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Modeling dry flux of ammonia and nitric acid between the atmosphere and Lake Balaton

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Abstract—N-deposition from atmosphere contributes to the eutrophication of Lake Balaton (Hungary). To estimate the share of N-input compared to the effect of other sources, measurements have started in the 70's of the last century. However, in previous calculations the flux of N-gases (NH₃ and HNO₃) was estimated using deposition velocity parameters determined for terrestrial ecosystems. These simplifications were accompanied by an overestimation of the role of these compounds. According to our results for years 2001–2004, ammonia has a mean net emission flux from the lake (32.7 t N year⁻¹), while nitric acid deposition takes –21.8 t N year⁻¹ that are one order of magnitude lower than sum of other deposition forms (esp. wet N-deposition). The pH range in lake water (pH = 8.3–8.9) allows the bi-directional flux for ammonia. Ammonia exchange can act as a buffering system, i.e., in case of a high N-load to the lake from other sources (rivers, waste water, run-off, etc.) N-accumulations can be buffered through nitrogen emission in form of NH₃ as a consequence of the elevated compensation-point concentration. From this reason, eutrophication of Lake Balaton is phosphorus limited. Comparing the measured ammonia flux with the fluxes calculated by compensation-point models based on single Henry's law theory and by Hales-Drewes theory, it can be concluded that in our case latter theory describes better the exchange processes, suggesting that effect of carbon dioxide on the solubility of ammonia can not be excluded. However, in contrast with Hales and Drewes who suggested a decreased solubility of ammonia in presence of CO₂, we find an opposite effect, i.e., CO₂ favors the solubility of ammonia in the slight alkaline pH-range representative to the lake.

Key-words: eutrophication, FLake model, Monin-Obukhov theory, resistance model, compensation-point model, ammonia flux, nitric acid flux

1. Introduction

Atmospheric load of trace materials is one of the most important nutrient sources for freshwater ecosystems. Nutrient enrichment causes change of ecosystem structure and function; this process is termed eutrophication (*Durand et al.*, 2011). Generally, the two limiting elements in eutrophication are the nitrogen and the phosphorus. According to an international survey (*ICLIF*, 2010), Lake Balaton nowadays is co-limited; i.e., both N and P are limiting factors for eutrophication.

The mean surface of Lake Balaton is 598 km² with a contributing area of 5775 km². Being a shallow lake (mean depth of water is 3 m), Balaton is especially sensitive to nutrient loading (*Jordan et al.*, 2005). The first serious extinction of fish caused by algal bloom as a consequence of nutrient enrichment was observed in 1975 (*Herodek*, 1977).

Since then, intensive investigations have been started to estimate the source and strength of nutrient loading to the lake for mitigation purposes. *Jolánkai and Bíró* (2005) compiled the load of N and P into the lake from different sources for a three-decade period between 1975 and 2004. According to this work, the atmospheric nitrogen deposition has varied within a wide range between 300 and 1,800 t N year⁻¹. The reason of this large variation is the lack of direct measurement of dry deposition of nitrogen compounds to the surface of the lake. In all of previous studies, dry deposition of nitrate and ammonium particles and nitric acid vapor was estimated by the inferential method taking into account deposition velocities determined for terrestrial surfaces (*Horváth et al.*, 1981; *Horváth*, 1990). It led to an overestimation of nitrogen load, especially as the consequence of different surface characteristics (e.g., roughness) between terrestrial and water systems. To eliminate these discrepancies, a field campaign has started in 2002 to measure the dry deposition of nitrogen compounds also providing direct measurement data for validation of modeled fluxes. In a previous study (*Kugler and Horváth*, 2004), it was pointed out that dry deposition rates of nitrate and ammonium particles over Lake Balaton are much lower than it was supposed before and takes a nearly negligible share in the total atmospheric N-load to the lake.

In another paper (*Kugler et al.*, 2008), results of a preliminary analysis concerning the atmospheric dry deposition of nitric acid and net flux of ammonia for a year period (March 2002–February 2003) was reported based on a simple compensation-point model. It was found that deposition rate for nitric acid is less by one order of magnitude compared to grass surfaces, and ammonia has bi-directional flux resulting in either monthly average net emission or net deposition as the function of physical and chemical conditions in air and water. As ammonia has bi-directional flux, it is a key component in the nitrogen balance between the atmosphere and the lake, since compensation-point concentration and emission rate of ammonia is increasing parallel with increase

of N-load from other sources (waste water, rivers, creeks, leaching of fertilizers, etc.). It means a negative feedback mechanism which probably emits the excess nitrogen in the form of ammonia into the atmosphere (Kugler *et al.*, 2008). Moreover, in other case, in the lack of nutrient-N the atmosphere may act as nitrogen (ammonia) source for this aquatic ecosystem.

The aim of the paper is to investigate in more details the dry fluxes of gaseous nitrogen compounds and to estimate their share in total atmospheric N-load. Our investigations are based on sophisticated models for a four-year period (2001–2004) validated by flux data measured by the gradient method.

2. Methodology

2.1. Measurements

Meteorological and chemical parameters have been measured at the Storm Warning Observatory of Hungarian Meteorological Service, at the shore of lake (46° 54' 48.88" N; 18° 2' 19.76" E) in the town Siófok.

Meteorological measurements as wind direction and velocity, air temperature, relative humidity, and air pressure were observed by standard meteorological instruments. The global radiation and long wave radiation components were calculated by different parameterization schemes (Holtslag and van Ulden, 1983; Mészáros, 2002; Foken, 2006).

Measurement protocol for ammonia and nitric acid concentrations are: i) for the compensation-point model calculations: March 2002–February 2003 by 24-h continuous sampling at the height of 12.3 m above lake surface; ii) for the gradient measurements: July 12, 2002–July 25, 2012, 3-hour samplings, 8 times a day at two levels above the lake surface (12.3 and 2.8 m); iii) for interpolation of concentration data to Siófok: K-pusztá and Farkasfa background air pollution monitoring stations (46° 58' N, 19° 33' E and 46° 55' N, 16° 18' E) (2001–2004). Ammonia and nitric acid were sampled by a NILU EK-type three-stage bulk filter-pack sampler (EMEP, 1996). Concentrations of nitrate and ammonium ions in the extract of filters water were determined by ion-chromatography and spectrophotometry, respectively. Minimum detection limit (MDL) was $0.1 \mu\text{g N m}^{-3}$ for both ions. The bulk relative error of sampling and measurements is 10%.

The $\text{NH}_3+\text{NH}_4^+$ concentration (by spectrophotometry) and pH in the lake water were sampled and measured on the basis of bi-weekly samplings by the Middle Transdanubian Inspectorate for Environmental Protection, Natural Protection, and Water Management and by the VITUKI, Research Centre for Environmental Protection and Water Management. Sampling points were selected at Balatonakali, Keszthely, Siófok, and Szigliget settlements.

For validation of models, dry fluxes of ammonia and nitric acid were measured by the gradient method as described in Section 2.3.

2.2. The compensation-point model

Net dry flux of a gas having bi-directional exchange can be estimated by a modified compensation-point model (first described by *Farquhar et al.*, 1980):

$$F = -(C(z_{ref}) - C(z_0)) \cdot \left(\frac{1}{R_a + R_b} \right), \quad (1)$$

where F is the flux of gases, $C(z_{ref})$ is the atmospheric concentration of gases measured at the level z_{ref} (in our case 12.3 m), $C(z_0)$ is the compensation-point concentration at z_0 (roughness length) level, R_a and R_b are the resistances of turbulent and laminar layers, respectively. In case of ammonia and nitric acid vapor above water surfaces, the canopy resistance (R_c) can be neglected according to *Erisman et al.* (1994) and *Shahin et al.* (2002).

The net dry flux of nitric acid vapor can be calculated by Eq. (1), taking into account that in the slightly alkaline water HNO_3 molecules are completely dissociated, i.e., $C(z_0) = 0$ (*Kugler et al.*, 2008).

