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Interactive comment on “Brightening of the global cloud field by nitric acid and the associated radiative forcing” *by* R. Makkonen et al.

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We thank reviewer 2 for the extensive comments. We believe, however, that most of the comments are based on a misconception about the purpose of the paper. We will improve the revised manuscript in order to make sure that the writing is not ambiguous. Our detailed responses are as follows (reviewer comments in bold):

This paper aims at quantifying the indirect aerosol effect caused by nitric acid and corresponding nitrate using a global climate model with explicit aerosol treatment and a two moment cloud microphysics taking the aerosol–cloud interactions into account. The incorporation of the effects of nitrate is performed via a parameterization derived from a cloud parcel model.

The aim of this paper is not to quantify the indirect effect caused by nitrate. The aim is to quantify the global enhancement of aerosol activation from the soluble gas effect caused by gaseous nitric acid (Kulmala et al., 1993; 1995; 1997; 1998; Korhonen et al., 1996; Laaksonen et al., 1997; 1998; Hegg, 2000; Charlson et al., 2001; Nenes et al., 2002; Kokkola et al., 2003a,b; Xue and Feingold, 2004; Romakkaniemi et al., 2005; McFiggans et al., 2006). These are two different things. It is true the issues are not completely separate as ammonium nitrate is formed from co-condensation of ammonia and nitric acid (thus influencing the nitric acid gas-phase concentrations), and on the other hand, ammonia can in some circumstances boost the soluble gas effect of nitric acid (Kulmala et al., 1998, Romakkaniemi et al., 2005). In our study, we treat neither effects. However, we believe that even without simulating ammonia and nitrate we can get a good first estimate of the magnitude of the soluble gas effect on cloud drop activation (see also our arguments below). We will clarify these issues in the revised manuscript.

This is the main weakness of the paper. It is explicitly stated that nitrate aerosols are not treated at all. The modifications of the activated cloud droplet number only depends on the parameterization, which mainly considers the change in maximum supersaturation mimicking modifications of the hygroscopicity and aerosol mass due to condensation of gaseous nitric acid during droplet formation. However, an underlying change in the aerosol distribution is not considered at all.

The parametrization is based on adiabatic cloud model simulations in which the condensation of nitric acid onto the different size distributions is explicitly calculated, and thus the underlying change in the aerosol size distribution during the cloud activation process (above 99% RH) is taken into account. The parametrization depends on the dry size distribution of the aerosol, and since we do not simulate nitrate, the effect of nitrate on the dry distribution is not considered. However, more important to the enhancement of the activated fraction by nitric acid than the exact shape of the size distribution (which of course has other sources of uncertainty than just the missing nitrate) is the number concentration of the aerosol. Thus, even though we certainly do not want to understate the importance of nitrate to the soluble gas effect, we at the same time believe that its effect via modification of the dry distribution is not the most important source of uncertainty in our study. As can be seen from Romakkaniemi et al (2005) presenting the parameterization, the strength of nitric acid effect on CDNC is not very sensitive to small changes on dry aerosol size distribution (Figure 3 in Romakkaniemi et al., 2005).

Furthermore, the nitric acid concentrations are taken from a monthly climatology (without any evidence of how realistic the used HNO_3 distributions are), since the corresponding paper describing the nitric acid distribution is not (yet) available.

Rast et al. (2012) will be made available soon. The chemistry of the simulations used to obtain the HNO_3 fields is similar to Horowitz et al. (2003), which includes a comparison of HNO_3 concentrations to observations. Although the simulation setup is somewhat different in Rast et al. (2012), results in Horowitz et al. (2003) indicate a good agreement with HNO_3 observations. It is shown in Rast et al. (2012) that the observed spatial patterns of NO_2 are well reproduced by the model, although NO_2 concentrations are generally underestimated in heavily industrialized regions and overestimated in areas with fire emissions. In addition to Fig. 4a (HNO_3 mixing ratio), we will include some information on the simulated HNO_3 fields. In the revised manuscript, we will add a sentence about the bias in HNO_3 concentrations to the text. We added the following reference under which the report about the RETRO run will appear from which the HNO_3 fields are taken.

