Response to Anonymous Referee #1 comments to paper "Tropospheric vertical column densities of NO₂ over managed dryland ecosystems (Xinjiang, P. R. China): MAX-DOAS measurements vs. 3D dispersion model simulations based on laboratory derived NO emission from soil samples"

The authors would like to thank Anonymous Referee #1 for his/her constructive comments.

Specific comments:

1. **Page 19361, line 15: please add "e.g." in the list of references.**
   - *"e.g." have been added in the revised MS.*
2. **Page 19362, line 27: a more recent reference, if it is available, would be beneficial.**
   - *In the revised MS, the reference "World Map of the Koeppen-Geiger classification updated" by Kottek et al (2006) will be used.*
3. **Page 19363, Line 26: add "nm" after "420-450".**
   - *"nm" have been added.*
4. **Page 19365, line 2: define what the "m a.gr." stands for, is this meters above ground?**
   - *Yes*
5. **Page 19366, line 16: Is the "59.8 dS m-1" the right value for natural forests? Please check.**
   - *Yes, it is the right value for the natural forest. The natural forest in study area are associated with mainly Tamarix species and P. eupharatica and they depends on groundwater. The plant species of Tamarix widespread in salty and sandy land in arid area. Natural forest, so called by the local people because the unique tree species makes it possible to reverse environmental degradation.*
6. **Page 19366, line 17: what "TDR" and "FDR" stand for?**
   - *TDR (Time-Domain-Reflectometry) and FDR (Frequent Domain Reflectometry) have been added.*
7. **Page 19366, line 25: please explain the "pF 4.2".**
   - *The relation between soil moisture and soil moisture content expressed as pF curve (soil moisture retention curve). When the soil becomes dry the soil moisture content reached the minimum value then the soil is at permanent wilting point or has a pF=4.2. This means, that the theta min is equal to the permanent wilting point.*
8. **Page 19378, section 3.3: what about the errors in both measured and simulated NO₂ VCDs? Please discuss further the results of Figure 5.**
   - *We would like to thank Anonymous Referee #1 for this suggestion. And we assume that the referee #1 wanted to say the Figure 7 (in MS version Fig. 8). This sentence has been added in revised MS "Both measured and simulated NO₂ VSDs in Figure 7 have with an average root mean square (RMS) error between the measured and simulated values of approx. 5-15% "*
9. **Page 19380, Conclusions: I suggest rewriting the first paragraph. I found it too difficult to follow its structure.**
   - *We acknowledge the suggestions of Anonymous Referee #1.*
10. **Page 19380, lines 22-24: please give a reference (or source) for the central European wheat field NO fluxes values.**
    - *The related references have been added in MS (Yamulki et al. 1995; Stohl et al. 1996; etc.)*
11. **Page 19393, Figure 6: at the color scale the white box corresponds to values greater than 10000. Shouldn't it be less than 10000? Please check it.**

- *The authors like to thank Anonymous Referee #1 for his comment concerning our typing mistake. There was a simple typo (">" instead of "<").*

Technical comments:

1. **Abstract, line 15: please add "(3-D)" after the "three dimensional"**
- *"three dimensional" has been added in revised MS.*
2. **Page 19363, line 3: please add the word "is" after "mean wind speed"**
- *"is" has been added in revised MS.*
3. **Page 19366, line 28: please remove "there"**
- *"there" has been removed in revised MS.*
4. **Page 19376, line 6: please delete "net" before "NO"**
- *"net" has been removed in revised MS.*
5. **Page 19378, lines 15: please delete "the" after "NO"**
- *"the" has been removed in revised MS.*

Response to Anonymous Referee #2 comments to paper "Tropospheric vertical column densities of NO₂ over managed dryland ecosystems (Xinjiang, P. R. China): MAX-DOAS measurements vs. 3D dispersion model simulations based on laboratory derived NO emission from soil samples"

The authors would like to thank Anonymous Referee #2 for his/her constructive comments.

Response to the comments listed as Major issues:

P19372, L5: it is not clear why the LASAT model is 'state-of-art'. From the description, it appears that chemistry is missing from the model, so that temporal evolution of the chemically active NO-species is difficult to track. Furthermore, it is unclear how pixel cross-talk, or advection, in the model (highly relevant with model resolution of 30 m) is described. The authors should improve the description of these issues.

The term "state-of-the-art" has been chosen since (a) LASAT is one of those air-pollution-transport-dispersion models of air-pollution which is (in Germany) officially licensed for legal use of environmental issues, and (b) among comparable micro-scale (e.g. street canyons) transport-dispersion models LASAT considers at least chemical transformations of 1ˢᵗ order and keeps nonetheless truly operational. Being a transport-dispersion-model, LASAT basically considers advection ("pixel cross-talk") applying the 3D-continuity equation for any chosen tracer; the interested reader is referred to the cited reference (German VDI Guidelines VDI3945, part 3; cf. Janicke Consulting, 2011).

P19372, L5: Calculation of concentration of NO₂ from the photochemical equilibrium between NO and O3 is in principle feasible. However, O₃ concentration increase with altitude, and J(NO2) also has a vertical profile. It is unclear how these vertical distributions are taken into account? If they are neglected, which seems to be the case, the authors should estimate the error associated with these assumptions.

Since the NO-NO₂-O₃ photochemical equilibrium could not be handled by the LASAT "chemical" algorithm, we decided to use measured data (O₃ mixing ratio, NO₂ photolysis rate, s. sect. 2.2.2) to convert the calculated 3D-NO mixing ratio to the photo-stationary 3D-NO₂ mixing ratio. As far as the distribution of O₃ mixing ratio within the boundary layer is concerned: a constant vertical O₃ mixing ratio (up to 1500 m a.gr.) is assumed over Milan oasis. This is justified by the fact, that particularly in arid and hyper-arid landscapes at mid-day conditions (maximum of insulation) the entire atmospheric boundary layer is intensively mixed, which is due to extensive convective heating of the surface by the sun which produces buoyant thermals that establish the so-called mixing layer. Consequently a uniform vertical mixing ratios is expected for trace gases without distinct local sources and lifetimes greater than exchanges times within the Boundary Layer. (c.f. Husar et al. 1978, Stull 1988). This assumption is valied for ozone. Vertically constant O₃ mixing ratio has been reported for the atmospheric boundary layer over semi-arid southern Africa (Meixner et al., 1993). As far as the vertical profile of j(NO₂) is concerned: basically, the downward component of the actinic flux increases with increasing elevation due to the decreasing optical thickness of the scattering air masses. However, the altitude effect on the actinic flux in the first kilometer of the troposphere is typically very small. Trebs et al. (2009) used the Tropospheric Ultraviolet Visible model (TUV, version 4.4; http://cprm.acd.ucar.edu/Models/TUV/) to calculate the typical vertical change of the actinic flux and found a vertical gradient of 1.1%/km. Consequently, our calculations of the NO to NO₂ conversion in

the boundary-layer over Milan oasis (1500 m a.gr.) have not considered any potential vertical change of the j(NO₂) values measured at ground level.

P19372, L5: More attention should be paid at the local time at which measurements and model simulations have taken place. For instance, in Figure 4, it is unclear what the local time was for the MAX-DOAS measurements shown. This is important, in view of the diurnal cycle in soil NO$_x$ emissions (presumably higher at mid-day in response to higher soil temperatures) and the diurnal cycle in NO₂ concentrations with a midday minimum in NO₂ reflecting higher mid-day OH-levels (e.g. Fig. 7).

The authors like to thank referee#2 for this comment. As far as Fig. 4 (in MS: Fig 5) is concerned, the MAX-DOAS measurements were performed between 6:00 and 19:00 (local time) and all the "labelling" of data points are in terms of the measurements time.

P19372, L5: The community would benefit from an evaluation of Eq. 10 with the laboratory net-derived potential net NO-fluxes. To my knowledge, such an evaluation with samples from the field has not yet been done.

Based on this important suggestion of referee#2 we evaluated the laboratory net-derived potential net NO-fluxes according to eq.(10). In the revised version of our manuscript one will find the following figure:
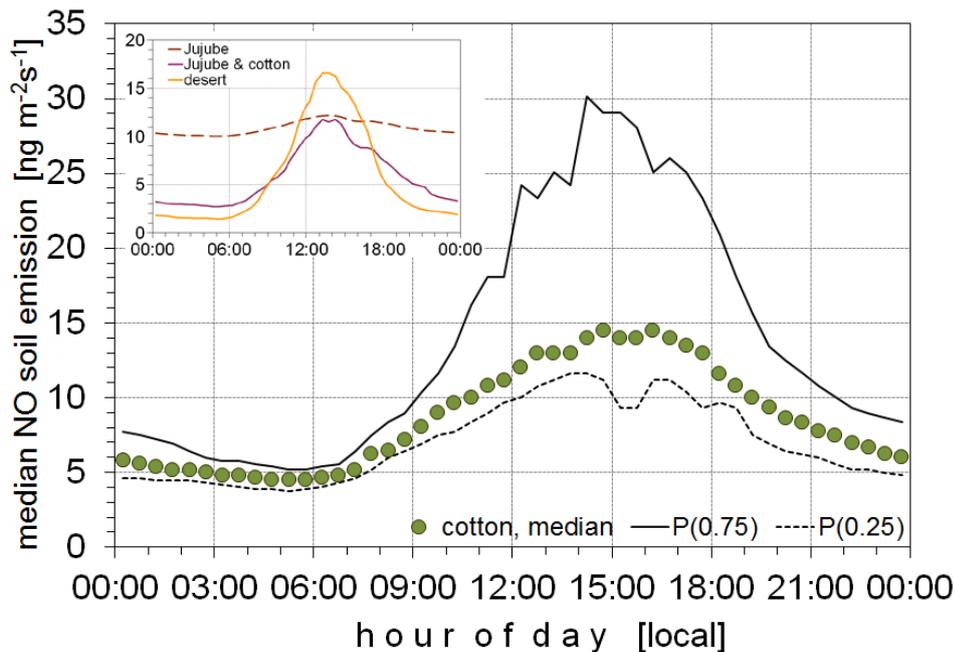
Figure 4: *median diel variation of the actual NO-flux (ng m^{-2}s^{-1}; in terms of mass of nitric oxide) from soils of the four major land-cover types of Milan oasis for the period 03 to 24 June, 2011. Data have been calculated according eq.(10) using (a) soil temperatures (medians) measured for each of the four major land-cover types, and (b) so-called "wilting point"-data for corresponding soil moisture contents at the four sites (s. section 2.2.3). Data for the cotton-site are given as medians, as well as 25 and 75% quantiles, those for the Jujube, Jujube-cotton and desert sites as medians only (s. figure insert).*

Within the revised version of our manuscript, the following text will replace lines 1-9 on page 19377 (section 3.2):

For the period 03 to 24 June, 2011, land-cover specific, actual NO fluxes were calculated according to eq.(10) for cotton, jujube, cotton/jujube, and desert soils from corresponding laboratory derived net potential NO fluxes. As input we used land-type specific, measured soil temperature data as well as land-type specific soil moisture data (so-called "wilting points", s. Sect. 2.2.3). The calculated NO fluxes are shown as median diel variation in Fig. 4. Since NO fluxes from Milan cotton fields dominate the total soil biogenic NO emission of the oasis, corresponding medians and quartiles are shown in Fig. 4, while – for the sake of clarity –for jujube, cotton/jujube, and desert only medians are given. Since land-type specific "wilting points" are constant, diel variations of actual NO fluxes mirror directly those of corresponding soil temperatures, showing the daily minimum around 06:00 local time for all four major land-cover types. The maximum of the actual NO-flux, however, is around 13:00 local time for jujube, cotton/jujube, and desert soils, and 15:00 local time for cotton. This is due to the increasing growth of the cotton plants, where at the beginning of the experimental period the bare soil surface was nearly 100% exposed to insolation, while towards the end of the experimental period the growing cotton canopy has shaded great parts of the soil surface. This is also reflected by the skewed distribution of actual NO-fluxes from cotton covered soil, indicated by the daytime non-symmetric inter-quartile range (upper quartile >> lower quartile). Actual NO-flux data of 09 June, 2011 (08:30-14:30 local time) were used for the comparison of LASAT and MAX-DOAS results. During this particular day (within the first week of the experimental period), the derived flux for "land-cover cotton" ranged from 15–64 ng $m^{-2}s^{-1}$ (in terms of mass of NO), those for jujube, cotton/jujube, and desert land-covers ranged from 11–13, 6–16, and 6–17 ng $m^{-2}s^{-1}$, respectively. These actual NO fluxes were then assigned to each individual source unit (i.e. to each of the 2500 polygons of Milan oasis' domain). The soil biogenic NO emission from all cotton fields between 08:30 and 14:30 was estimated to 28.7 kg (in terms of mass of NO), equivalent to 76% of the total soil biogenic NO emission of the entire Milan oasis.