During the measurement campaign, the compensation-point concentrations for ammonia were calculated by two different methods. First, the simple Henry's law was used to determine the compensation-point concentration:

$$C(z_0) = \frac{C_w}{\left[\text{H}^+ \right] \frac{K}{K_w} H_1 + H_1}, \quad (2)$$

where C_w and $[\text{H}^+]$ are concentrations of sum of ammonia+ ammonium and hydrogen ion in water phase, respectively, H_1 is the Henry's law constant of ammonia, K , K_w are constants at a given temperature (*Horváth*, 1982).

According to *Hales and Drewes* (1979), the simple Henry's law cannot be applied to calculate the compensation-point concentration, since carbon dioxide decreases the solubility of ammonia in water phase that must be taken into account in compensation-point calculation by the following formula:

$$C(z_0) = \frac{C_w (H_1 H_2 [\text{CO}_2] Q + 1)}{H_1 H_2 P [\text{CO}_2] + \left[\text{H}^+ \right] \frac{K}{K_w} H_1 + H_1}, \quad (3)$$

where, Q , P , K , K_w are constants at a given temperature, H_2 is the Henry's law constant of carbon dioxide, $[\text{CO}_2]$ is the concentration of carbon dioxide in the air (calculated from the average mixing ratio of 380 ppm, in 2002–2003).

Later on, laboratory experiments (*Ayers et al.*, 1985; *Dasgupta and Dong*, 1986) demonstrated by laboratory experiments that theory of *Hales and Drewes* (1979) is not suitable, and the classical Henry's law should be used to calculate the compensation-point concentration. Due to the obvious contradiction among different authors and results between field and laboratory measurements, we have calculated the compensation-point concentrations using single Henry's law and the modified solubility theory of Hales-Drewes as well.

2.3. The gradient method

The gradient method was applied for validation of compensation-point models and in case of ammonia to verify two different outputs of models based on different solubility theories. The net gradient flux of a gas can be determined by the following equation supposed the similarity in exchange of heat and trace gases (*Weidinger et al.*, 2000; *Foken*, 2006):

$$F = -\rho_m \bar{K}_H \frac{\Delta C}{\Delta z}, \quad (4)$$

where \bar{K}_H is the turbulent diffusion coefficient of the heat flux in a certain layer, ΔC is the concentration difference between two heights above surface, Δz is the difference between the two heights, ρ_m is the average density of the moist air. Turbulent diffusion coefficient at dimensionless height ($\zeta = (z - d)/L$) can be calculated using the similarity theory by the following formula:

$$K_H(\zeta) = \frac{\kappa u_* (z - d)}{\varphi_H(\zeta)}, \quad (5)$$

where κ is the Kármán constant (usually set to 0.4), u_* is the friction velocity, z is the height, d is the displacement height, L is the Monin-Obukhov length, φ_H is the universal function of sensible heat flux. Above water surface the displacement height is zero. Parameterizations of *Businger et al.* (1971) and *Dyer* (1974) were used for determination of the universal functions in different stratifications. The calculations of the friction velocity are described in Section 2.4.

2.4. The micrometeorological input

Turbulent diffusion coefficient for the gradient method and different resistances for compensation-point model were calculated by two different micrometeorological methods. First, we used the Monin-Obukhov theory to determine the turbulent sensible heat fluxes, the Monin-Obukhov length, and the friction velocity. It is named as resistance model (RM), since it was applied to

calculate the resistances (*Weidinger et al.*, 2000; *Ács and Szász*, 2002; *Ács*, 2003). Another model, namely the 1D numerical FLake model (FM) was also used to determine the same characteristics (*Mironov*, 2008).

At first, both models calculate the net radiation (Q_S) by the following equation:

$$Q_S = Q_H + Q_E + Q_G, \quad (6)$$

where Q_H , Q_E are the sensible and latent heat fluxes, Q_G is the heat flux into the water.

Calculation of momentum flux (τ), sensible heat flux (Q_H), latent heat flux (Q_E), and trace gas fluxes (Q_C) can be described by the following equations (*Foken*, 2006):

$$\tau = \rho_m u_*^2 = \rho_m K_M \frac{\partial \bar{u}}{\partial z}, \quad (7)$$

$$Q_H = -c_{pm} \rho_m u_* T_* = -\rho_m c_{pm} K_H \frac{\partial \bar{\theta}}{\partial z}, \quad (8)$$

$$Q_E = -\lambda \rho_m u_* q_* = -\lambda \rho_m K_E \frac{\partial \bar{q}}{\partial z}, \quad (9)$$

$$Q_C = -\rho_m u_* c_* = -\rho_m K_C \frac{\partial \bar{c}}{\partial z}, \quad (10)$$

where c_{pm} is the specific heat at constant pressure, λ is the phase transition energy, z is the height, $\bar{\theta}$, \bar{q} , \bar{c} , \bar{u} are average potential temperature, specific humidity, trace gas concentration, and wind velocity, respectively, u_* , T_* , q_* , c_* are dynamical parameters for wind velocity, air temperature, specific humidity, and trace gas concentration, respectively. K_s is the turbulent diffusion coefficient of a certain property $s \in (M, H, E, C)$ as momentum, sensible, latent heat, and trace gas. We assume that eddy diffusivity coefficients of sensible and latent heat and trace gases are similar $K_H = K_E = K_C$.

With the knowledge of the gradient of certain micrometeorological parameters (*Weidinger et al.*, 2000; *Mészáros*, 2002), the universal functions of momentum, heat, humidity, and trace gases can be calculated as:

$$\frac{\partial \bar{u}}{\partial z} = \frac{u_*}{\kappa(z-d)} \varphi_M(\zeta), \quad (11)$$

$$\frac{\partial \bar{\theta}}{\partial z} = \frac{T_*}{\kappa(z-d)} \varphi_H(\zeta), \quad (12)$$

$$\frac{\partial \bar{q}}{\partial z} = \frac{q_*}{\kappa(z-d)} \varphi_E(\zeta), \quad (13)$$

$$\frac{\partial \bar{c}}{\partial z} = \frac{c_*}{\kappa(z-d)} \varphi_C(\zeta), \quad (14)$$

where $\zeta = (z-d)/L$ is the dimensionless height and L is the so-called Monin-Obukhov length. Other parameters have been described previously. φ_s $s \in (M, H, E, C)$ is the universal function of a certain property as momentum, heat, humidity, and trace gas.

The Monin-Obukhov length is determined by this formula:

$$L = \frac{u_*^2}{\kappa \beta T_*}, \quad (15)$$

where $\beta = g/\bar{\theta}$ is the stability parameter, g is the acceleration of gravity.

The general forms of universal functions (Arya, 2001) of momentum and sensible heat are described as:

$$\varphi_M = (1 - \gamma_1 \zeta)^{-\frac{1}{4}}, \quad \text{if } 0 > \zeta \quad (\text{unstable}), \quad (16)$$

$$\varphi_M = 1 + \beta_1 \zeta, \quad \text{if } 0 \leq \zeta \quad (\text{stable}), \quad (17)$$

$$\varphi_H = \alpha (1 - \gamma_2 \zeta)^{-\frac{1}{2}}, \quad \text{if } 0 > \zeta \quad (\text{unstable}), \quad (18)$$

$$\varphi_H = \alpha + \frac{\beta_2}{\alpha} \zeta = \alpha (1 + \beta_2 \zeta), \quad \text{if } 0 \leq \zeta \quad (\text{stable}), \quad (19)$$

where $\alpha, \beta_1, \beta_2, \gamma_1, \gamma_2$ are constants derived from the micrometeorological experiments of *Businger et al.* (1971) and *Dyer* (1974).

By integration of the Eqs. (11–12), turbulent characteristics for a certain layer are described as follows:

$$u(z_2) - u(z_1) = \frac{u_*}{\kappa} \left[\ln \frac{z_2}{z_1} - \int_{\zeta_1}^{\zeta_2} (\varphi_M - 1) d \ln \zeta \right] = \frac{u_*}{\kappa} \left[\ln \frac{z_2}{z_1} - (\Psi_M(\zeta_2) - \Psi_M(\zeta_1)) \right], \quad (20)$$

$$\theta(z_2) - \theta(z_1) = \frac{T_*}{\kappa} \left[\ln \frac{z_2}{z_1} - \int_{\zeta_1}^{\zeta_2} (\varphi_H - \alpha) d \ln \zeta \right] = \frac{T_*}{\kappa} \alpha \left[\ln \frac{z_2}{z_1} - (\Psi_H(\zeta_2) - \Psi_H(\zeta_1)) \right], \quad (21)$$

where Ψ_M , Ψ_H are integral forms of stability function of momentum and sensible heat.