It has been shown before, that aerosol nitrate has a considerable influence on the direct aerosol effect (e.g. Bauer et al, ACP, 2007). Since the radiative properties of nitrate are not so different from those of sulphate, the resulting differences cannot be only an effect of additional uptake of nitric acid, but a substantial modification of the aerosol size distribution due to the additional aerosol mass.

The paper by Bauer et al. (2007) investigates the direct radiative effect caused by nitrate aerosols, but neglects the indirect effects caused by either nitrate aerosol or condensation of nitric acid. Our study neglects nitrate aerosols, and focuses on the effect of gaseous nitric acid condensation on cloud droplet activation: we are not trying to simulate the indirect effect caused by nitrate. We are simulating the enhancement of aerosol activation due to uptake of gaseous HNO_3 at relative humidities above 99%. As noted above, modification of the size distribution due to nitrate may have an influence on the soluble gas effect, but we do not believe it is the most important source of uncertainty in our study.

Aerosol nitrate is known to be semivolatile; consequently using the total nitric acid as a proxy does not resemble realistically the aerosol fraction of nitrate.

We are not using HNO_3 as a proxy for total nitrate. The important quantity to get right in order to calculate the soluble gas enhancement to the activated fraction is the concentration of gaseous nitric acid at cloud base, and we believe that the offline nitric acid fields represent a reasonable approximation of that.

Due the diurnal temperature cycle the aerosol fraction in especially warm climate regions is lowest during the day and consequently the effect on clouds is lower during the day than during the night. Since the short wave spectrum is dominating the cloud forcing, the effect of nitrate is relatively low under those conditions. On the other hand, the gaseous HNO_3 concentrations mostly increase during the day due to the photochemical production, which cannot be resembled by monthly mean concentrations. Consequently the monthly mean concentrations applied in this study are not a realistic representation of the effects of nitrate.

Nor are they meant to be. As stated above, the input needed for the simulations is the gaseous nitric acid concentration. As pointed out by the referee, the gas-phase HNO_3 concentrations are highest at daytime, and thus applying climatological means would tend to underestimate the daytime gas-phase concentrations when the effect of nitric acid on the radiation budget via enhancement of cloud activation is largest. On the other hand, nitrate aerosols are not included in ECHAM5 MOZ, hence the applied nitric acid concentration includes also the aerosol-phase nitrate. This leads to an overestimation of the nitric acid concentration, especially during nighttime. The applied nitric acid fields are quantitatively similar to those in Xu and Penner (2012), with a surface concentrations of 165 pptv and 174 pptv in this study and Xu and Penner (2012), respectively. Surface HNO_3 concentrations over remote oceans are slightly higher in ECHAM5-MOZ, while Xu and Penner (2012) show generally higher concentrations over continents. We will make this clear in the revised manuscript.

Additionally, the nitrate aerosol fraction is known to substantially depend on the chemical composition of the aerosol, e.g. in marine environment NaNO3 can be formed, forcing a release of HCl into the gas phase as an acid replacement process. However, since NaNO3 has a lower hygroscopicity than NaCl the activation potential of the aerosol should decrease, which cannot be reproduced by the applied parameterisation. On the other hand, if no replacement reactions take place additional mass (mostly in form mostly of NH4NO3) is added to the aerosol distribution. This aerosol mass (due to condensation on existing particles) alters the size distribution, affecting coagulation and other microphysical aerosol properties similarly (such as conversion of hydropho- bic to hydrophilic material via coating) as the aerosol hygroscopicity (and subsequent water uptake) and therefore the ambient aerosol size. Both of these effects can play a significant role in the activation process of the total aerosol.

In the clean marine environment, gas-phase nitric acid concentrations are generally below 0.1 ppb and thus the soluble gas effect will in any case be very small. Furthermore, hydrochloric acid that is driven out of the aerosol due to uptake of nitric acid is almost as efficient in producing the soluble gas effect as nitric acid itself (Kulmala et al., 1998). Thus we do not think that explicitly accounting for processes taking place in a clean marine environment that are not represented in our model would in any major

way alter our results.

However, the amount of nitrate formed does not only depend on the available nitric acid, but also on other neutralizing compounds, mainly NH3. Consequently, a scheme not taking the ammonia concentration into account is not able to reproduce a realistic nitric acid effect.