P19372, L5: Also, the paper would improve greatly if the authors could indicate whether their evaluation of the LASAT simulations with the MAX-DOAS observations is consistent with the parametrization of the diurnal cycle in soil NO_x emissions that follows Eq. (10).

Referee#2 is most likely pointing to the fact, that the actual NO emissions (irrespective of the land-cover type) have their maximum in the early afternoon (s. above), while the highest height-integrated NO_2 concentrations as simulated by LASAT (on the basis of the actual NO emissions) are in the morning (08:30–10:00), followed by rather constant values for the reminder of the day (s. Fig. 7, in MS Fig. 8). The apparent discrepancy between both diurnal variations can be simply explained by the diurnal variation of the wind direction and the specific viewing geometry of the MAX-DOAS instrument. The MAX-DOAS instrument was located at the south-west corner of the oasis, and the observations at zenith and low elevation angles probed air masses located at different locations accross the oasis. The wind direction was from north-east in the morning and turned to north-west in the afternoon. Hence, air masses of lower concentration crossed the viewing directions in the afternoon compared to those in the morning. This explains that in spite of the larger NO_x emissions smaller column densities have been observed in the afternoon.The apparent discrepancy of the diurnal cycles of NO emissions and measured NO_2 column densities indicates the importance to exactly consider the 3-dimensional NO_2 distribution (due to the soil-emitted NO) for the comparison of the model results with MAX-DOAS observations. We added this information to the text

P19379, L7: In section 3.5, the authors state that 'there is remarkable good agreement' between measured and simulated data. Inspection of Figure 7 however shows that there is a discrepancy of 25-30% between the LASAT model and most reliable MAX-DOAS measurement (at 15 deg elevation), with LASAT being too high. While I agree that the authors have done an impressive job in describing the spatial and temporal detail of soil

NOx emissions from the area, I think it is a bridge too far to claim that the agreement between simulated and measured NO2 is remarkable. I think the discrepancy needs more attention. It could be caused by the lack of chemistry in the LASAT simulation (NO2 too long-lived).

Nevertheless, for the case of our measurements the locally enhanced NO values caused by the soil emissions have a small but systematic effect on the ozone concentration, and thus also on the Leighton ratio: Close to the surface (below about 50m) the NO concentrations can be quite large, with maximum values up to about 10 ppb. Consequently, the ozone concentration will be reduced due to the reaction with NO by up to about 10 ppb. This means that the Leighton ratio will be reduced by up to about 25%. Although the reduction of the ozone mixing ratio wil be partly compensated by mixing with air from higher altitudes, the simulated NO_2 mixing ratios might overestimate the true NO_2 mixing ratios by up to about 25%. Probably the true overestimation for our measurements is much smaller because the typical NO mixing ratio within the lowest 100m is much lower than 10 ppb. However, the LASAT simulation overestimate slightly the true NO_2 VCD. The both measured and simulated NO_2 VSDs in Figure 7 (in MS Version Figure 8) have with an average root mean square (RMS) error between the measured and simulated values of approx. 5-15%. The overestimation of LASAT simulation is well suited to the fact that in reality a little less NO can be converted to the NO_2 because of lower ozone concentration at the surface. We added this information to the text.

It is also intriguing that the 2 and 4 deg elevation cases (for which the geometrical AMF will lead to errors) show better agreement than the 15 deg elevation case (for which the simple geometrical AMF works fine). These aspects should be discussed in more detail than just claiming 'remarkable agreement'.

The reviewer is right that in principle the accuracy of the geometric approximation is much higher for the high elevation angles than for the loewer elevation angles. However, for the specific cases studied here, this is not the case. First, close to the sources, the height of the layer with elevated NO_2 is quite low (in our case the bulk of NO_2 is located below 50 m). Secondly, also the aerosol load is usually very low at Milan oasis. Thus the probability of scattering events inside the layer of enhanced NO_2 is very low, and consequently the accuracy of the geometric approximation is relatively high. To further quantify the associated uncertainties, we performed radiative transfer simulations and found that the deviations of the geometric approximation are similar for the different elevaton angles (about 5% for 2°, 3% for 4° and 3% for 15°).
However, because of the shorter light paths through the NO_2 layer, the relative error caused by the uncertainty of the spectral analysis is higher than for the low elevation angles. Thus for the case of our measurements, we indeed expect lower uncertainties for the low elevation angles. We added this information to the text.

Specific comments:

1. P19362, L25-26: I'm not sure if the assumption that free tropospheric NO_2 advection is negligible holds. In the study-area, considerable contributions from lightning and soil (from other areas) resulting in summertime NO2 maxima have been reported (e.g. van der A et al., 2008; Miyazaki et al., ACP, 2012 – Figure 14).
- *We agree that in principle tropospheric NO2 retrievals might be also affected by NOx produced from lightning. Very fortunately, the study area is typically only little affected by clouds and aerosols. Also the lightning activity is rather weak. The selected study area provides rather good pre-requisites to achieve this aim of the study, since they are supposed not to be strongly affected by other, neighboring substantial NOx sources, such as e.g. traffic or power plants; also NOx emissions due to lightning can be neglected over Milan oasis. It should also be noted that*

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lightning (and soil emissions from other areas) would affect both the upwind and downwind areas in the same way.

2. P19363, L8: here 'NE' is mentioned, but in L11 'NW' is mentioned. Should it be NW everywhere? Please clarify if NW means 'North West'.

- *The authors like to thank Anonymous Referee #2 for his/her comment concerning our typing mistake. There was a simple typo ("NW" instead of "NE")*

3. P19363, L19: please have the list of references preceded by e.g.

"e.g." have been added in the revised MS.

4. P19365, L5-6: Strongly suggest to provide references that confirm that scattering may be neglected at elevation angles > 15 degrees.

- *The potential importance of scattering on the interpretation of the MAX-DOAS measurements depends on two main aspects: first on the height of the trace gas layer. Second on the amount of aerosols. In our case the trace gas layer is shallow and the aerosol amount is low. Thus scattering effects can be neglected. (see discussion of last major point above).*

5. P19365, L8: I don't think the abbreviation or meaning of LASAT has been introduced at this stage. Suggest to do so.

- *In abstract the abbreviation of LASAT (Lagrangian Simulation of Aerosol-Transport) was explained. However, here "Lagrangian Simulation of Aerosol-Transport " has been added.*

6. P19367, L4: the section title should read 'NO fluxes', not 'NO2 fluxes'.

- Many thanks to Anonymous Referee #2 for his/her comment concerning our typing mistake. There was a typo ("NO_2" instead of "NO")

7. P19368, L7: please clarify why the soil T variation between 20 and 30 degrees is 'desired'. Do ambient temperatures in July never drop below 20 C?

- *The control of the soil temperature via the temperature controlled cabinet of the soil laboratory must allow the frequent (and fast) change at least between two temperatures differing by 10 K (T_0 and T_1) during an individual drying-out experiment (please see Behrendt et al. 2014). Normally, the ambient temperatures in July of the study area are above 20 °C. We added the reference to the text.*

8. P19368, L17: after 'As shown during the last two decades', a few citations would be appropriate.

- *„Yang and Meixner, 1997; Otter et al., 1999; Kirkman et al., 2001; van Djik and Meixner, 2001; van Dijk et al., 2002; Garrido et al., 2002; Meixner and Yang, 2006; Yu et al., 2008, 2010; Feig et al., 2008; Ashuri, 2009; Feig, 2009; Laville et al., 2009; Gelfand et al., 2009; Bargsten et al., 2010" have been added.*

9. P19371, L2: 'methods' should be 'method'.

- *"methods" has been corrected for "method" in revised MS.*

10. P19371, L5: the closing bracket after plant cover is redundant.

- *"the closing bracket" was removed.*

11. P19372, L23: in terms of stability classes.

- *"of" has been added.*

12. P19377, L9: 76% of total, 24-hour soil biogenic NO emissions? Please clarify.

- *That is not 76% of 24-hour soil biogenic NO emissions, but also 75% of the total soil NO emission between 08:30 and 14:30. Here additional "within 6 hours" has been added.*

13. P19378, L14-16: the resolution of Figure 6 is a bit low. I think the Figure is so nice that it would merit an improvement in resolution so the spatial detail can be better distinguished.

- *We followed the suggestions of Anonymous Referee #2.*

Stull, R.B. (1988), An Introduction to Boundary-Layer Meteorology, Kluwer Academic Publishers, Dordrecht, The Netherlands.

Husar, R.B., Patterson, D.E., Husar, J.D., Gillani, N.V., Wilson Jr., W.E. (1978), Sulfur budget of a power plant plume, Atmospheric Environment, 12 (1-3), 549-568.

Meixner, F.X., Ajavon, A.-L., Helas, G., Scharffe, D., Zenker, T., Harris, G.W., Andreae, M.O. (1993), Vertical distribution of ozone over southern Africa: Airborne measurements during SAFARI-92, AGU Fall Meeting, San Francisco, U.S.A.

Trebs, I., Bohn, B., Ammann, C., Rummel, U., Blumthaler, M., Königstedt, R., Meixner, F. X., Fan, S., Andreae, M.O. (2009), Relationship between the NO_2 photolysis frequency and the solar global irradiance, Atmospheric Measurement Techniques, 2, 725–739.

Tropospheric vertical column densities of NO₂ over managed dryland ecosystems (Xinjiang, P. R. China): MAX-DOAS measurements vs. 3-D dispersion model simulations based on laboratory derived NO emission from soil samples

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Abstract

We report on MAX-DOAS observations of NO_2 over an oasis-ecotone-desert ecosystem in NW-China. There, local ambient NO_2 concentrations originate from enhanced biogenic NO emission of intensively managed soils. Our target oasis "Milan" is located at the southern edge of the Taklimakan desert, very remote and well isolated from other potential anthropogenic and biogenic NO_x sources. Four observation sites for MAX-DOAS measurements were selected, at the oasis center, downwind and upwind of the oasis, and in the desert. Biogenic NO emissions in terms of (i) soil moisture and (ii) soil temperature of Milan oasis' (iii) different land-cover type sub-units (cotton, Jujube trees, cotton/Jujube mixture, desert) were quantified by laboratory incubation of corresponding soil samples. Net potential NO fluxes were up-scaled to oasis scale by areal distribution and classification of land-cover types derived from satellite images using GIS techniques. A Lagrangian dispersion model (LASAT, Lagrangian Simulation of Aerosol-Transport) was used to calculate the dispersion of soil emitted NO into the atmospheric boundary layer over Milan oasis. Three dimensional NO concentrations (30 m horizontal resolution) have been converted to 3-D (three dimensional) NO_2 concentrations, assuming photostationary state conditions. NO_2 column densities were simulated by suitable vertical integration of modeled 3-D NO_2 concentrations at those downwind and upwind locations, where the MAX-DOAS measurements were performed. Downwind-upwind differences (a direct measure of Milan oasis' contribution to the areal increase of ambient NO_2 concentration) of measured and simulated slant (as well as vertical) NO_2 column densities show excellent agreement. This agreement is considered as the first successful attempt to prove the validity of the chosen approach to up-scale laboratory derived biogenic NO fluxes to ecosystem field conditions, i.e. from the spatial scale of a soil sample (cm^2) to the size of an entire agricultural ecosystem (km^2).