Stability functions in cases of stable and unstable stratifications are:

$$\Psi_M(\zeta) = \ln \left[\left(\frac{1 + x_M^2}{2} \right) \left(\frac{1 + x_M}{2} \right)^2 \right] - 2 \tan^{-1} x_M + \frac{\pi}{2}, \quad \text{if } 0 > \zeta, \quad (22)$$

$$\Psi_H = 2 \ln \left(\frac{1 + x_H^2}{2} \right), \quad \text{if } 0 > \zeta, \quad (23)$$

$$\Psi_M = -\beta_1, \quad \Psi_H = -\frac{\beta_2}{\alpha}, \quad \text{if } 0 \leq \zeta, \quad (24)$$

where $x_M = (1 - \gamma_1 \zeta)^{1/4}$, $x_H = (1 - \gamma_2 \zeta)^{1/4}$.

RM model uses Eqs. (16-19) for calculation, where the constants used have been measured at the Kansas experiment of *Businger et al.* (1971):

$$\alpha = 0,74; \beta_1 = 4,7; \beta_2 = 4,7 / \alpha; \gamma_1 = 15; \gamma_2 = 9. \quad (25)$$

After calculation of radiation balance, RM is resolving the Eqs. (15, 20–21). We considered $z_1 = z_0 = 0.0003$ m, and water temperature was applied at height z_1 . Model uses iteration method to calculate friction velocity (u_*), dynamic temperature (T_*), and sensible heat flux using Eq. (8). Sensible heat flux was calculated using the assumption that $\varphi_E = \varphi_H$ based on the difference in specific humidity. At the end of calculations, heat flux into the water is determined as residual term in radiation balance.

Since RM uses measured water temperatures at depth of 1 m for calculations, we tried to find a lake model which is able to predict the surface

temperature of a shallow lake. The FLake model (FM) is able to predict a vertical temperature structure in lakes at various depths on time scales from a few hours to a year.

The change in water temperature is described by the following equation in FM:

$$h \frac{\partial T_S}{\partial t} = \frac{1}{\rho_w \cdot c_w} [Q_w + I_w - Q_M - I(h)], \quad (26)$$

where h is the depth of mixed layer, T_s is the surface temperature of water (the same as the temperature in the upper water layer), ρ_w is the density of water, c_w is the specific heat capacity of water, Q_w is the heat flux through air-ice-water or air-water interface, I_w is the radiation flux through air-ice-water or air-water interface, Q_M is the heat flux at the bottom of mixed layer, $I(h)$ is the radiation flux at the bottom of depth layer (h). Terms Q_w and I_w are defined as $Q_G = Q_w + I_w$ for Q_G referring to Eq. (6).

FM uses the following method for calculations. First, prognostic and diagnostic values of the model are set to their initial values. As next step, the albedo of water, ice, and snow and also optical characteristics of water are determined. It follows the calculation of long wave radiation from surface and shortwave heat balance. With the Monin-Obkuhov theory momentum, sensible, and latent heat fluxes plus the dynamic velocity are derived. At the parameterization of the universal functions Eqs. (16–19), FM uses constants of *Dyer* (1974):

$$\alpha = 1; \beta_1 = \beta_2 = 5; \gamma_1 = \gamma_2 = 16. \quad (27)$$

For further calculations FM uses the Euler explicit scheme. In all time steps all model variables are derived. As the next step, heat flux through air-ice-water or air-water interface, a heat flux utilized in calculations of the convective boundary-layer evolution in the lake water, then heat flux through water-bottom sediment interface are computed. Later on, it follows to determine change in thickness and temperature of ice and snow, mean temperature of water column, mixed-layer depth, mixed-layer temperature, bottom temperature, and shape factor with respect to temperature profile in thermocline. Depth of upper layer of bottom sediments penetrated by thermal wave and temperature at that depth are computed. At the end, lake surface temperature is updated. That is set equal to either temperature of the water-surface temperature, or to surface temperature of ice or snow. The model applies a 10-step iteration method. More details for the FLake model description refer to *Mironov* (2008) and *Mironov et al.* (2010).

Both models determine the turbulent fluxes dynamic velocity, and also stratification. Then, aerodynamic resistances can be derived to solve the following equation (Ács *et al.*, 2000) using Eq. (5):

$$R_a = \int_{z_0}^z \frac{1}{K_H(z)} dz, \quad (28)$$

where K_H is the turbulent diffusion coefficient of sensible heat flux in a certain layer.

The boundary layer resistance can be calculated by the following formula (Kramm *et al.*, 1996):

$$R_b = \frac{2}{\kappa u_*} \left(\frac{Sc}{Pr} \right)^P, \quad (29)$$

where Sc is the Schmidt-number, Pr is the Prandtl-number, and P is an empirical constant (2/3). The quotient of Schmidt- to Prandtl-numbers are 0.96 for ammonia and 1.44 for nitric acid (Hicks *et al.*, 1987).

3. Results and discussions

3.1. Calculation of resistances and turbulent diffusion coefficients

Turbulent heat and momentum fluxes and diffusion coefficient were parallel determined by resistance (RM) and Flake models (FM) (Ács and Szász, 2002; Mironov, 2008) between January 2001 and December 2004 on hourly base.

Input data for resistance model are: water and air temperature, wetness characteristics (e.g., specific humidity), wind velocity and direction, cloudiness, and global radiation. Output data are: hourly averages of momentum flux (τ), sensible (Q_H) and latent (Q_E) heat fluxes, turbulent diffusion coefficients (K_H), resistances (R_a , R_b), and Monin-Obukhov length (L) on the basis of methods described by Ács *et al.* (2000), Weidinger *et al.* (2000), and Foken (2006).

Input data for FLake model are: rate of snow accumulation, global radiation, longwave radiation, wind velocity, and temperature, humidity, and pressure of air. Initial conditions (Table 1) were determined by Vörös *et al.* (2010) based on measurements and sensitivity analysis. Initial mean water temperature was always set to the measured water temperature of the lake.

Table 1. Initial conditions and predicted variables in FLake model

Type	Symbol	Name	Setting/ initialization
Initial conditions	Depth _w	Depth of lake*	0.9 m
	Fetch	Wind fetch	3000 m
	T _{bs0}	Sediment temperature	283.15 K
	Depth _{bs}	Depth of sediment	3 m
	Latitude	Geographical situation	47°
	Albedo	Albedo	0.095
Prognostic variables	T _{snow}	Snow temperature	273.15 K
	T _{ice}	Ice temperature	273.15 K
	T _{mnw}	Mean water temperature	274.25 K
	T _{wML}	Temperature in boundary layer	274.25 K
	T _{bot}	Temperature at boundary of water/sediment	274.25 K
	T _{B1}	Temperature at the bottom of upper sediment	283.15 K
	C _θ	Shape factor	0.50
	h _{snow}	Snow depth	0 m
	h _{ice}	Ice depth	0 m
	h _{ML}	Thickness of mixing layer	0.9 m
	h _{B1}	Depth of upper layer of sediment	3 m
	T _{sfc}	Temperature in the previous time step	274.25 K

*Based on the sensitivity analysis of FLake model for Lake Balaton after Vörös *et al.* (2010)

Output data of FLake model are: turbulent fluxes over lake, turbulent diffusion coefficient of sensible heat flux, aerodynamic and boundary layer resistances, and Monin-Obukhov length.

Data of calculated hourly energy balance components by the two methods were governed mainly by the water temperature and input meteorological variables. Extreme figures caused by i) difference of measured (RM) and modeled (FM) water temperature, ii) high negative value of sensible heat flux during stable conditions at high wind velocity, and iii) by overestimation of latent heat flux during very unstable stratifications were filtered. Corrections were applied for cases with extreme large deviations between the figures calculated by the two methods caused by unreliable output data at least from one of the methods. Filtration criteria were as follows:

- i) radiation balance must not be lower than -120 W m^{-2} ,
- ii) latent heat flux must not reach 450 W m^{-2} ,
- iii) lower and upper thresholds for sensible heat flux were -75 W m^{-2} and 175 W m^{-2} , respectively.

