

Interactive comment on “Diurnal fluxes of HONO above a crop rotation” by Sebastian Laufs et al.

Anonymous Referee #2

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Review of “Diurnal fluxes of HONO above a crop rotation” by Laufs et al.

This paper describes three field investigations into the surface emission fluxes of nitrous acid (HONO) above soil / low crops in France. This topic relates to a series of recent studies which have demonstrated that additional fluxes of HONO to the boundary layer (beyond gas phase / heterogeneous reactions and dark NO₂/H₂O interactions) are required to explain observed daytime steady-state HONO levels. This is of importance as HONO is an important precursor to OH in many continental boundary layer settings, and the paper addresses a current high profile topic in atmospheric chemistry using state-of-the-science approaches.

HONO fluxes were measured using the gradient method, employing a pair of LOPAP monitors sampling at different heights above the soil / crops. The resulting fluxes are found to be comparable in magnitude to those inferred previously (although HONO flux observations are few and far between), and significantly larger than those which would

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be inferred by the temperature and soil moisture dependence of biotic emissions from previous laboratory studies (but see my comments below).

The correlation between the observed flux and some potential controlling factors are observed, and the best correlation obtained for NO₂, photolysis (j_{NO_2}), and temperature, adjusted for RH. This result is qualitatively attributed to photoenhanced NO₂ conversion to HONO upon humic-acid type surfaces.

The paper is well written (a few minor language suggestions are given below) and clearly phrased / easy to follow. The experiments are clearly described and analysed (NB suggestions for a couple of expanded explanations below) and the conclusions, although correlation rather than definitive causation, are reasonable and advance our understanding. Subject to the points below being satisfactorily addressed, I recommend publication in ACP.

Minor points

L48 PSS also fails where there are significant heterogeneity in the co-reactants of the species in the PSS – notable OH – i.e. significant heterogeneity in VOC loading causes problems for HONO PSS analyses, even if the NO and HONO components are in a homogeneous environment.

L103 the key for PNA (HNO₄) interference in the flux measurements is not the absolute amount but the different in PNA across the flux measurement heights. Can the authors comment on this.

L111 It is not appropriate to “ignore” the potential interference – please calculate (estimate) the anticipated PAN levels making reasonable assumptions and hence quantify the potential interference in the NO₂.

Section 2.3 – how well was the stability criterion satisfied – what fraction of the data had to be discarded ?

L166 the diurnal averaging will address precision but not accuracy – please clarify.

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Please give some more details of the “events” which were excluded – what proportion of the total were they, what criteria were used to identify them as abnormal.

L190 how often were the LOPAPs intercompared – please give details. This is critical to the flux derivations / to be confident no drift in instrument response biased the results

L313 the Oswald data derived from lab experiments in which “transient” HONO fluxes were derived as soil was dried – i.e. they would have sampled an immediate response to the changing conditions, over a period of a few hours, potentially different from the field in which conditions were much more stable. Also the samples were previously dried and reconstituted (not intact cores). Does this affect the comparison / conclusion ? Given the temperature link described subsequently – also a possible indicator of biotic influences ?

L330 were any other parameters considered in the correlations – in particular aerosol loading (ideally aerosol surface area) ?

L339 still not clear – a little unsatisfactory

L403 HNO₃ sometimes shows a diurnal profile with a maximum in the afternoon as inferred here, but quite different mean diurnal profiles have also been reported (e.g. Murphy et al ACP 6 5321 2006) – which would affect the nitrate photolysis conclusion here.

L459 I wasn't quite clear how the reference RH aspect worked for the data or the fitting – please expand / clarify. May be useful to show the regression (in addition to the mean diurnal timeseries for each campaign).

Wording

Abstract line 16 – suggest reword to “. . .these results are consistent with HONO formation by. . .”

Line 38 HO₂xH₂O is not a nomenclature I am familiar with – use a period . ?

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L55-56 reword the REA phrase

L61 an NO₂ driven mechanism

L152 the abbreviations for previous decades reads a little awkwardly

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-1030, 2016.

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