1 Introduction

Emissions of nitric oxide (NO) are important in regulating chemical processes of the atmosphere (Crutzen, 1987). Once emitted into the atmosphere, NO reacts rapidly with ozone (O_3) to nitrogen dioxide (NO_2) which, under daylight conditions, is photolyzed back to NO ($\lambda \leq$ 420 nm). For that reason, NO and NO_2 are usually considered as NO_x ($NO_x = NO + NO_2$). Ambient NO_x is a key catalyst in atmospheric chemistry: during the atmospheric oxidation of hydrocarbons its ambient concentration determines whether ozone (O_3) is photochemically generated or destroyed in the troposphere (Chameides et al., 1992). While the combustion of fossil fuels (power plants, vehicles) is still the most important global NO_x source (approx. 25 Tg a^{-1} in terms of mass of N), biogenic NO emissions from soils have been estimated to range between 6.6 and 9.6 Tg a^{-1} (Denman et al., 2007). The considerable uncertainty about the range of soil biogenic NO emissions stems from widely differing estimates of the NO emission. Moreover, the uncertainties in the NO emission data from semi-arid, arid, and hyper-arid regions are very large (mainly due to a very small number of measurements being available). These ecosystems, however, are considered to contribute more than half to the global soil NO source (Davidson and Kingerlee, 1997), and make approx. 40% of planet Earth's total land surface (Harrison and Pearce, 2000).

Production (and consumption) of NO in the soil depends mainly on soil microbial activity and is mainly controlled by soil temperature, soil moisture, and soil nutrient concentration (Conrad, 1996; Meixner and Yang 2006; Ludwig et al., 2001). Any natural or anthropogenic action that result in the inputs of nutrients (e.g. by fertilizer application) and/or modification of soil nutrient turnover rates has a substantial effect on soil biogenic NO emission. The rapid (economically driven) intensification of arid agriculture (oasis agriculture), particularly by enlargement of the arable area and by enhancement of necessary irrigation leads inevitably to the increase of soil biogenic NO emissions. Since those microbial processes which underlay NO production and NO consumption in soils are confined to the uppermost soil layers (<0.0 5 m depth, Rudolph et al., 1996), the most direct method for their characterization and quantification is usually realized by laboratory incubation of soil samples; corresponding measurements result in the determination of so-called net potential NO fluxes, which are explicit functions of soil moisture, soil temperature, and ambient NO concentration (Behrendt et al., 2014).

Tropospheric NO_2 column densities can be retrieved from satellite observations using differential optical absorption spectroscopy (DOAS) (e.g. Leue et al., 2001; Richter and Burrows, 2002, Beirle et al., 2004). Identification and quantification of the sources of

3

79 tropospheric NO_2 column densities are important for monitoring air quality, for understanding

80 radiative forcing and its impact on local climate. Ground-based Multi Axis Differential

81 Optical Absorption Spectroscopy (MAX-DOAS) is a novel measurement technique

82 (Hönninger et al., 2004) that represents a significant advantage over the well-established

83 zenith scattered sunlight DOAS instruments, which are mainly sensitive to stratospheric

84 absorbers. From NO_2 slant column densities, retrieved from measurements at different

85 elevation angles, information about tropospheric NO_2 profiles and/or tropospheric vertical

86 column densities can be obtained (e.g. Sinreich et al., 2005; Wittrock et al., 2004; Wagner et

87 al., 2011).

88 In this paper we concentrate (a) on ground-based MAX-DOAS measurements of slant and

89 vertical NO_2 column densities over an intensively used oasis of the Taklimakan desert (NW-

90 China), (b) on biogenic NO emissions derived from laboratory incubation measurements on

91 oasis soil samples, (c) on up-scaling of the laboratory results to the oasis level, (d) calculation

92 of atmospheric boundary layer NO_2 concentrations by suitable $NO{\rightarrow}NO_2$ conversion and

93 3 dimensional dispersion modelling, and (e) on simulating slant and vertical NO_2 column den-

94 sities from the calculated 3-D-NO_2 distributions by integration along the MAX-DOAS light

95 path. The final aim is comparison and discussion of the results obtained under (a) and (e).

96

97 **2   Materials and methods**

98 **2.1   Research area**

99   After two 'searching field campaigns' (2008 and 2009) in the Xinjiang Uighur Autonomous

100 Region of NW-China, the oasis "Milan" has been identified as the target oasis for the

101 presented research. The contemporary oasis Milan, identical to the ancient silk-road post

102 "Miran", belongs to the county "Ruoqiang" of the Xinjiang province and is located in the

103 southern Taklimakan Desert on the foot of the Altun Shan Mountains (39.25 °N, 88.92 °E,

104 998 m a.s.l.). In the early 1950s, the delta-shaped oasis (see Fig. 1) has been established as an

105 agricultural co-operative "state farm" (*Xinjiang Production and Construction Crop*) and

106 covers nowadays about $100\,km^2$. Milan oasis can be geomorphologically classified as a

107 "mountain-oasis-ecotone-desert system (MOED system)" consisting of Gobi (gravel) desert, a

108 salty transition zone surrounding the oasis, and dryland farming with irrigation. The latter

109 consists only of two crops, cotton and jujube trees (*Ziziphus Jujuba* L., "*red date*"), which are

110 planted, irrigated, and fertilized following standardized protocols and growing on rectangular

111 fields (approx. 10 ha) of pure cultures or mixtures of it. The general energy supply of Milan

4

112 oasis is entirely provided by nearby hydropower plants, and battery powered trikes dominate

113 the local public and private transport. Consequently, anthropogenic NO_x emissions of Milan

114 oasis are considered as very low, if not negligible. Beyond that, Milan oasis is isolated by the

115 desert from neighbouring oases by 80 to 400 km. Therefore, the dominant NO_x source of Mi-

116 lan oasis are biogenic NO emissions from its intensively managed crop fields; the oasis can be

117 undoubtedly considered as a large "hotspot in the middle of nothing". Given this very specific

118 situation, it is certainly justified to assume that (a) NO_2 concentrations in the atmospheric

119 boundary layer over Milan oasis are only caused by the oasis itself, and (b) free tropospheric

120 NO_2 concentrations, which are usually due to large-scale tropospheric NO_2 advection, are

121 negligible.

122 According to Koeppen classification (Koeppen, 1931; Kottek et al., 2006), Milan oasis owns

123 a cold desert climate (BWk), which is dominated by long hot summers (30 years' mean:

124 29°C) and cold winters (30 years' mean: − 6°C). Mean annual precipitation amounts

125 28.5 mm, mean annual evaporating capacity is 2920 mm, mean wind direction is NE to E, and

126 mean wind speed is 2.7 m s^{-1}.

2.2 In-situ measurements

128 A field campaign has been performed at Milan oasis, from 24 May to 26 June, 2011. A total

129 of 32 individual MAX-DOAS measurements (approx. 20 min) have been performed by two

130 Mini-MAX-DOAS instruments (partially simultaneously) on 21 days during the 2011 cam-

131 paign at the NE natural forest site (1), desert site (2), jujube site (3) and hotel station in Milan

132 oasis center (4). Accompanying data of wind direction, wind speed, air temperature,

133 barometric pressure, global and net radiation have been observed at sites (1) – (5) at 1.8 m

134 above ground (at NE natural forest: 11 m; at hotel station: 23 m). Soil temperature (at 0.05 m

135 depth), as well as rainfall (amount and intensity) were recorded at all sites in 2011.

2.2.1 Ground-based measurements of vertical column densities of NO_2

137 Multi-Axis-Differential Optical Absorption Spectroscopy (MAX-DOAS) observes scattered

138 sun light under various (mostly slant) elevation angles. From combinations of the retrieved

139 NO_2 slant column densities (SCDs) obtained at different elevation angles, information on the

140 vertical NO_2 profile and/or on the corresponding vertical column density (VCD) can be

141 obtained (e.g. Hönninger et al., 2002; Sinreich et al., 2005; Wittrock et al., 2004; Wagner et

142 al., 2011). Spectral calibration of the MAX-DOAS instruments was performed by fitting a

143 measured spectrum to a convoluted solar spectrum based on a high resolution solar spectrum

144 (Kurucz et al., 1984). Several trace gas absorption cross sections of NO_2 at 294 K (Vandaele

145 et al., 1996), H_2O at 290 K (Rothman et al., 2005), Glyoxal at 296 K (Volkamer et al., 2005),

146 O_3 at 243 K (Bogumil et al., 2003) and O_4 at 286K (Hermans et al., 1999) were convolved to

147 match the resolution of the instrument and then used in the spectral analysis using a

148 wavelength range of 420-450 nm (also a Ring spectrum was included in the fitting process).

149 The output of the spectral analysis is the NO_2 SCD, which represents the NO_2 concentration

150 integrated along the corresponding light paths through the atmosphere.

151 Since a spectrum measured in zenith direction (a so called Fraunhofer reference spectrum) is

152 included in the fit process to remove the strong Fraunhofer lines, the retrieved NO_2 SCD ac-

153 tually represents the difference between the SCDs of the measurement and the Fraunhofer

154 reference spectrum; it is usually referred to as differential SCD or $DSCD_{meas}$. The troposphe-

155 ric DSCD for the elevation angle α can be derived from MAX-DOAS observation by subtract-

156 ing the NO_2 DSCD for the closest zenith observation ($\alpha_0 = 90°$):

157 $$DSCD_{trop}(\alpha) = DSCD_{meas}(\alpha) - DSCD_{meas}(\alpha_0) \qquad (1)$$

158 DSCDs are converted into VCDs (the vertically integrated concentration) using so called air

159 mass factors (AMF, Solomon et al., 1987), which is defined by:

160 $$AMF = SCD / VCD \qquad (2)$$

161

162 In many cases AMF are determined from radiative transfer simulations (Solomon et al.,

163 1987). However, if trace gas column densities are retrieved from MAX-DOAS observations at

164 high elevation angles (> 10°), the AMF can be determined by the so called geometric approxi-

165 mation (Hönninger et al., 2002; Brinksma et al., 2008; Wagner et al., 2010):

166 $$AMF_{trop} \approx \frac{1}{\sin(\alpha)} \qquad (3)$$

167

168 In this study, the tropospheric vertical column density (VCD_{trop}) is obtained from $DSCD_{trop}(\alpha)$

169 as discussed by Wagner et al. (2010):

170 $$VCD_{trop} = \frac{DSCD_{trop}(\alpha)}{AMF_{trop}(\alpha) - AMF_{trop}(\alpha_0)} \qquad (4)$$

171 During the field experiments, the MAX-DOAS instruments have been mounted on solid

172 tables (aluminium structure) at approx. 11 m a.gr. (NW natural forest, hotel station) and 3.5 m

173 a.gr. (remainder of sites) with the telescope facing northwards. Observations were always
174 made on elevation angles of 0°, 2°, 4°, 6°, 8°, 10°, 15°, 20°, 45° and 90°. VCD_{trop}s were
175 determined from measurements at 15°. The potential importance of scattering on the
176 interpretation of the MAX-DOAS measurements depends on two main aspects: first on the
177 height of the trace gas layer and second on the amount of aerosols. In our case the trace gas
178 layer is shallow and the aerosol amount is low (see 2.2.8). Thus scattering effects can be
179 neglected. However, for comparison of the $DSCD_{trop}$ data obtained by MAX-DOAS with the
180 simulated SCDs obtained from 3 D distributions of NO_2 concentration (calculated with
181 LASAT (Lagrangian Simulation of Aerosol-Transport)) on the basis of laboratory derived net
182 potential NO_2 fluxes) the lower elevation angles (2°, 4°) for $DSCD_{trop}(\alpha)$ have been used,
183 which have a much higher sensitivity to the observed NO_2.
184 For classifying all MAX-DOAS measurements whether they were made up-wind, down-wind,
185 or in the center of Milan oasis, their observation position was related to the mean wind
186 direction during each measurement period. Wind measurements were part of accompanying
187 *in-situ* measurements (see below).