Application of these criteria is justified by, e.g., Liu *et al.* (2011) in calculation of direct fluxes for a water reservoir. Data over or below these limits

were replaced by the limit figure itself. Hourly energy balance was closed in these cases by change of heat flux into water.

Corrections were applied in cases when difference in heat fluxes into water was larger than 200 W m^{-2} . In these cases by proportional variation of sensible and latent heat fluxes – keeping the Bowen-ratio constant calculated by the two methods –, the difference between heat flux into water was kept below 200 W m^{-2} . According to the criteria above, corrections were applied in 3 to 6% of cases in the different years.

For validation of results we compared the monthly evaporation rates with that of calculated by Central-Transdanubian Water Directorate on the basis of Meyer-formula (Anda and Varga, 2010), for the period of 2001–2004. According to Kovács (2011) and Szilágyi and Kovács (2011), the Meyer-formula (MF) simulates well the real evaporation for Balaton. The monthly evaporation rates calculated by the different methods can be seen in Fig. 1. Correlations between model results (MF)–(FM) and (MF)–(RM) are $r=0.93$ and $r=0.80$, respectively, both are significant relations at $p=0.01$ probability level.

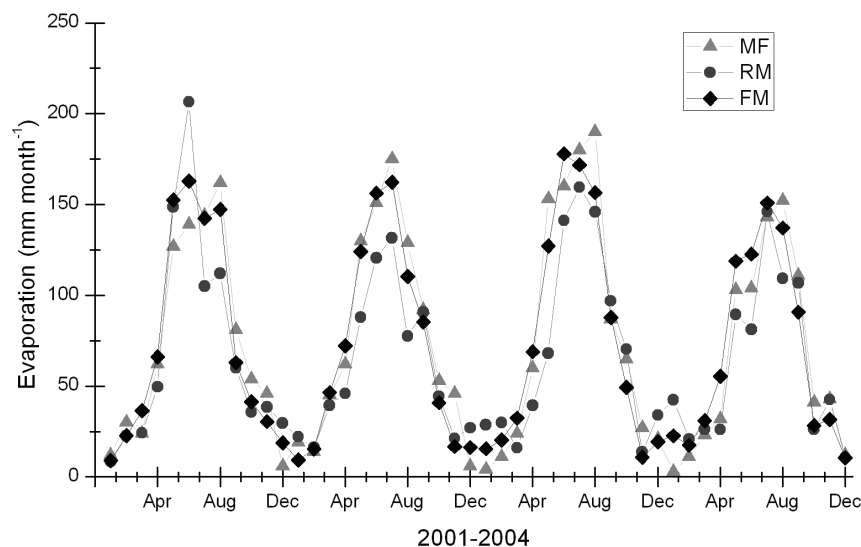


Fig. 1. Monthly evaporation rate calculated by three different ways for Lake Balaton (MF: Meyer-formula, FM: FLake model, RM: resistance model)

Yearly sum of evaporation calculated by the three different methods can be seen in Table 2. There is a good agreement between the mean values of MF and FM models, while RM underestimates the evaporation in comparison to others. The deviations among the mean values of three models are below 20%.

Table 2. Yearly evaporation (in mm) calculated by three different methods ((MF: Meyer-formula, FM: FLake model, RM: resistance model))

Year	MF	FM	RM
2001	887	892	841
2002	922	855	725
2003	982	938	843
2004	778	817	728
Mean	892	876	784

Mean monthly sensible heat fluxes were also determined by both FM and RM methods (Fig. 2a). It is generally a small value for lakes in comparison to radiation balance (Fig. 2b), because the stratifications over the lake are close to the neutral. The differences probably derive from differences between measured (RM) and calculated (FM) water surface temperatures.

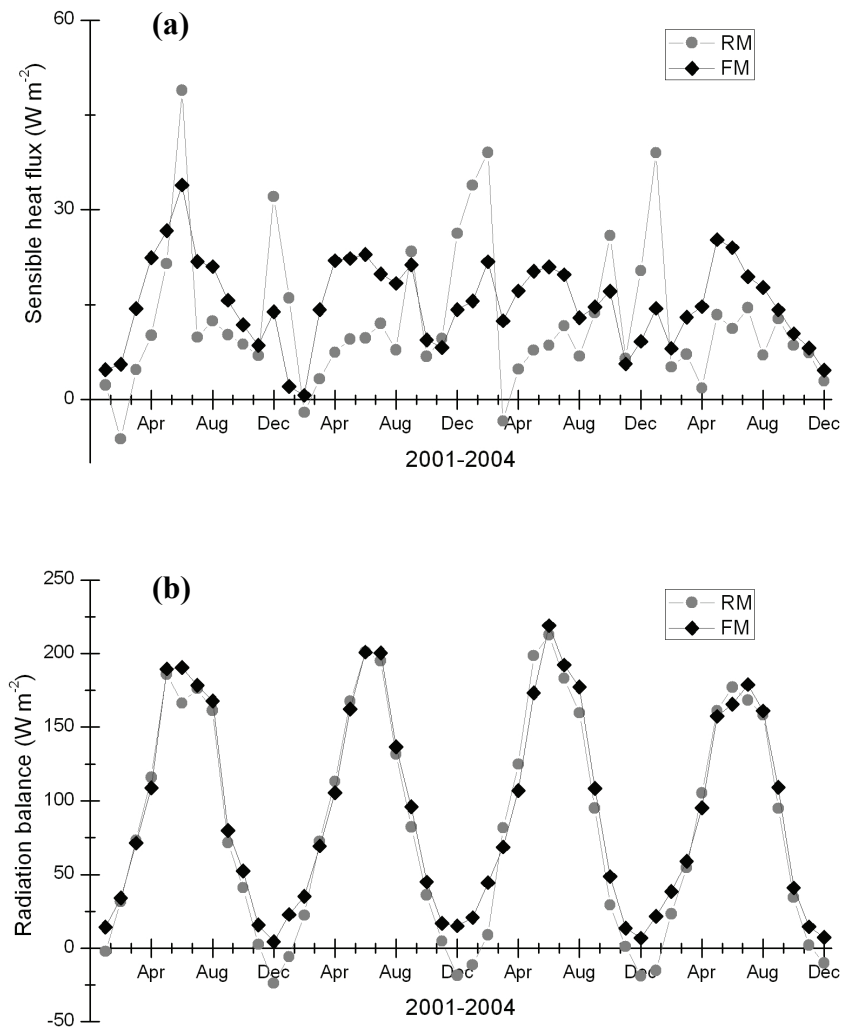


Fig. 2. Variation of monthly mean of sensible heat flux, Q_H (a) and radiation balance, Q_S (b) calculated by two different models (FM: FLake model, RM: resistance model)

Fig. 2b shows the course of monthly mean of radiation balance. Parameterization of surface energy budget components can be described by Eq. (6). The agreement between the two models is appropriate. Calculated turbulent diffusion coefficient of sensible heat between the heights of 12.3 and 2.8 meters using FM and RM methods for the period of experiment carried out in July 2002 gives also a good agreement as it can be seen in *Fig. 3a*. By the knowledge of K_H , we can estimate the exchange rate of gases by the gradient method supposing that exchange for heat and for trace gases are similar as mentioned above. Correlation between the diffusion coefficients determined by the two methods is $r=0.96$ ($p=0.01$).

