environment 40, 1869–1888.

Nussbaum, S., Remund, J., Rihm, B., Mieglitz, K., Gurtz, J., Fuhrer, J., 2003. High-resolution spatial analysis of stomatal ozone uptake in arable crops and pastures. Environment International 29, 385–392.

Paoletti, E., Manning, W.J., 2007. Toward a biologically significant and usable standard for ozone that will also protect plants. Environmental Pollution 150, 85–95.

Pleijel, H., Danielsson, H., Emberson, L., Ashmore, M.R., Mills, G., 2007. Ozone risk assessment for agricultural crops in Europe: further development of stomatal flux and flux–response relationships for European wheat and potato. Atmospheric Environment 41, 3022–3040.

Saltelli, A., Scott, E.M., Chen, K. (Eds.), 2000. Sensitivity Analysis. Wiley, Chichester.

Saltelli, A., Tarantola, S., Campolongo, F., Ratto, M., 2004. Sensitivity Analysis in Practice. Wiley, Chichester.

Schaub, M., Emberson, L., Büker, P., Kräuchi, N., 2007. Preliminary results of modeled ozone uptake for *Fagus sylvatica* L. trees at selected EU/UN-ECE intensive monitoring plots. Environmental Pollution 145, 636–643.

Simpson, D., Ashmore, M.R., Emberson, L., Tuovinen, J.-P., 2007. A comparison of two different approaches for mapping potential ozone damage to vegetation. A model study. Environmental Pollution 146, 715–725.

Stich, S., Cox, P.M., Collins, W.J., Huntingford, C., 2007. Indirect radiative forcing of climate change through ozone effects on the land-carbon sink. Nature 448, 791–794.

Tomlin, S.A., 2006. The use of global uncertainty methods for the evaluation of combustion mechanisms. Reliability Engineering and System Safety 91, 1219–1231.

Tuovinen, J.-P., Simpson, D., Emberson, L., Ashmore, M., Gerosa, G., 2007. Robustness of modelled ozone exposures and doses. Environmental Pollution 146, 578–586.

Turányi, T., Zalotai, L., Dóbé, S., Bérces, T., 2002. Effect of the uncertainty of kinetic and thermodynamic data on methane flame simulation results. Physical Chemistry Chemical Physics 4, 2568–2578.

Várallyay, Gy., Szűcs, L., Murányi, A., Rajkai, K., Zilahy, P., 1980. Map of soil factors determining the agro-ecological potential of Hungary (1:100 000) II. Agrokémia és Talajtan 29, 35–76 (In Hungarian).

Zádor, J., Wagner, V., Wirtz, K., Pilling, M.J., 2005a. Quantitative assessment of uncertainties for a model of tropospheric ethene oxidation using the European Photoreactor (EUPHORE). Atmospheric Environment 39, 2805–2817.

Zádor, J., Zsély, I.Gy., Turányi, T., Ratto, M., Tarantola, S., Saltelli, A., 2005b. Local and global uncertainty analyses of a methane flame model. Journal of Physical Chemistry A 109, 9795–9807.

Zhang, L., Moran, M.D., Brook, J.R., 2001. A comparison of models to estimate in-canopy photosynthetically active radiation and their influence on canopy stomatal resistance. Atmospheric Environment 35, 4463–4470.

Zhang, L., Moran, M.D., Makar, P.A., Brook, R., Gong, S., 2002. Modelling gaseous dry deposition in AURAMS: a unified regional air-quality modelling system. Atmospheric Environment 36, 537–560.

Zsély, I.Gy., Zádor, J., Turányi, T., 2005. Uncertainty analysis backed development of combustion mechanisms. Proceedings of the Combustion Institute 30, 1273–1281.

Zsély, I.Gy., Zádor, J., Turányi, T., 2008. Uncertainty analysis of NO production during methane combustion. International Journal of Chemical Kinetics 40, 754–768.