2.2.2 Accompanying measurements

189 Wind direction, wind speed, air temperature, relative humidity, barometric pressure, and
190 rainfall intensity have been measured by combined weather sensors (weather transmitter
191 WXT510, Vaisala, Finland). All five weather sensors have been operated side-by-side for one
192 week before they have been mounted at the individual measurement sites (1) – (5). Based on
193 these results, all meteorological data, which have been measured between 3 – 24 July, 2011
194 have been corrected using one of the sensors as reference. All combined weather sensors'
195 data, as well as those of net radiation (4 component net radiation sensor, model NR01,
196 Hukseflux, The Netherlands) and soil temperature (thermistor probe, model 109, Campbell
197 Scientific, U.S.A.) have been recorded every minute. Ambient O_3 concentrations and NO_2
198 photolysis rates have also been measured in-situ; both quantities are necessary to calculate the
199 NO→NO_2 conversion factor (see Sect. 2.2.8). Ozone concentrations have been measured by
200 UV-absorption spectroscopy (model 49i, ThermoFisher Scientific, U.S.A.) and NO_2 photoly-
201 sis rate by a filter radiometer (model 2-Pi-JNO2, metcon, Germany) in 1 minute intervals.

2.2.3 Soil samples

203 Microbial processes responsible for biogenic NO emission are confined to the uppermost soil
204 layers (Galbally and Johansson, 1989; Rudolph et al., 1996; Rudolph and Conrad, 1996).

205 Consequently, composite soil samples (1 kg of top soil, 0–5 cm depth) have been collected at
206 the individual sites of Milan oasis (natural forest, cotton, jujube, cotton & jujube mixture,
207 desert). All samples (air dried) were sent from Xinjiang to Germany by air cargo and stored
208 refrigerated ($+ 4°C$) until laboratory analysis of the net potential NO flux (see below). Sub-
209 samples have been analyzed for dry bulk soil density (ISO 11272), pH (ISO 10390), electrical
210 conductivity (salinity, ISO 11265), contents of nitrate and ammonium (ISO 14256), total
211 carbon and total nitrogen (ISO 10649 and ISO 13878), texture (ISO 11277), as well of soil
212 water potential (pF values 1.8, 2.5, 4.2, Hartge and Horn, 2009).

213 Electrical conductivity varied between 1.6 to 9.5 dS m^{-1} within the managed soils, and was
214 59.8 and 3.0 dS m^{-1} in the natural forest and desert soils, respectively. Commercially available
215 soil moisture probes (e.g. TDR (Time-Domain-Reflectometry) and FDR (Frequence-Domain-
216 Reflectometry)) show extreme interferences for soils of >2 dS m^{-1} (c.f. Kargas et al., 2013)
217 and their calibration for such soils is extremely challenging, if possible at all. Indeed, FDR-
218 signals monitored in Milan oasis' soils were extremely noisy and spurious. Nevertheless, up-
219 scaling of the laboratory derived net potential NO fluxes needs data of the uppermost layer of
220 each soil of Milan oasis land-types (see Sect. 2.2.6). For that, as most reasonable
221 approximation, it was decided to use that individual (constant) gravimetric soil moisture
222 content, which corresponds to the so-called "wilting point". The latter was determined by
223 laboratory water tension measurements (pF 4.2) on undisturbed soil cores from each land-
224 cover type. The wilting point is defined as that soil moisture in the root zone, which would
225 cause irreversible wilting of plants. Wilting point conditions in the uppermost soil layers
226 (2 cm) of soils in the Taklimakan Desert are easily reached, since evaporation there is
227 extremely high (evaporating capacity 2920 mm a^{-1}). Even after flooding irrigation of Milan
228 oasis' crop fields, these conditions have repeatedly been observed within at least 3 days by
229 visual inspections.

230 **2.2.4 Laboratory determination of net potential NO_2 fluxes**

231 The methodology for the laboratory measurement of the NO flux from soil has been deve-
232 loped at the end of the nineties (Yang and Meixner, 1997) and has been continuously used
233 during the last two decades (Otter et al., 1999; Kirkman et al., 2001; van Dijk and Meixner,
234 2001; Feig et al., 2008a; Feig et al., 2008b; Yu et al., 2008; Ashuri, 2009; Feig, 2009; Gelfand
235 et al., 2009; Yu et al., 2010a, 2010b; Bargsten et al., 2010). The methodology has been
236 significantly improved in the frame of this study and is described in detail by Behrendt et al.
237 (2014).

238 Generally, the release of gaseous NO from soil is the result of microbial NO production and
239 simultaneous NO consumption. The latter is, as shown by Behrendt et al. (2014), particularly
240 for arid and hyper-arid soils, negligible. Applying the laboratory dynamic chamber method,
241 the release of NO is determined by incubating aliquots of the soil samples in a dynamic
242 chamber system under varying, but prescribed conditions of soil moisture, soil temperature,
243 and chamber's headspace NO concentrations. From the difference of measured NO concentra-
244 tions at the outlets of each soil containing chamber and an empty reference chamber, actual
245 net potential NO fluxes (in terms of mass of nitric oxide per area and time) is calculated as
246 function of soil moisture and soil temperature. For that, a known mass (approx. 60 g dry
247 weight) of sieved (2 mm) and wetted (to water holding capacity) soil is placed in one of six
248 Plexiglas chambers (volume 9.7×10^{-4} m^3) in a thermo-controlled cabinet (0 – 40°C). After
249 passing through a purification system (PAG 003, Ecophysics, Switzerland), dry pressurized,
250 zero (i.e., "NO free") air is supplied to each chamber, controlled by a mass flow controller
251 (4.167×10^{-5} $m^3 s^{-1}$). The outlet of each chamber is connected via a switching valve system to
252 the gas-phase chemiluminescence NO analyzer (model 42i-TL, Thermo Fisher Scientific Inc.,
253 U.S.A.) and to the non dispersive infrared analyzer CO_2/H_2O-analyzer (model LI-COR 840A,
254 LI-COR Biosciences Inc., U.S.A.). During a period of 24 – 48 h, the soil samples are slowly
255 drying out, hence providing the desired variation over the entire range of soil moisture (i.e.
256 from water holding capacity to wilting point conditions and completely dry soil). During the
257 drying out period, the temperature of thermo-controlled cabinet is repeatedly changed from 20
258 to 30°C, hence providing the desired soil temperature variation (Behrendt et al. 2014). Occa-
259 sionally, nitric oxide standard gas (200 ppm) is diluted into the air purification system via a
260 mass flow controller; this allows the control of the chamber headspace NO concentration
261 when determining NO consumption rate of the soil sample. The actual soil moisture content
262 of each soil sample is determined by considering the H_2O mass balance of each chamber,
263 where the temporal change of the chamber's headspace H_2O concentration is explicitly related
264 to the evaporation rate of the soil sample. Tracking the chamber's headspace H_2O concen-
265 tration throughout the drying-out period and relating it to the gravimetrically determined total
266 soil mass at the start and end of the measurement period delivers the actual gravimetric soil
267 moisture content of the soil sample (Behrendt et al., 2014).
268 As shown during the last two decades (Yang and Meixner, 1997; Otter et al., 1999; Kirkman
269 et al., 2001; van Djik and Meixner, 2001; van Dijk et al., 2002; Meixner and Yang, 2006; Yu
270 et al., 2008, 2010; Feig et al., 2008; Ashuri, 2009; Feig, 2009; Gelfand et al., 2009 and
271 Bargsten et al., 2010), the dependence of NO release from gravimetric soil moisture and soil

9

272 temperature can be characterized by two explicit dimensionless functions, the so-called opti-

273 mum soil moisture curve $g(\theta_g)$ and the exponential soil temperature curve $h(T_{soil})$

$$274 \quad g(\theta_g) = \left(\frac{\theta_g}{\theta_{g,0}}\right)^a \exp\left[-a\left(\frac{\theta_g}{\theta_{g,0}} - 1\right)\right] \tag{5}$$

$$275 \quad h(T_{soil}) = \exp\left[\frac{\ln Q_{10,NO}}{10}(T_{soil} - T_{soil,0})\right] \tag{6}$$

276 where θ_g is the dimensionless gravimetric soil moisture content, $\theta_{g,0}$ the so-called optimum

277 gravimetric soil moisture content (i.e., where the maximum NO release has been observed), a

278 is the soil moisture curve's shape factor (solely derived from NO release and gravimetric soil

279 moisture data which have been observed during the drying-out measurements, see Behrendt et

280 al. 2014), T_{soil} is the soil temperature (in °C), $T_{soil,0}$ is the reference temperature (here: 20°C),

281 and $Q_{10,NO}$ is the (logarithmic) slope of $h(T_{soil})$, defined by

$$282 \quad Q_{10,NO} = \frac{\ln F_{NO}(\theta_{g,0},T_{soil,1}) - \ln F_{NO}(\theta_{g,0},T_{soil,0})}{T_{soil,1} - T_{soil,0}} \tag{7}$$

283 where $T_{soil,1}$ is a soil temperature which is 10 K different from $T_{soil,0}$ (here: 30°C). The actual

284 NO fluxes F_{NO} (ng m^{-2} s^{-1}; in terms of mass of nitric oxide) are defined by

$$285 \quad F_{NO}(\theta_{g,0},T_{soil,0}) = \frac{Q}{A_{soil}}\left[m_{NO,cham}(\theta_{g,0},T_{soil,0}) - m_{NO,ref}\right]f_{C,NO} \tag{8}$$

$$286 \quad F_{NO}(\theta_{g,0},T_{soil,1}) = \frac{Q}{A_{soil}}\left[m_{NO,cham}(\theta_{g,0},T_{soil,1}) - m_{NO,ref}\right]f_{C,NO} \tag{9}$$

287 where Q is the purging rate of the dynamic chambers (m^3 s^{-1}), A_{soil} is the cross-section of the

288 dynamic chamber (m^2), and $m_{NO,cham}$ and $m_{NO,ref}$ are the NO mixing ratios (ppb) observed un-

289 der conditions $(\theta_{g,0},T_{soil,0})$ and $(\theta_{g,0},T_{soil,1})$ at the outlets of each soil chamber and the reference

290 chamber, respectively. The conversion of NO mixing ratios to corresponding NO concentra-

291 tions (ng m^{-3}, in terms of mass of nitric oxide) is considered by $f_{C,NO}$ (= 572.5 ng m^{-3} ppb^{-1}

292 under STP conditions). Finally, the net potential NO flux, $F_{NO}(\theta_g,T_{soil})$ is given by

$$293 \quad F_{NO}(\theta_g,T_{soil}) = F_{NO}(\theta_{g,o},T_{soil,0})g(\theta_g)h(T_{soil}) \tag{10}$$

294   This net potential NO flux is specific for each soil sample, hence for sites (1), (2), (4), and (5)

295   of Milan oasis; the actual NO flux of the sites is calculated applying corresponding field data

296   of gravimetric soil moisture and soil temperature. This procedure has been successfully

297   applied for a variety of terrestrial ecosystems (e.g., Otter et al., 1999; van Dijk et al., 2002;

298   Ganzeveld et al., 2008). For soils of the Zimbabwean Kalahari (Ludwig et al., 2001; Meixner

299   and Yang, 2006), for a German grassland soil (Mayer et al., 2011), but also for Brazilian

300   rainforest soils (van Dijk et al, 2002), soil biogenic NO fluxes derived from the described

301   laboratory incubation method have been successfully verified by field measurements using

302   both, field dynamic chamber and micrometeorological (aerodynamic gradient) techniques.