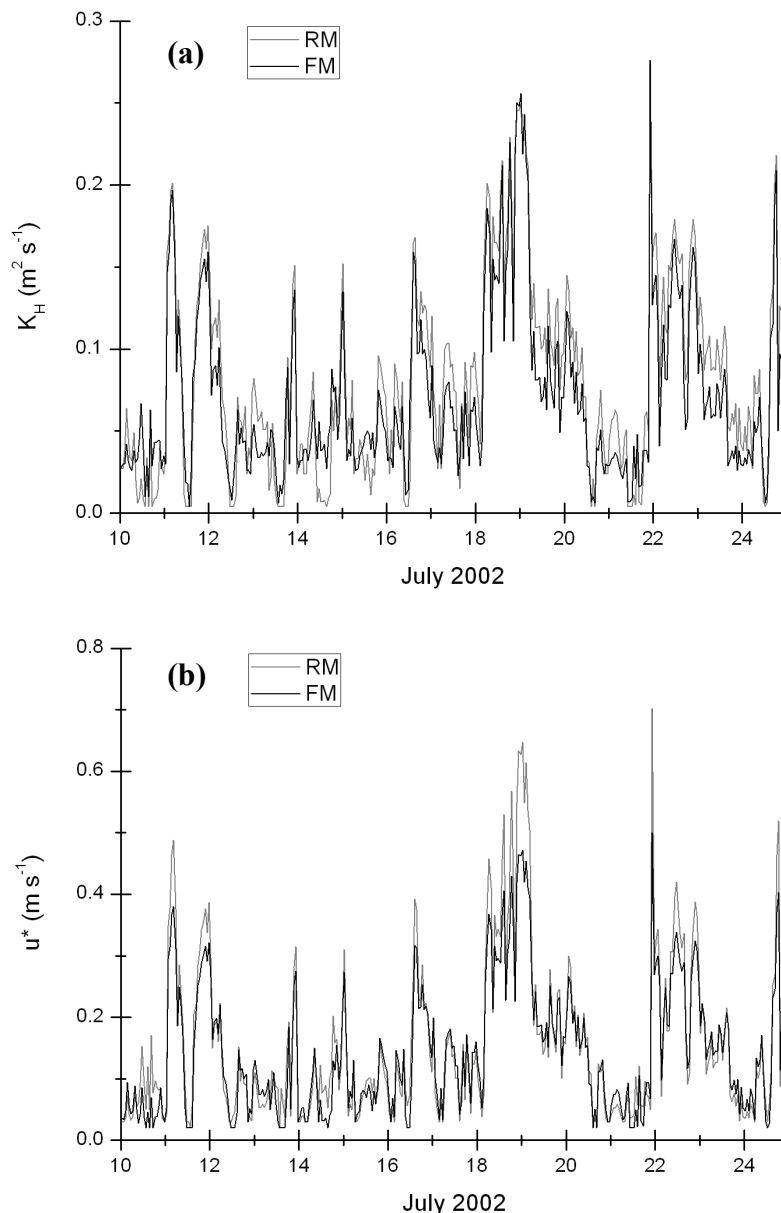


Fig. 3. Turbulent diffusion coefficients of sensible heat flux, K_H for the height between 12.3 and 2.8 meters (a) and friction velocity (b) calculated by the two different methods (July 10–25, 2002)

Finally, friction velocities (u_*) were also compared derived from RM and FM models (*Fig. 3b*). Agreement is good between results of the two models; systematic deviations can only be observed in case of higher values. Correlation is significant, $p=0.97$ ($p=0.01$).

In summary, it can be stated that the agreement between turbulent fluxes calculated by the two models is reasonable providing appropriate input data for determination of gas fluxes.

3.2. Modeling of fluxes

Ammonia and nitric acid fluxes were modeled at first for the period of July 12–25, 2002 for intercomparison (validation) of modeled fluxes by the results of gradient flux measurements conducted in the same period (*Figs. 4a,b*).

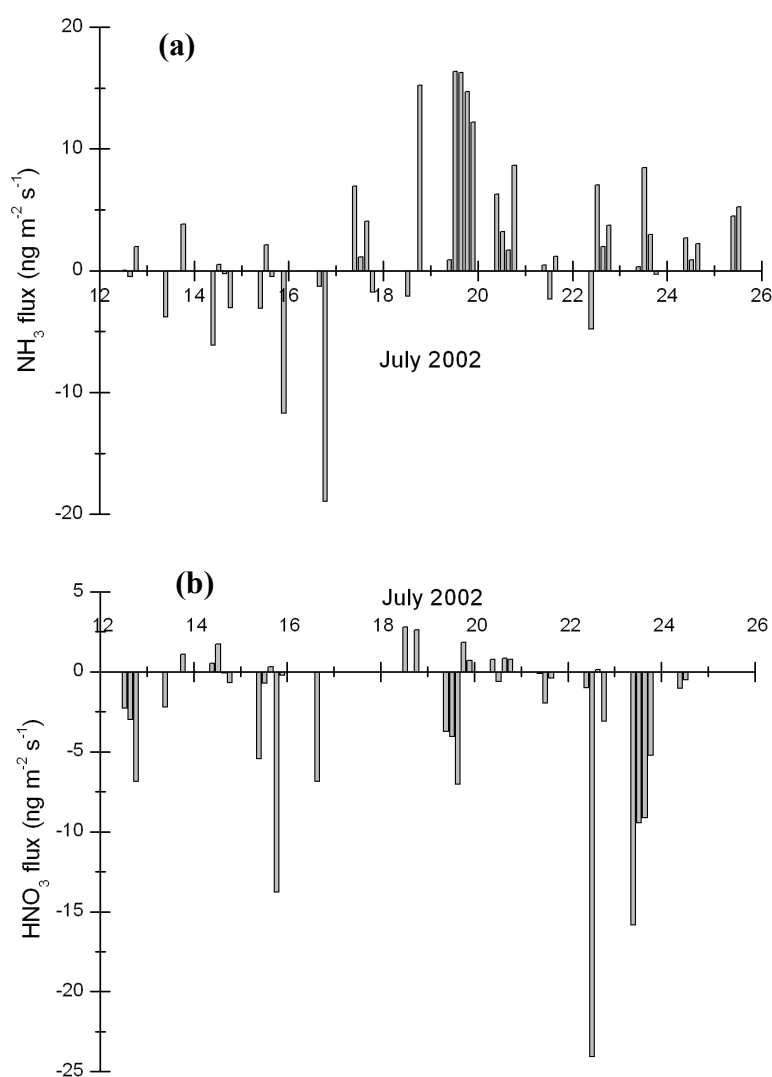


Fig. 4. Ammonia (a) and nitric acid (b) fluxes measured by the gradient method during a summer campaign at Siófok observatory

Ammonia exchange between the lake and the atmosphere was calculated on the basis of hourly micrometeorological parameters and 3-hour measured concentrations by means of the compensation-point model Eq. (1) using RM and FM methods for calculation of resistances. Only good fetch cases (wind from lake dominantly during duration of 3-hour samplings) were taken into consideration in evaluation. Compensation-point concentration of ammonia was calculated parallel by using the simple Henry's law equation and by the modified solubility theory of Hales-Drewes taking into account the effect of carbon dioxide on the solubility of ammonia in water at low concentrations. Ammonia concentration in air (at $h = 12.3$ m above water surface), ammonium+ammonia concentration and pH in water were measured as described in Section 2.1. Average of the 3-hour eddy diffusion coefficients for sensible heat was used in calculation.

The pH is a crucial parameter in controlling ratio the of ammonia to ammonium in diluted water solutions. It follows from Eqs. (2) and (3), that one unit decrease in pH results in one order decrease in compensation-point concentration. Ammonia in acidic solutions ($\text{pH} < 7$) – being a weak base – exists dominantly in protonated form (NH_4^+) prohibiting the escape of ammonia gas from the water. In the range of pH of the lake ($\text{pH} = 8.3\text{--}8.9$), ammonia and ammonium exist together making the bi-directional change (either volatilization or absorption) of ammonia between the water and the atmosphere possible. Sign of the flux is determined by the difference in compensation-point and atmospheric concentration of ammonia according to the Eq. (1).

Other two input parameters of compensation-point model were the aerodynamic and boundary-layer resistances; they were calculated using both the resistance and FLake models as described in Section 2.4. Average resistances calculated by the two models were used (for details refer to 3.5).

Flux of nitric acid was modeled by the same way as of ammonia, the only difference is that HNO_3 does not exist in molecular form in diluted solutions, especially in the pH range of 8.3–8.9. It follows, that in Eq. (1) the compensation-point concentration of nitric acid equals to zero. Nitric acid concentrations in air were sampled by 3-hour sampling and analyzed as described in Section 2.1.