303   2.2.5 Classification and actual distribution of Milan fields

304   Image classification is likely to assemble groups of identical pixels found in remotely sensed

305   data into classes that match the informational categories of user interest by comparing pixels

306   to one another and to those of known identity. For the purposes of our study, land-cover

307   classification was carried out based on two Quickbird images (0.6 m ground resolution,

308   DigitalGlobe, http://www.digitalglobe.com) acquired on 09 April and 31 August 2007

309   respectively, with the aid of a recent ETM+ Landsat image (141/033,

310   http://earthexplorer.usgs.gov/) acquired on 25 April 2011 (15 and 30 m spatial resolution). A

311   major advantage of using Quickbird images of high spatial resolution images is that such data

312   greatly reduce the mixed-pixel problem (a "mixed pixel" consists of several land-cover

313   classes) and provide a greater potential to extract much more detailed information on land-

314   cover structures (e.g. field borders, buildings, roads) than medium or coarse spatial resolution

315   data using whether on screen digitizing or image classification.

316   However, we take the advantage of resolution merge processing to increase the spatial

317   resolution of the Landsat image from 30 to 15 meters for the bands 1-5 and 7 for better land-

318   cover mapping and for updating the land-cover map from 2007 to 2011. Then, we defined

319   different areas of interests (AOIs) to represent the major land-covers with the aid of in-situ

320   GPS data collection (45 points). Next, we increased number of AOIs based on image spectral

321   analysis method. After that supervised classification was performed using the maximum

322   likelihood parametric rule and probabilities. This classifier uses the training data by means of

323   estimating means and variances of the classes, which are used to estimate Bayesian

324   probability and also consider the variability of brightness values in each class. For that, it is

325   the most powerful classification methods when accurate training data is provided and one of

326   the most widely used algorithms (Perumal and Bhaskaran, 2010). As a result, five major

327 ecosystems were determined: cotton, jujube, cotton/jujube mixture fields, desert, and plant

328 cover). The cotton and the jujube fields are the most dominant types. Finally, the classified

329 land-cover image was converted into vector format using polygon vector data type to be

330 implemented in LASAT analysis as sources of NO flux and for the purpose of estimating NO

331 concentrations. The map includes 2500 polygons of different sizes as sub-units of Milan

332 major land-cover.

333 2.2.6 Two dimensional distribution of soil NO emissions of Milan oasis

334 The soil NO emission sources of Milan oasis were defined by individual source units, which

335 have been identified as those sub-units (polygons) of the land-cover vector map consisting of

336 natural forest or desert, or covered by cotton, jujube, cotton/jujube mixture. Two identifiers

337 have been attributed to each source unit, (a) a metric coordinate whose numerical format re-

338 fers to the corner of the corresponding polygon, and (b) a unique ID number followed by a de-

339 scription of its land cover type. The soil NO source strength (i.e., actual NO flux, see Sect.

340 2.2.4) of each source unit has been calculated from the corresponding net potential NO flux,

341 the land-cover type specific gravimetric soil moisture content ("wilting point"), and the actual

342 soil temperature, which has been *in-situ* measured for each of the land-cover types of Milan

343 oasis (see Sect. 2.2.2). Those polygons which are not matching the mentioned land-cover

344 types and other tiny polygons generated by digital image processing techniques were

345 dismissed to avoid intricate geometric errors affecting NO emission data. In other words,

346 these "other classes" were dissolved before performing LASAT analysis to avoid extreme

347 values.

348 2.2.7 Three dimensional distribution of NO concentrations by Lagrangian dispersion
349   modelling (LASAT)

350 Having the actual NO source units of the Milan oasis available, the 3-D distribution of NO

351 concentrations in the atmospheric boundary layer $(0 – 1500\,m\,a.gr.)$ over Milan oasis have

352 been calculated by the Lagrangian dispersion model LASAT (German VDI Guidelines

353 VDI3945, part 3; c.f. Janicke Consulting, 2011). LASAT is a state-of-the-art model, since (a)

354 LASAT is one of those transport-dispersion models of air-pollution which is officially

355 licensed for legal use of environmental issues (in Germany), and (b) among comparable

356 micro-scale (e.g. street canyons) transport-dispersion models LASAT considers at least

357 chemical transformations of 1st order and keeps nonetheless truly operational. Being a

358 transport-dispersion-model, LASAT basically considers advection ("pixel cross-talk")

359 applying the 3D-continuity equation for any chosen tracer (see German VDI Guidelines

360 VDI3945, part 3, cf. Janicke Consulting, 2011). For that, pre-processing of meteorological pa-

361 rameters (i.e. 3-D wind distributions, based on meteorological in-situ measurements, see Sect.

362 2.2.2) and calculation of dispersion parameters (σ_y, σ_z) have to be performed. Unfortunately,

363 it was difficult to obtain fine resolution using LASAT individually. Therefore, LASAT model

364 was integrated with Geographic Information System (ArcGIS) by using an advanced module

365 namely LASarc (IVU Umwelt GmbH, 2012). LASarc allowed us to calculate NO

366 concentrations using relatively fine resolution of 30m×30m and taking the advantages of

367 using integrated map colour scheme in ArcGIS. This module has been used to realize Milan

368 oasis' complex NO source configuration and to setup calculations of LASAT.

369 The model was designed to calculate NO-concentrations at 16 different vertical layers (0–3,

370 3–5, 5–10, 10–20, 20–30, 30–50, 50–70, 70–100, 100–150, 150–200, 200–300, 300–400,

371 400–500, 500–700, 700–1000, and 1000–1500 m a.gr.). The horizontal resolution is 30 m, in

372 x-direction (W-E) as well in y-direction (S-N), which results in 656 (x) and 381 (y) grids for

373 the Milan oasis domain. LASAT's meteorological input data contain a variety of parameters,

374 namely start and end time (T_1, T_2), wind speed (U_a) and wind direction (R_a) at anemometer

375 height (H_a), average surface roughness (Z_0), and atmospheric stability (in terms of stability

376 classes). These parameters have been provided in a time-dependent tabular form, up-dated

377 every 30 minutes (except Z_0). Average (30 min) wind speed and wind direction data have

378 been calculated from *in-situ* measurements (1 min resolution, see Sect. 2.2.2).

379 LASAT's pre-processing module determines the vertical profile of wind speed according to

380 the well-known logarithmic relation,

381 $$U(z) = \frac{u_*}{k} \ln\left(\frac{z}{Z_0}\right) \tag{11}$$

382 where $U(z)$ is the horizontal wind speed (m s^{-1}) at height z (m), u_* is the friction velocity

383 (m s^{-1}), k is the dimensionless von Karman constant (= 0.4, Simiu and Scanlan, 1996), and Z_0

384 is the surface roughness length (m). LASAT's pre-processing module accepts only one indivi-

385 dual value for Z_0; nevertheless, the required mean value has been calculated from all Z_0's of

386 Milan oasis domain, which have been assigned to each of the sub-units (polygons) of the

387 vector land-cover map (see Sect. 2.2.5). For individual Z_0's, we calculated land-cover specific

388 NDVI data (normalized differential vegetation index) from Landsat ETM+ image (141/033)

389 $$NDVI = \frac{r_{NIR} - r_{RED}}{r_{NIR} + r_{RED}} \tag{12}$$

390 where *NIR* is the reflectance in the near-infrared bandwidth (0.77-0.90 μm) and *RED* is the

391 reflectance in the red bandwidth (0.63-0.69 μm). In Landsat ETM+ images, these correspond

392 to bands 4 and 3, respectively. Finally, r_{NIR} and r_{RED} are the corresponding ratios of reflected

393 and incident energy as a function of wavelength (see Chander and Markham, 2003). Then,

394 surface roughness grid data was estimated as:

395 $$Z_0(x,y) = \exp(a_{xy} NDVI(x,y) + b_{xy}) \tag{13}$$

396 where a_{xy} and b_{xy} are constants, which are, according to Morse et al. (2000), derived from

397 $NDVI(x,y)$ and $GPS(x,y)$ data for known sample pixels representing the earlier classified land-

398 cover types, namely natural forest, desert, cotton, jujube, and cotton/jujube mixture.

399 Corresponding land-cover type Z_0's are 0.45, 0.01, 0.18, 0.26, and 0.22 m, respectively; the

400 required average value over the entire LASAT model domain results in $Z_0 = 0.22 \pm 0.158$ m.

401 Besides mechanical turbulence (Z_0), atmospheric stability affects most the dispersion of trace

402 substances. For Milan oasis' atmospheric boundary layer, atmospheric stability has been cal-

403 culated according to the "solar radiation/delta T (SRDT)" method in 30 min intervals. This

404 method (c.f. Turner, 1994) is widely accepted because of its simplicity and its representative-

405 ness for atmospheric stability over open country and rural areas, like the Milan oasis domain.

406 Daytime stability classes are calculated from *in-situ* measurements of solar radiation and

407 horizontal wind speed (see Sect. 2.2.2).

408 Finally, 30 min means of all parameters and input variables of LASAT have been calculated.

409 Using these, about 4×10^6 gridded data points of 3-D NO concentration have been calculated

410 for each time period considered in Section 3.2.

411 **2.2.8 Simulation of SCD$_{NO2}$ and VCD$_{NO2}$ by spatial integration of LASAT results**

412 There is only one tool to provide a robust relationship between biogenic soil NO emissions on

413 one hand and MAX-DOAS observed SCD's and VCD's on the other hand: the exact simula-

414 tion of the MAX-DOAS measurement through spatial integration of three dimensional NO

415 concentrations calculated by LASAT (followed by NO→NO$_2$ conversion). At a given

416 location of the MAX-DOAS measurement, integration must be performed from the height

417 where the MAX-DOAS instrument has been set-up ($h_{MAXDOAS}$) to the end of the atmospheric

418 boundary layer ($h_{ABL} = 1500$ m a.gr.) along two virtual light paths, (a) the vertical up path

14

419 (VCD), and (b) the slant path (SCD) according to the selected elevation angle of each MAX-

420 DOAS measurement.

421 Calculation of simulated VCD's for NO ($VCD_{NO,sim}$) at the location of a MAX-DOAS

422 instrument is achieved as follows: (a) determination of the NO mass density (ng m^{-2}) of the

423 vertical column between $h_{MAXDOAS}$ and h_{ABL}; this is obtained by adding NO concentrations

424 (ng m^{-3} in terms of mass of nitric oxide) of all LASAT cells in vertical direction over that

425 30 m $\times$ 30 m grid, which contains the location of the MAX-DOAS instrument, multiplied by

426 the height difference $\Delta h = h_{ABL} - h_{MAXDOAS}$ (in m), (b) multiplying that NO mass density by

427 the ratio of Avogadro's number (6.02217×10^{26} molecules kmol^{-1}) and the molecular weight of

428 NO (30.0061×10^{12} ng kmol^{-1}) delivers the desired value of $VCD_{NO,sim}$ in units of molecules

429 m^{-2} ($\times 10^{-4}$: molecules cm^{-2}) at the location of the MAX-DOAS instrument. Calculation of

430 simulated SCD's for NO ($SCD_{NO,sim}$) requires the determination of the 3-D light path through

431 the trace gas layered. Positioning of MAX-DOAS's telescope was always to the north, the

432 selected MAX-DOAS elevation angle α and h_{ABl} deliver the length of the slant light path

433 (= $h_{ABL}/\sin\alpha$). The desired $SCD_{NO,sim}$ (in molecules m^{-2}) results from the NO mass density of

434 the slant column multiplied by the length of the slant light path, where the NO mass density is

435 equivalent to the sum of all NO concentrations of those LASAT cells which are intersected by

436 the slant light path from the position of the MAX-DOAS instrument to h_{ABL}.