3.3. Measurement of fluxes of ammonia and nitric acid by the gradient method

For validation of models, dry fluxes of ammonia and nitric acid were measured during a summer campaign at the shore of the lake by the gradient method between July 12 and 25, 2002. Concentration gradients were determined by concentrations measured at 2.8 m and 12.3 m heights near/above the water surface by 3-hour samplings according to Eq. (4). Turbulent diffusion coefficient was derived from Eq. (5). Averages of 3-hour diffusion coefficient were used in calculation. Fluxes of ammonia and nitric acid by the gradient

method during expedition can be seen in *Figs. 4a,b*. The 3-hour mean fluxes were varied between $-18.9 \text{ ng m}^{-2} \text{ s}^{-1}$ and $16.3 \text{ ng m}^{-2} \text{ s}^{-1}$ for ammonia and between $2.8 \text{ ng m}^{-2} \text{ s}^{-1}$ and $-24.1 \text{ ng m}^{-2} \text{ s}^{-1}$ for nitric acid. (Positive figures derive from the 10% uncertainty of nitric acid concentration measurements.) Certainly, only good fetch cases (wind dominantly from lake during the duration of 3-hour samplings) were taken into consideration in the evaluation. Concentrations – especially for nitric acid – sometimes were below the detection limit; in these cases fluxes were not computed.

3.4. Validation, comparison of modeled and measured fluxes

The 3-hour mean of ammonia fluxes measured by the gradient method and modeled by the compensation-point model (using both resistance and FLake models for calculation of resistances) were compared for the period of summer campaign in 2002. The regression of the measured and modeled fluxes can be seen in *Figs. 5a,b*. Compensation-point concentrations for models were calculated both by simple Henry's law and Hales-Drewes solubility theory. Three-hour averages of calculated and modeled fluxes were plotted. Modeled fluxes are calculated as the mean of the results of the resistance and the FLake models. (The deviation between results of resistance and FLake models can be seen in *Table 2*.)

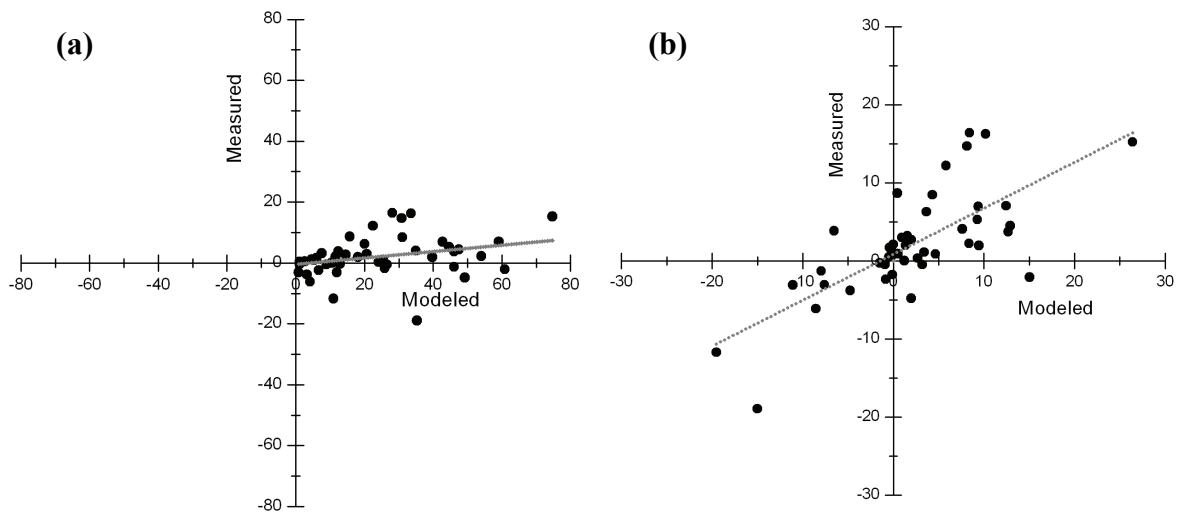


Fig. 5. Comparison of measured ammonia fluxes with results of compensation-point model used a) Henry's law; and b) Hales-Drewes theory for calculation of compensation-point concentration in $\text{ng m}^{-2} \text{ s}^{-1}$ for the period of July 12–25, 2002

The main parameters of comparison can be seen in *Table 3*. According to *Fig. 5* and *Table 3*, the difference between results of the two solubility theories

is significant. In contrast of finding of *Ayers et al.* (1985) and *Dasgupta and Dong* (1986), who demonstrated by laboratory measurement that classical Henry's law is applicable for solubility of ammonia, it seems that modeled fluxes by the theory of Hales and Drewes ranges much better with our gradient method measurements. Though, according to theory of *Hales and Drewes* (1979), carbon dioxide decreases the solubility of ammonia (increases the compensation-point concentration as a probable effect of carbamic acid), a reversed picture can be observed from our results. As *Fig. 5* and *Table 3* show, the fluxes are much lower calculated by Hales-Drewes theory suggesting that solubility of ammonia is rather increasing in the pH regime representative for the lake water. The supposed effect of carbon dioxide as the function of pH is illustrated in *Fig. 6* calculated at 20° C with the average $[\text{NH}_4^+]_w + [\text{NH}_3]_w$ concentrations measured in the modeled period ($1.61 \cdot 10^{-6}$ M) by Eq. (3). As it can be seen, the effect of carbon dioxide strongly depends on the pH. At $\text{pH} < 8.25$, CO_2 enhances the volatilization of ammonia above that the influence turns to the inverse. This relationship explains our results, because during the summer experiment the pH of lake water was always above 8.65.

Table 3. Mean parameters in comparison of ammonia fluxes measured and modeled by the two solubility theories

	Hales-Drewes theory	Henry's law
Water temperature		22–29 °C
pH		8.65–8.72
C_w (ammonia + ammonium)		48–58 μM
Mean flux	2.21 $\text{ng m}^{-2} \text{s}^{-1}$	24.4 $\text{ng m}^{-2} \text{s}^{-1}$
Degree of freedom		46
Correlation	$r = 0.72$	$r = 0.24$
Significance (probability level)	$p = 0.01$	Non significant

Data in *Table 3* suggest the applicability of Hales-Drewes solubility theory instead of the classical Henry's law in calculation of compensation-point concentration in flux modeling, since correlation is significant, furthermore, the measured ($2.11 \text{ ng m}^{-2} \text{ s}^{-1}$) and modeled ($2.21 \text{ ng m}^{-2} \text{ s}^{-1}$) average fluxes were practically the same ($\text{SD}=6.59$ and 8.08 , respectively). In contrast, modeled fluxes using the single Henry's law equilibrium constant only for ammonia (excluding CO_2) gives a mean flux higher by one order without significant relationship with the measured fluxes. Deviation from single Henry's law solubility theory was found in earlier investigations as well (*Lau and Charlson*, 1977; *Horváth*, 1982), underlying the disagreement among field and laboratory measurements in estimating the effect of CO_2 on the solubility of ammonia. To clarify the reason of this disagreement, further research is needed in this field.

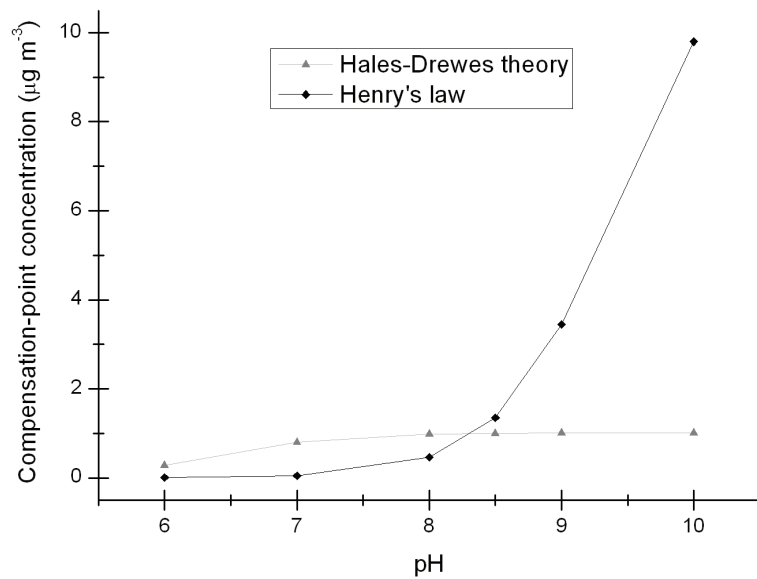


Fig. 6. Compensation-point concentration of ammonia in diluted water solution at 20 °C in the function of pH calculated by the Henry's law and the Hales-Drewes theory at $[\text{NH}_4^+]_w + [\text{NH}_3]_w = 1.61 \cdot 10^{-6} \text{ M}$

Modeled fluxes of nitric acid were verified by fluxes measured by the gradient method similarly to ammonia. Samplings, gradient measurements, and gradient flux calculations were the same. Regression is illustrated by Fig. 7. The correlation between the calculated and modeled fluxes is $r=0.68$ ($p=0.01$).

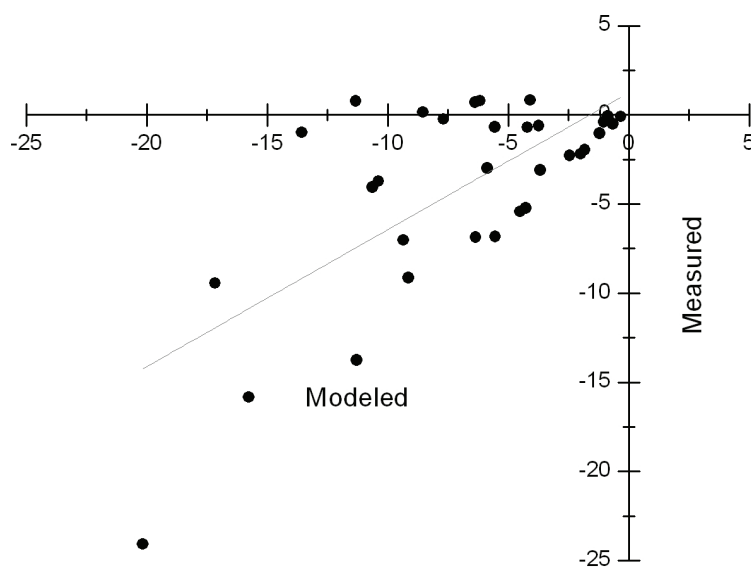


Fig. 7. Comparison of measured nitric acid fluxes with results of compensation-point model ($\text{ng m}^{-2} \text{ s}^{-1}$) for the period of July 12–25, 2002

3.5. Flux calculation by the RM and FM models using new solubility theory

Ammonia exchange between the lake and the atmosphere was modeled on the basis of hourly micrometeorological parameters and daily concentration measurement of atmospheric ammonia between 2001 and 2004 by the compensation-point model Eq.(1) using the RM and FM models for calculation of resistances. Daily ammonia concentrations were measured near the lake between March 2002 and February 2003, while for the remaining period, interpolated data were used from two Hungarian background air pollution monitoring stations (*Farkasfa* and *K-pusztá*). The agreement is relatively good (*Fig. 8a*), showing a uniform pattern of background ammonia concentration all over Hungary.

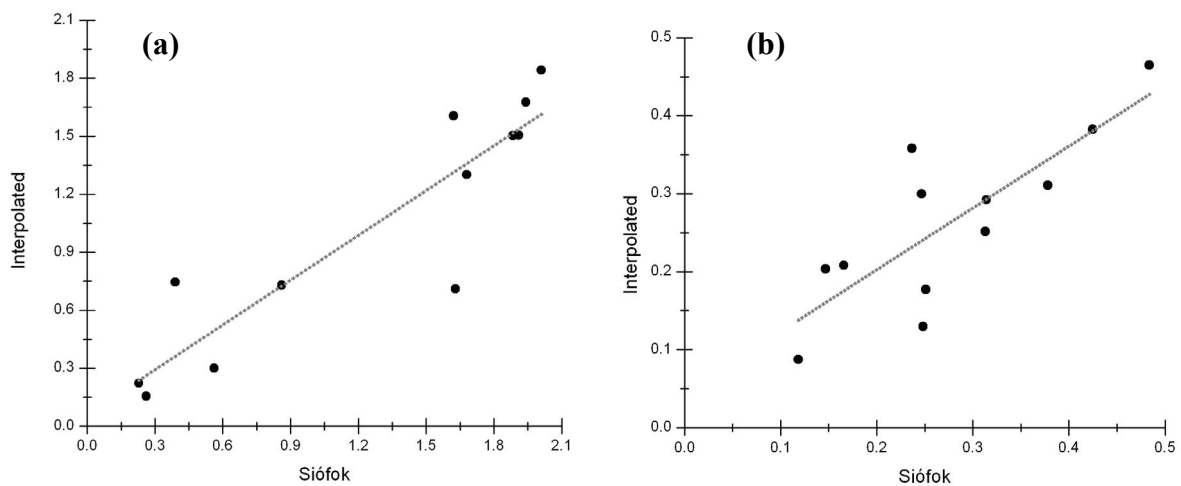


Fig. 8. Comparison of monthly mean ammonia (a) and nitric acid (b) concentrations in $\mu\text{g N m}^{-3}$ measured near the lakeside (Siófok) and the average of two background air pollution monitoring stations (K-pusztá, Farkasfa) in $\mu\text{g m}^{-3}$, between March 2002 and February 2003 ($r = 0.90$ and 0.78 for ammonia and nitric acid, respectively, and $p = 0.01$)

For calculation of the compensation-point concentration, the knowledge of pH, and sum of NH_3 and NH_4^+ concentrations in water were necessary. They were provided by the Middle Transdanubian Inspectorate for Environmental Protection, Natural Protection, and Water Management, measured on the basis of periodic measurement at five sampling points around the lake (*Figs. 9a,b*).

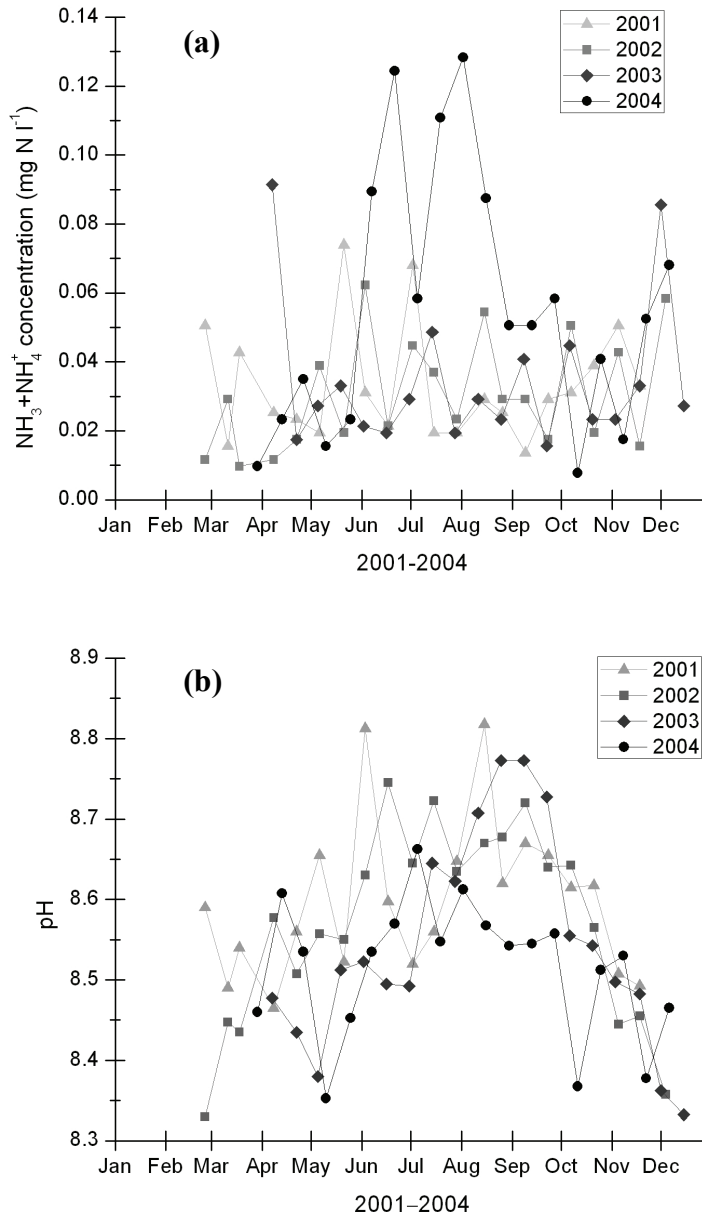


Fig. 9. Concentration of ammonia + ammonium (a) and pH (b) in the lake water, mean of 5 sampling points

Flux rates calculated by the two models had to be selected according to the wind direction. Determined by the location of the measurement point, the fetch criteria (homogeneous open water surface within at least 1 km) are fulfilled in the sector of 203 to 68 degrees clockwise. In the “wrong” sector, air temperature and wind velocity – both determining the exchange processes – are different from parameters measured in the “good fetch” sector.