437 For conversion of $VCD_{NO,sim}$ to $VCD_{NO2,sim}$ and $SCD_{NO,sim}$ to $SCD_{NO2,sim}$ it is assumed, that

438 the photostationary state (PSS) of the triad NO, NO$_2$, and O$_3$ is established in Milan oasis'

439 atmospheric boundary layer. According to Leighton (1961) this chemical equilibrium state is

440 due to fast photochemical reactions, namely NO+O$_3$ $\rightarrow$ NO$_2$+O$_2$ and NO$_2$+hυ $\rightarrow$ NO+O, from

441 which the so-called photostationary state NO$_2$ concentration (NO$_{2,PSS}$) can be derived as

442
$$\left[NO_{2,PSS}\right] = \frac{\left[O_3\right]\left[NO\right]k_1}{j\left(NO_2\right)} \tag{14}$$

443 where [O$_3$] is the ozone number density (molecules cm^{-3}; calculated from *in-situ* measured O$_3$

444 concentrations, see Sect. 2.2.2), [NO] is the NO number density, k_1 is the reaction coefficient

445 of the NO+O$_3$ $\rightarrow$ NO$_2$+O$_2$ reaction (cm^3 molecules^{-1} s^{-1}; Atkinson et al., 2004), and j(NO$_2$) is

446 the *in-situ* measured NO$_2$ photolysis rate (in s^{-1}; see Sect. 2.2.2). Finally, $VCD_{NO2,sim}$ and

447 $SCD_{NO2,sim}$ are calculated from $VCD_{NO,sim}$ and $SCD_{NO,sim}$ by

448
$$VCD_{NO2,sim} = CF_0 \times VCD_{NO,sim} \text{ and } SCD_{NO2,sim} = CF_0 \times SCD_{NO,sim} \tag{15}$$

449   where the NO→NO$_2$ conversion factor is defined by $CF_0 = [O_3]\, k_1\, /\, j(NO_2)$.

450   Since the NO-NO$_2$-O$_3$ photochemical equilibrium could not be handled by LASAT's
451   "chemical" algorithm, we decided to use measured data (O$_3$ mixing ratio, NO$_2$ photolysis rate,
452   s. sect. 2.2.2) to convert the calculated 3D-NO mixing ratio to the photo-stationary 3D-NO$_2$
453   mixing ratio. For that, a constant vertical O$_3$ mixing ratio (up to 1500 m a.gr.) is assumed over
454   Milan oasis. This is justified by the fact, that particularly in arid and hyper-arid landscapes at
455   mid-day conditions (maximum of insulation) the entire atmospheric boundary layer is
456   intensively mixed, which is due to extensive convective heating of the surface by the sun
457   which produces powerful buoyant thermals that establish the so-called mixing layer.
458   Consequently an uniform vertical mixing ratio is expected for trace gases with chemical
459   lifetimes greater than the exchange time of the atmospheric boundary layer. (c.f. Husar et al.
460   1978, Stull 1988). This assumption is valid for ozone. Vertically constant O$_3$ mixing ratio
461   has been reported for the atmospheric boundary layer over semi-arid southern Africa
462   (Meixner et al., 1993). Concerning the vertical distribution of j(NO$_2$) it is obvious, that the
463   downward component of the actinic flux increases with increasing elevation due to the
464   decreasing optical thickness of the scattering air masses. However, the altitude effect on the
465   actinic flux in the first kilometer of the troposphere is typically very small. Trebs et al. (2009)
466   used the Tropospheric Ultraviolet Visible model to calculate the typical vertical change of the
467   actinic flux and found a vertical gradient of 1.1%/km. Consequently, our calculations of the
468   NO to NO$_2$ conversion in the boundary-layer over Milan oasis (1500 m a.gr.) have not
469   considered any potential vertical change of the j(NO$_2$) values measured at ground level.

470   Nevertheless, for the case of our measurements the locally enhanced NO values caused by the
471   soil emissions have a small but systematic effect on the ozone concentration, and thus also on
472   the Leighton ratio: Close to the surface (below about 50m) the NO concentrations can be
473   quite large, with maximum values up to about 10 ppb. Consequently, the ozone concentration
474   will be reduced due to the reaction with NO by up to about 10 ppb. This means that the
475   Leighton ratio will be reduced by up to about 25%. Although the reduction of the ozone
476   mixing ratio wil be partly compensated by mixing with air from higher altitudes, the
477   simulated NO$_2$ mixing ratios might overestimate the true NO$_2$ mixing ratios by up to about
478   25%. Probably the true overestimation for our measurements is much smaller because the
479   typical NO mixing ratio within the lowest 100m is much lower than 10 ppb.

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3   Results and Discussion

3.1   Land-cover type specific net potential NO fluxes

Net potential NO fluxes (as functions of soil temperature and moisture) have been determined by incubation of samples which have been taken from the top-soil of Milan oasis' major land-cover types, i.e. natural forest, desert, cotton, jujube, and cotton/jujube mixture (see Sect. 2.2.4). Figure 2 shows the laboratory derived net potential ~~net~~ NO flux, F_{NO} from soils of the most contrasting land-cover types of Milan oasis (irrigated & fertilized fields of cotton, jujube, cotton/jujube mixture, and desert).

Net potential NO fluxes of the natural forest land-cover type are not shown, because laboratory incubation measurements have shown that there is no significant NO release from these soils, most likely due to its high electrical conductivity (salt content). Optimum gravimetric soil water contents (i.e., where the maximum of F_{NO} is observed) for desert, managed cotton, and managed jujube soils have one in common, very low values of $\theta_{g,opt}$ (0.009–0.017) for soil temperatures of 50°C. During the vegetation period (April – September), soil temperatures of > 40°C are easily reached for the soils of Milan oasis, particularly for the desert soils. While the nature of all Milan oasis' soils is arid/hyper-arid, maximum net potential NO fluxes are 7600, 63, 270, and 98 ng m^{-2} s^{-1} (in terms of mass of nitric oxide) for cotton, jujube, jujube/cotton mixture, and desert soils, respectively.

3.2   Land-cover types of Milan oasis and actual NO fluxes

As mentioned in Section 2.2.5, land-cover classification and actual distribution of Milan oasis' fields have been identified from satellite images (Quickbird, Landsat ETM+). The 2011 distribution of fields and the corresponding land-cover is shown in Figure 3.

The dominant crop was cotton, representing 18% (64 km^2) of the total field area of Milan oasis (jujube 7%, 28 km^2), cotton/jujube mixture 0.89 % (3 km^2), natural forest 18% (64 km²), residential area 1.62% (5.5 km²) and desert 52% (174 km^2). Land-cover specific, actual NO fluxes (30 min means) from cotton, jujube, cotton/jujube, and desert soils were calculated from corresponding laboratory derived net potential NO fluxes, land-type specific soil moisture and soil temperature data (see Sect. 2.2.6). These NO fluxes (ng m^{-2} s^{-1}, in terms of mass of nitric oxide) were then assigned to each individual source unit (i.e. to each of the 2500 polygons of Milan oasis' domain).

For the period 03 to 24 June, 2011, land-cover specific, actual NO fluxes were calculated

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according to eq.(10) for cotton, jujube, cotton/jujube, and desert soils from corresponding laboratory derived net potential NO fluxes. As input we used land-type specific, measured soil temperature data as well as land-type specific soil moisture data (so-called "wilting points", s. Sect. 2.2.3). The calculated NO fluxes are shown in Fig. 4 as median diel variation (for the entire period of 03 to 24 June, 2011). Since NO fluxes from Milan cotton fields dominate the total soil biogenic NO emission of the oasis, corresponding medians and quartiles are shown in Fig. 4, while – for the sake of clarity – for jujube, cotton/jujube, and desert only medians are given. Since land-type specific "wilting points" are constant, diel variations of actual NO fluxes mirror directly those of corresponding soil temperatures, showing the daily minimum around 06:00 local time for all four major land-cover types. The maximum of the actual NO-flux, however, is around 13:00 (local time) for jujube, cotton/jujube, and desert soils, and 15:00 local time for cotton. This is due to the growth of the cotton plants: while at the beginning of the experimental period the bare soil surface was nearly 100% exposed to insolation, the growing cotton canopy has shaded great parts of the soil surface towards the end of the experimental period . This is also reflected by the skewed distribution of actual NO-fluxes from cotton covered soil, indicated by the daytime non-symmetric inter-quartile range (= upper quartile – lower quartile). As shown in sect. 3.5, actual NO-flux data of 09 June, 2011 (08:30-14:30 local time) were used for the comparison of LASAT and MAX-DOAS results. During this particular day (within the first week of the experimental period), the derived flux for "land-cover cotton" ranged from 15–64 ng $m^{-2}s^{-1}$ (in terms of mass of NO), those for jujube, cotton/jujube, and desert land-covers ranged from 11–13, 6–16, and 6–17 ng $m^{-2}s^{-1}$, respectively. These actual NO fluxes were then assigned to each individual source unit (i.e. to each of the 2500 polygons of Milan oasis' domain). The soil biogenic NO emission from all cotton fields between 08:30 and 14:30 was estimated to 28.7 kg (in terms of mass of NO), equivalent to 76% of the total soil biogenic NO emission of the entire Milan oasis within 6 hours.

3.3 Vertical NO₂ column densities by MAX-DOAS

We performed 32 individual MAX-DOAS measurements within 21 days of the 2011 field campaign to examine the spatial variation between the observed sites. In Fig. 5, all observed vertical NO$_2$ column densities (in molecules cm^{-2}) observed at sites (1) - (4) of Milan oasis are shown in polar coordinates with reference to corresponding wind directions measured *in-situ* at the individual sites.

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544   Wind speeds (30 min means) ranged between 1.5 and 7.7 m s^{-1} and wind direction was mostly

545   (78%) from the northern quadrants (59%, 9%, 13%, and 19% from NE, SE, SW, and NE

546   quadrants, respectively). As expected, highest VCDs (10^{15} – 10^{16} molecules cm^{-2}) were

547   observed at site (4) (Milan oasis center), regardless of wind direction. When the wind

548   direction is from the NE quadrant, site (3) (jujube fields) is down-wind of Milan oasis (see

549   Fig.1); then its VCDs are as high as those obtained in the oasis' center ($5 - 7 \times 10^{15}$ molecules

550   cm^{-2}). The few VCD data points of 1×10^{15} molecules cm^{-2} at the jujube site, attributed to

551   winds from SE and SW quadrants, are mainly due to NO emissions from traffic on the

552   National Road 315 which passes the southern margins of Milan oasis. Lowest VCDs

553   ($3 \times 10^{13} - 3 \times 10^{14}$ molecules cm^{-2}) have been observed at site (1) (natural forest) and site (2)

554   (desert). Alone from these spatially resolved VCD observations in the Milan oasis' domain,

555   the increase of VCD due to the oasis itself can be estimated in the order of at least one order

556   of magnitude.

557   Fortunately, we have been able to perform simultaneous measurements with two MAX-

558   DOAS instruments at sites (1) and (3) on 09 and 13 June, 2011. Since winds (approx. 3 m s^{-1})

559   were from the NE quadrant during these two days, site (1) has been up-wind, and site (3)

560   downwind of Milan oasis. Corresponding VCD results are shown in Figure 6. NO$_2$ VCDs at

561   the downwind site exceeded those at the upwind site by factors 5 – 9. This difference between

562   downwind and upwind MAXDOAS signals is considered to be a direct measure for the areal

563   increase of ambient NO$_2$ concentration. In the absence of anthropogenic NO$_x$ sources (see

564   Sect. 2.1), this provides first evidence for the considerable impact of the biogenic NO emissi-

565   ons from the fields of Milan oasis.

3.4   3-D distribution of ambient NO-concentration

567   The LASAT model has to be used to calculate the dispersion of soil emitted NO into the at-

568   mospheric boundary layer over Milan oasis. An example for the resulting distribution of NO

569   ~~the~~ concentration in the first four vertical layers of LASAT (0-3, 3-5, 5-10, and 10-20 m) is

570   shown in Figure 7 (09 June, 2011; 11:30-13:00 local time). The shown results are the mean of

571   three LASAT model runs, since a new LASAT calculation of 3-D distribution of NO

572   concentration is started for every set of meteorological parameters which are provided every

573   30 min from means of the *in-situ* measured meteorological quantities (see Sect. 2.2.2). During

574   11:30-13:00, mean wind direction was 15°, 38°, and 50°, wind speed was rather constant

575   (2.60 – 2.67 m s^{-1}), and atmospheric stability class has been generally neutral (3.2).

576 By comparing the NO ambient concentrations, particularly in the first vertical LASAT layer
577 ($0-3$ m) of oasis area with the surrounding desert, it becomes obvious that the great differ-
578 ences of ambient NO concentrations mirror the corresponding differences of actual soil NO
579 fluxes from each source-unit; within this layer calculated mean NO concentrations are 13, 12,
580 10, and 1 ng m^{-3} (in terms of mass of nitric oxide; or 10.6, 9.8, 8.2, and 0.8 ppb) for the oasis
581 centre, jujube fields, cotton/jujube mixture, and desert, respectively. The value at the oasis
582 center exceeds those over desert by more than an order of magnitude, similar as the
583 corresponding VCD values (see above). As expected under the prevailing conditions of well
584 developed atmospheric turbulence, NO concentrations rapidly decreases with height (see
585 panels "$0-3$ m", "$3-5$ m", "$5-10$ m" in Fig. 7), and with prevailing northerly winds, the NO
586 concentration centre shifting southwards with increasing altitude.

587 **3.5 Simulated SCDs and VCDs *vs.* SCDs and VCDs by MAX-DOAS**

588 For those periods where simultaneous "upwind" and "downwind" MAX-DOAS
589 measurements have been performed (09 and 13 June, 2011), corresponding SCD_{sim} and
590 VCD_{sim} have been simulated by suitable vertical integration (see Sect. 2.2.8) of LASAT-
591 calculated 3-D NO concentrations, followed by NO$\rightarrow$NO$_2$ conversion (based on
592 photostationary state assumption of Milan oasis' atmospheric boundary layer). Since SCD_{sim}
593 and VCD_{sim} represent only that part of true SCDs and VCDs of NO$_2$, which are due to the
594 contribution of the oasis' soil NO emissions, SCD_{sim} and VCD_{sim} are compared to the
595 difference of those SCDs and VCDs which have been simultaneously measured by two
596 MAX-DOAS instruments at corresponding "downwind" and "upwind" sites (see Fig. 8). For
597 elevation angles of 2° and 4°, SCD_{sim} and $\Delta SCD = SCD_{down} - SCD_{up}$ are shown in Figure 8a.
598 In Figure 8b, VCD_{sim} and $\Delta VCD = VCD_{down} - VCD_{up}$ are shown for 15° elevation.
599 Here it should be noted that in principle the accuracy of the geometric approximation is
600 higher for the high elevation angles than for the lower elevation angles. However, for the
601 specific cases studied here, this is not the case. First, close to the sources, the height of the
602 layer with elevated NO$_2$ is quite low (in our case the bulk of NO$_2$ is located below 100 m).
603 Second, also the aerosol load is usually very low. Thus the probability of scattering events
604 inside the layer of enhanced NO$_2$ is very low, and consequently the accuracy of the geometric
605 approximation is relatively high. To further quantify the associated uncertainties, we
606 performed radiative transfer simulations and found that the deviations from the geometric
607 approximation are similar for the different elevation angles (about 5% for 2°, 3% for 4° and
608 3% for 15°). However, because of the shorter light paths through the NO$_2$ layer, the relative

error caused by the uncertainty of the spectral analysis is higher than for the low elevation angles. Thus for the case of our measurements, we indeed expect lower uncertainties for the low elevation angles.

Since soil NO emission data used in the LASAT dispersion model were calculated from land-cover type specific potential net NO fluxes, which in turn were derived from laboratory incubation experiments on corresponding soil samples, the results in Figure 8 are also considered as an excellent quality assurance of the chosen up-scaling of laboratory results to the oasis scale. There is remarkable good agreement between measured and simulated data. However, the actual NO emissions (irrespective of the land-cover type) have their maximum in the early afternoon (s. Fig. 4), while the highest height-integrated NO_2 concentrations as simulated by LASAT (on the basis of the actual NO emissions) are in the morning (08:30–10:00), followed by rather constant values for the reminder of the day (s. Fig. 8). The apparent discrepancy between both diurnal variations can be simply explained by the diurnal variation of the wind direction and the specific viewing geometry of the MAX-DOAS instrument. The MAX-DOAS instrument was located at the south-west corner of the oasis, and the observations at zenith and low elevation angles probed air masses located at different locations accross the oasis. The wind direction was from north-east in the morning and turned to north-west in the afternoon. Hence, air masses of lower concentration crossed the viewing directions in the afternoon compared to those in the morning. This explains that in spite of the larger NO_x emissions smaller column densities have been observed in the afternoon. The apparent discrepancy of the diurnal cycles of NO emissions and measured NO_2 column densities indicates the importance to exactly consider the 3-dimensional NO_2 distribution (due to the soil-emitted NO) for the comparison of the model results with MAX-DOAS observations.

The Figure 8b shows that the LASAT simulations overestimate slightly the true NO_2 VCD. The both measured and simulated NO_2 VSDs have with an average root mean square (RMS) error between the measured and simulated values of approx. 5-15%. However, the overestimation of LASAT simulation is well suited to the fact that in reality a little less NO can be converted to the NO_2 because of lower ozone concentration at the surface.

4   Conclusion

This study has been focused on the following activities: (1) representative soil sampling from the uppermost soil layer (< 0.05 m) of all land-cover type units (natural forest, cotton fields,

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642 jujube fields, cotton/jujube mixture, desert) of Milan oasis (Xinjiang, NW China), (2) labora-

643 tory incubation experiments (dynamic chamber system) to characterize the biogenic NO emis-

644 sion from these soil samples in form of net potential NO fluxes as function of soil moisture

645 and soil temperature, (3) determination of the actual size, areal distribution, and land-cover

646 type of Milan oasis' field units from satellite remote sensing information, (4) field measure-

647 ments of slant (SCD) and vertical (VCD) NO_2 column densities (by MAX-DOAS) and

648 additional quantities (soil moisture, soil temperature, ozone concentration, NO_2 photolysis

649 rate, meteorological parameters) during an extended field campaign of 4 weeks at Milan oasis,

650 (5) using data from (2), (3) and (4): calculation of Milan oasis' 2D distribution of actual, land-

651 cover specific NO fluxes, (6) calculation of 3-D NO concentrations in Milan oasis' atmosphe-

652 ric boundary layer originating from the dispersion of biogenic NO soil emissions determined

653 by (5) with help of the Lagrangian dispersion model LASAT, (7) simulation of SCDs and

654 VCDs by suitable vertical integration of calculated 3-D NO concentrations followed by

655 suitable $NO \rightarrow NO_2$ conversion factors derived from *in-situ* measurements, (8) comparison of

656 measured and simulated SCDs and VCDs.

657 Results of the laboratory derived NO fluxes have shown that the extensively managed (fertili-

658 zed and efficiently irrigated) cotton fields of Milan oasis release large amounts of soil bio-

659 genic NO; NO fluxes range between 10–30 ng $m^{-2}\,s^{-1}$ (in terms of mass of N), that is approx.

660 5–10 times more than from a typical central European wheat field (Yamulki et al. 1995; Stohl

661 et al. 1996).

662 Applying two MAX-DOAS instruments, simultaneous measurements have been performed at

663 upwind and downwind sites of Milan oasis. Downwind site VCDs exceeded those from the

664 upwind site by factors 5 – 9. Differences of VCD and SSC ("downwind" minus "upwind") are

665 a direct measure for the areal increase of ambient NO_2 concentration caused by the oasis

666 itself. The measured differences of VCDs and SCDs were compared with the simulated VCDs

667 and SCDs and excellent agreement was found.

668 This agreement is considered as the first successful attempt to prove the validity of the chosen

669 approach to up-scale laboratory derived biogenic NO fluxes to ecosystem level field con-

670 ditions, i.e. from the spatial scale of a soil sample (cm^2) to field size (ha), and from field size

671 (ha) to the size of an entire (agro-) ecosystem (km^2). Furthermore, in the absence of anthropo-

672 genic NO sources of Milan oasis (hydropower energy, battery powered trikes), it is obvious,

673 that the areal increase of ambient NO_2 concentration in the atmospheric boundary layer of the

674 isolated (in terms of NO_2 advection) Milan oasis is entirely due to biogenic NO emission from

675 the arid/hyper-arid soils of the oasis itself. Extensive agricultural management of Milan oasis'

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676 crop fields (fertilization (350- 600 kg N ha^{-1}a^{-1}) and effective irrigation of cotton and jujube

677 fields) obviously provides considerable contribution of biogenic NO$_x$ (NO+NO$_2$) from

678 arid/hyper-arid soils of the Taklimakan desert to the local tropospheric NO$_x$ budget.

679 About 80% of the Chinese cotton production originates from the 3000 km long belt of oases

680 surrounding Taklimakan Desert (1.65×10^6 km^2) in Xinjiang (NW-China); cotton cultivated

681 land area in Xinjiang occupies the first place of entire China. Since 1955, Xinjiang's output of

682 cotton increased 294 times (Lei et al., 2005). Fast economic growth in the region (+11% GDP

683 a^{-1}), inevitably accompanied by large anthropogenic NO$_x$ emissions (traffic, energy producti-

684 on), may be countervailed or even exceeded by the "hotspot" character of Xinjiang's oases,

685 namely by soil biogenic NO emissions from agriculturally dominated oases. Most likely, they

686 will contribute most to the regional tropospheric NO$_x$ budget. This is all the more likely,

687 given the continued intensification of oasis agriculture around the Taklimakan desert which

688 will be accompanied by corresponding land use change (desert→dryland farming with

689 irrigation) in the coming decades.