Fluxes by the compensation-point model based on RM and FM were calculated on hourly base. Mean monthly fluxes can be seen in *Fig. 10a*. The compensation-point concentration of ammonia was generally higher in summer

half-year compared to the atmospheric concentrations resulting in emission peaks in this season. As a yearly average, net flux can be calculated in each year.

Deposition model of nitric acid is similar to the compensation-point model of ammonia. Only difference is that compensation-point concentration of nitric acid is zero in Eq. (1). Calculation method of nitric acid fluxes was the same as for ammonia using direct concentration measurements (March 2002–February 2003) and interpolated concentrations from the 2 background monitoring stations. The correlation between direct measurements and interpolated concentrations can be seen in *Fig. 8b*. *Fig. 10b* shows the mean monthly nitric acid fluxes for the four-year period.

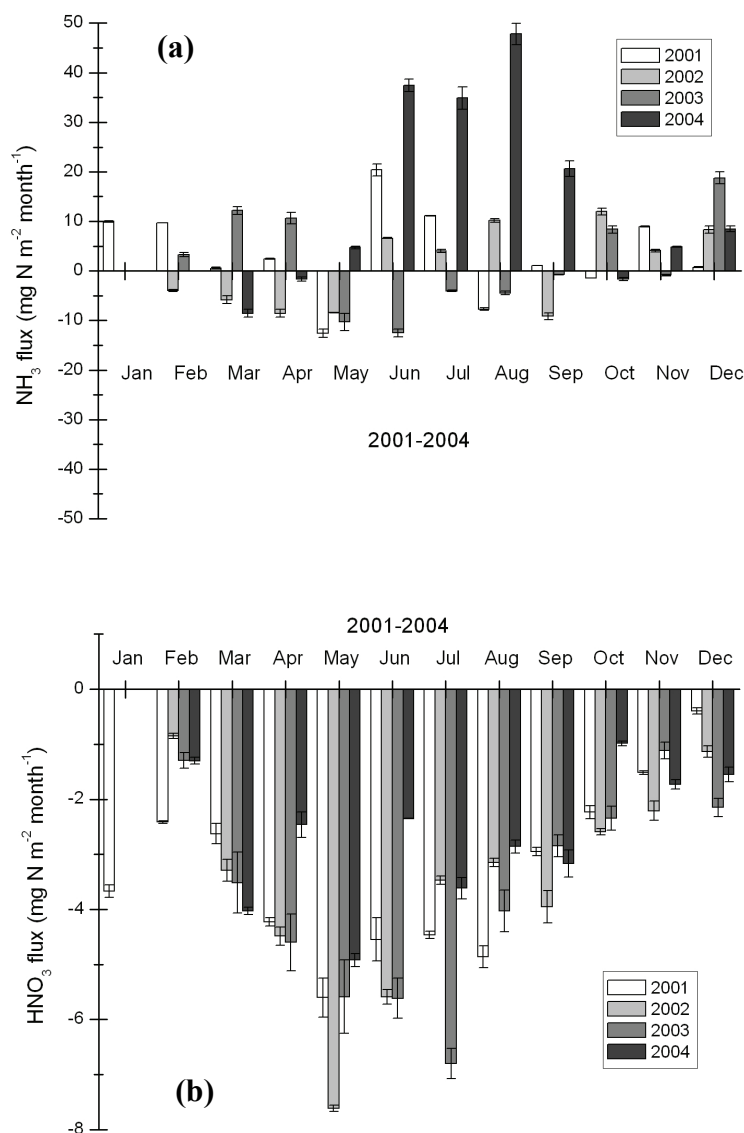


Fig. 10. Modeled mean monthly rates of ammonia (a) and nitric acid (b) fluxes (error bars denote the difference between two modeled fluxes by RM and FM)

In frozen periods (typically between the end of December to middle of February), fluxes were not computed since compensation-point concentration of ammonia is unambiguously zero, because the frozen surface prevents emission. Theoretically, deposition (adsorption) is possible onto ice surface probably followed by emission (desorption). Moreover, concentrations of ammonia and nitric acid in winter season are much lower since the equilibrium of $(\text{NH}_3)_{\text{gas}} + (\text{HNO}_3)_{\text{gas}} \leftrightarrow (\text{NH}_4\text{NO}_3)_{\text{particle}}$ process highly depends on air temperature and humidity (Stelson and Seinfeld, 1982). Low temperature and high humidity favor aerosol formation in frozen periods. For these reasons, deposition during frozen lake event was estimated to be negligible.

Yearly average of ammonia (by Hales-Drewes theory) and nitric acid dry fluxes calculated by FLake (FM) and resistance (RM) models are compiled in Table 4. For ammonia, upward (emission) fluxes were modeled in each year with large difference among years caused by extremely high ammonia+ammonium concentrations in lake water in different years (Fig. 9a). For nitric acid, the pattern is more even, there are no large differences among years.

Table 4. Yearly mean of ammonia and nitric acid fluxes over Lake Balaton (2001–2004) using the different turbulence models (FM: Flake model, RM: resistance model)

models	2001	2002	2003	2004	mean
	(mg N m⁻² year⁻¹)				
FM NH ₃	42.6	6.01	17.3	138	51.0
RM NH ₃	43.8	12.5	23.4	156	58.9
mean	43.2	9.27	20.4	147	54.9
FM HNO ₃	-38.3	-37.8	-39.7	-28.5	-36.1
RM HNO ₃	-40.6	-38.9	-40.0	-29.4	-37.2
mean	-39.5	-38.3	-39.9	-29.0	-36.7

4. Conclusions

Dry flux of ammonia gas and nitric acid vapor were modeled both by a simple resistance model and by the more sophisticated FLake model.

Between the years of 2001 and 2004, net yearly ammonia emission and nitric acid deposition were observed at Lake Balaton. Calculated net NH₃ emission and HNO₃ deposition to the whole surface of lake between 2001 and 2004 were 32.7 t N year⁻¹ and -21.8 t N year⁻¹, respectively. The magnitude of these figures is less by one order of magnitude compared to nitrogen load from wet deposition and from dry deposition of aerosol particles that takes

–437 t N year⁻¹ in the same period (Kugler and Horváth, 2008). It means that dry fluxes of ammonia and nitric acid do not play important role in the N-budget and in the eutrophication of Lake Balaton in those years.

The pH range in the lake water allows bi-directional flux of ammonia. Direction of net flux (emission or deposition) depends mainly on concentrations in the water and air. Ammonia exchange can act as a buffering system, i.e., in case of a high N-load into the lake from other sources (rivers, waste water, runoff, etc.), the effect can be buffered through nitrogen emission in form of NH₃ as a consequence of the elevated compensation-point concentration. In contrast, in lack of enough nitrogen for living systems, ammonia can be absorbed (deposited) parallel with decrease of compensation-point concentration controlled by the water. The main consequence of this phenomenon can be that eutrophication of Lake Balaton (and probably of other lakes with similar pH) is probably phosphorus limited.

Comparing the measured ammonia flux with the fluxes calculated by compensation-point model based on the single Henry's law theory and by the modified solubility theory of Hales-Drewes, it can be concluded that in our case latter theory describes better the exchange processes, suggesting that effect of carbon dioxide on the solubility of ammonia can not be excluded. However, in contrast with Hales-Drewes, who suggested the decrease the solubility of ammonia in presence of CO₂, we find an opposite effect, i.e., CO₂ favors the solubility of ammonia in the pH-range of the lake. To eliminate the obvious contradiction among the different solubility theories, further researches are needed in the future.

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