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896　**Figures:**
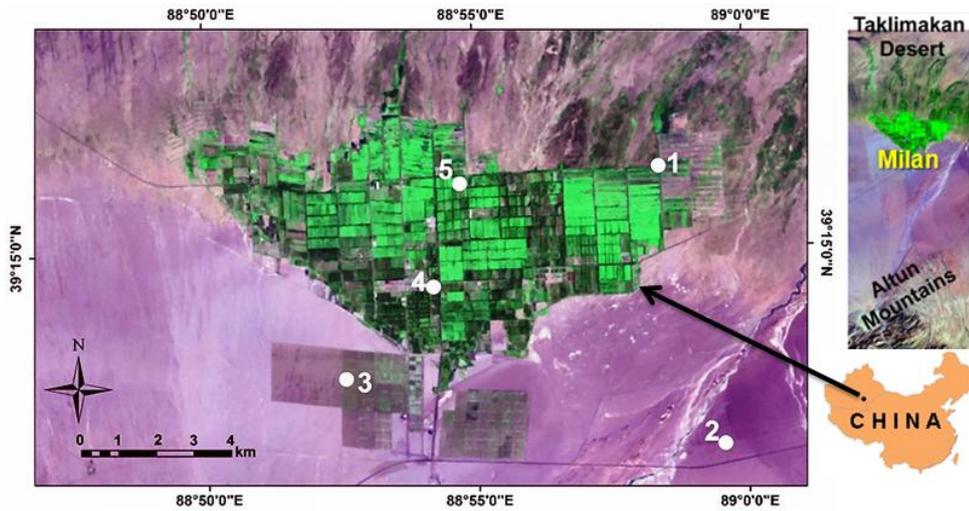
897

898　**Fig. 1**: Satellite map (Landsat ETM+; 2011) of Milan oasis, Xinjiang, NW-China (The map
899　has an area of 338 km^2). The white circles show the sites of *in-situ* measurements: natural
900　forest (1), desert (2), jujube (3), hotel/oasis station (4) and cotton field (5).
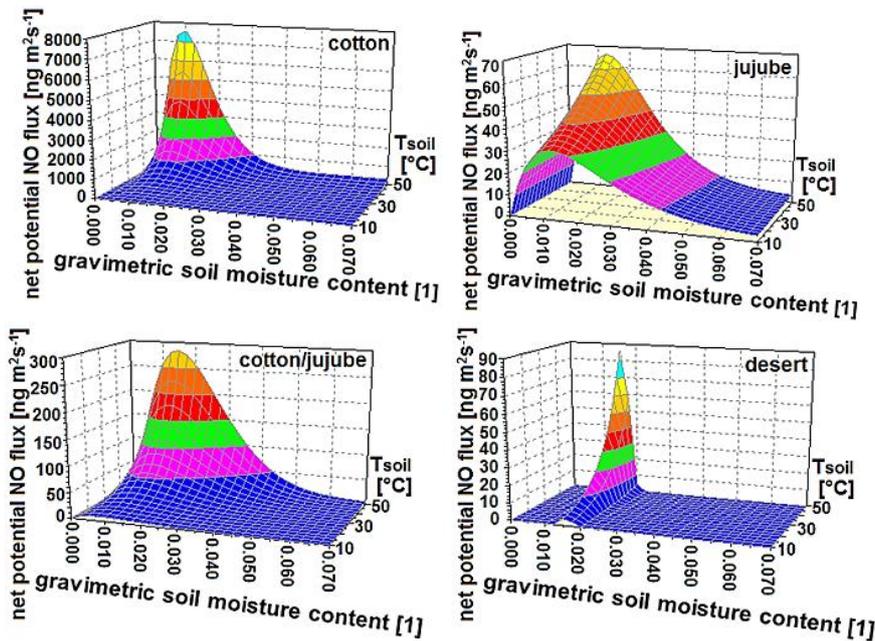
901

902　**Fig. 2**: Net potential NO fluxes F_{NO} (ng m^{-2} s^{-1}; in terms of mass of nitric oxide) from soils of
903　the four major land-cover types of Milan oasis as functions of soil temperature (°C) and
904　dimensionless gravimetric soil moisture content.

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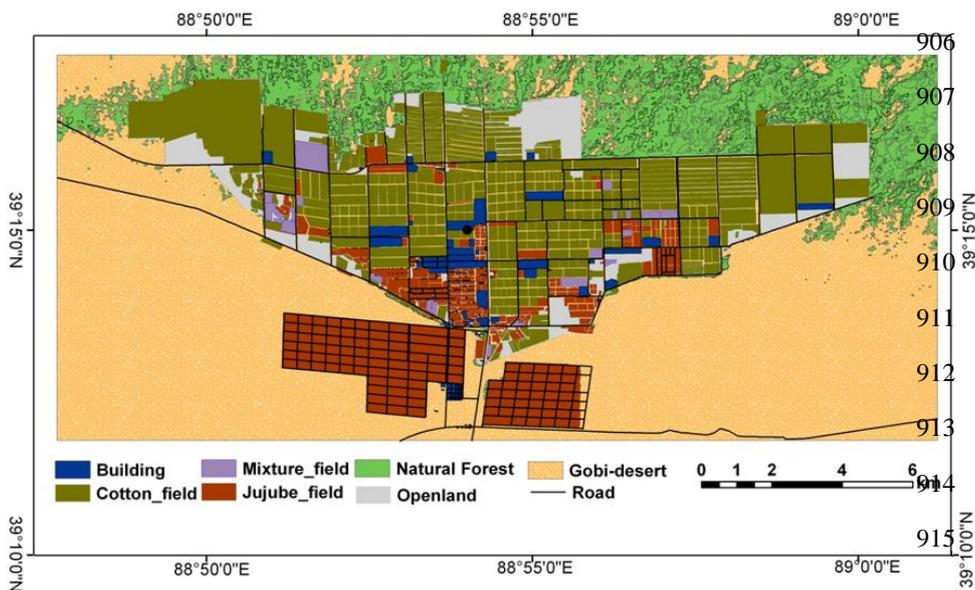
Fig. 3: 2011 map of land-cover types of Milan oasis as derived from satellite images (Quickbird, Landsat ETM+, see Sect. 2.2.5).

Fig 4: median diel variation of the actual NO-flux (ng m^{-2}s^{-1}; in terms of mass of nitric oxide) from soils of the four major land-cover types of Milan oasis for the period 03 to 24 June, 2011. Data have been calculated according eq.(10) using (a) soil temperatures (medians) measured for each of the four major land-cover types, and (b) so-called "wilting point"-data for corresponding soil moisture contents at the four sites (s. section 2.2.3). Data for the cotton-site are given as medians, as well as 25 and 75% quantiles, those for the Jujube, Jujube-cotton and desert sites as medians only (s. figure insert).

Fig. 5: Results of MAX-DOAS measurements performed at sites oasis/hotel (4), Jujube (3), Natural forest (1), and Desert (2) of Milan oasis from 23 May to 26 June, 2011 (see Fig. 1). Vertical NO_2 column densities (in molecules cm^{-2}; 20-30 min averages) are shown in relation to in-situ measured wind direction at each location of MAX-DOAS measurements. The MAX-DOAS measurements were performed between 6:00 and 19:00 (local time). Note the radial logarithmic scale of VCD data.
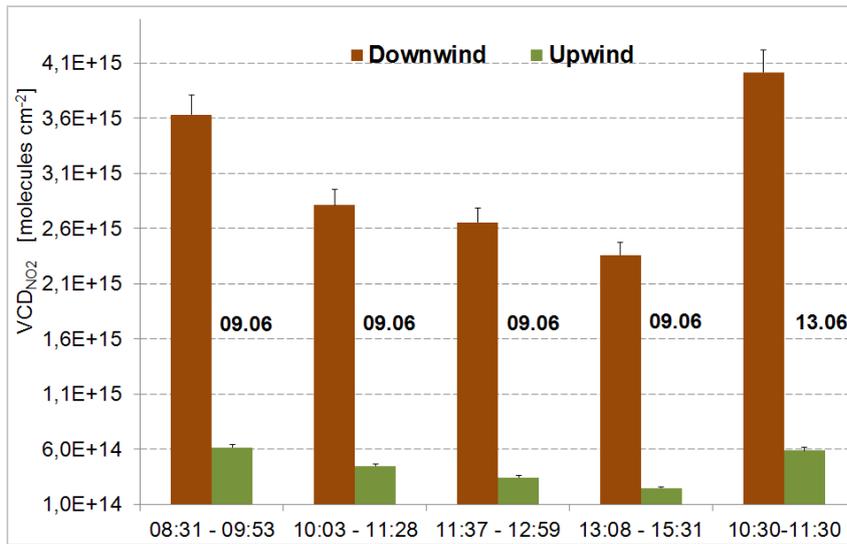
Fig. 6: Results of NO_2-VCD measured simultaneously with two MAX-DOAS instruments upwind (natural forest, site (1)) and downwind (jujube field, site (3)) of Milan oasis on 09 and 13 June, 2011.
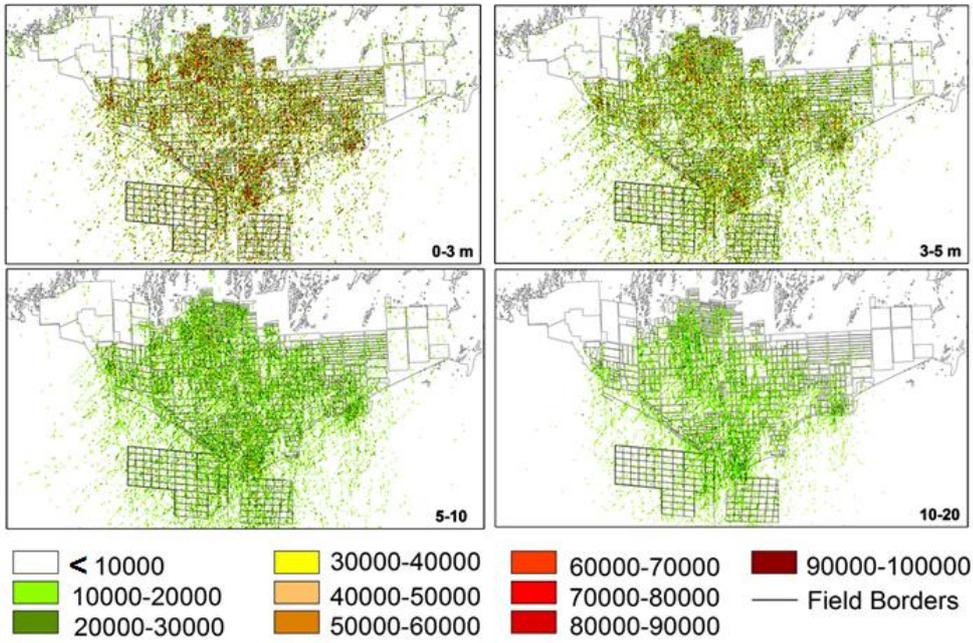
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Fig. 7: Results of NO concentrations (ng m^{-3}; in terms of mass of nitric oxide) calculated by the LASAT dispersion model for the first four vertical levels on 09 June, 2011, 11:30 to13:00 (local time).
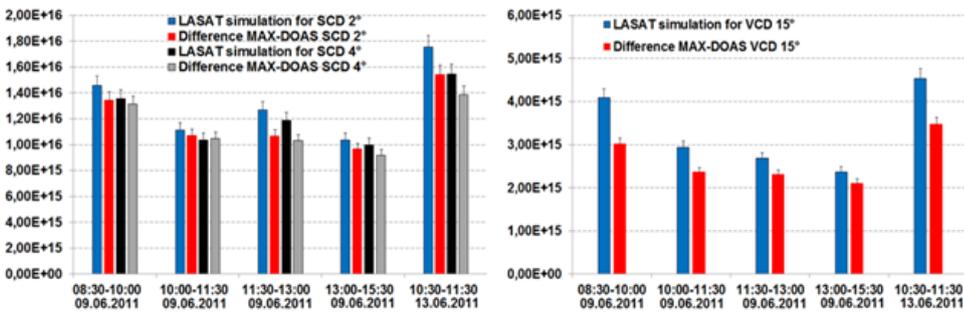
Fig. 8: Simulated SCDs vs. SCDs measured by MAX-DOAS (a) and simulated VCDs vs. VCDs measured by MAX-DOAS (b) on 09 and 13 June, 2011 at Milan oasis. SCDs have been measured and simulated for elevation angles of 2° and 4°, VCDs were measured at 15°.

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