The lack of ammonia is a major source of uncertainty in our simulations. We have previously shown (Romakkaniemi et al., 2005) that ammonia can either enhance or decrease the soluble gas effect by nitric acid. Consider an air parcel containing gaseous nitric acid and ammonia which has a relative humidity of, say, 90%, and which is experiencing cooling. If the cooling is rapid, most of the HNO_3 and NH_3 are still in the gas phase when cloud formation starts, and the NH3 will act to enhance the soluble gas effect of HNO_3. On the other hand, if the cooling is very slow, nitric acid and ammonia will form ammonium nitrate, which may partition to the large particles before cloud formation starts. In such a case, ammonia will inhibit the soluble gas effect of HNO_3. It is thus a question of air parcel history what the effect of ammonia is. However, the relevant “dividing” timescale below which ammonia enhances the HNO_3 effect is on the order of hours to days and with less time for system to equilibrate ammonia enhances nitric acid effect. On the global scale, the effect of ammonia may thus be either to enhance or to decrease the HNO_3-effect, but that can only be known with a sophisticated enough global model that can take all of the effects into account. As such a model is not currently available, we believe that our simulations represent the best estimate possible at the moment.

Even though the parameterization tries to mimick some of the effects it is not evident, if all of those processes are properly taken into account or if e.g. the temperature is only used as a measure for the change of HNO_3 solubility.

The parametrization is based on state-of-the-art adiabatic cloud model simulations which explicitly calculate the condensation kinetics of both water and nitric acid onto the growing droplets at relative humidities above 99%. It does not account for any temperature effects below 99%RH.

Since neither in this paper nor the parameterization derivation by Romakkaniemi et al. (ACP, 2005) it is shown how well the parameterization reproduces "real conditions" from either chamber or field measurements, the quality of the numerically derived theoretical considerations is ambiguous.

We do not agree with this statement. It has been shown for example that the equations on which our cloud parcel model is based on can well reproduce the growth rates of droplets in binary nitric acid-water condensation experiments (Rudolf et al., 2001). Thus, although there are no laboratory experiments available on the nitric acid effect on cloud drop activation (such experiments would certainly be very welcome!) we are quite confident that the effects we have been simulating with our cloud model and that are incorporated in the parametrization are realistic. As noted in the manuscript, the observations of Ma et al. (2010) in China indicate that nitric acid contributes to persistent clouds which may activate even at RH's slightly below 100% (Ma et al., 2010), and that experimental evidence of the role of HNO_3 in cloud drop formation has been obtained by Henin et al. (2011) (albeit at ppm-levels).

The parameterization is able to reproduce the fact that HNO_3 is highly soluble and will be taken up by the activated cloud droplets; this dissolution will occur mainly after the activation process and more during the droplet growth due to diffusional limitations, such that even though a reduction in the critical supersaturation is achieved, this mainly occurs after the droplets have reached the critical radius and will anyhow continue to grow.

Our cloud parcel model (Kokkola et al., 2003b) explicitly calculates the diffusion of gaseous nitric acid into the droplets and the time dependence of nitric acid uptake, before and after the activation, to the droplets has been shown in several publication also others than ours (e.g. Korhonen et al. 1996, Xue and Feingold 2004). The activation timescale is slow enough so that the activated fraction is increased even in cases when most of the acid condenses after activation, except in the cases of really acidic aerosol and low nitric acid concentrations (Hegg 2000).

After obtaining the modified cloud droplet numbers, this paper is a consistent study using state of the art techniques to analyse the indirect effects. The obtained numbers of modifications of the indirect effect are mainly within the order of uncertainty associated with the total indirect effect (based on the multi-model spread from model intercomparison studies).

The fact that the importance of aerosol nitrate will potentially increase in future scenarios is realistic, equally the assumption that it will replace some of the ammoniumsulphate. However, the quantification of this effect is again difficult without taking the aerosol interactions of nitrate into account. Furthermore, to apply for the future conditions based on an emission scenario the HNO_3 field should be consistent (modified by the different NOx emissions and the altered oxidation capacity of the atmosphere). The reduction in the NOx emissions in the scenario will lead to a smaller aerosol load; the increase in the activated fraction is unlikely to compensate the reduced aerosol in such a way that the indirect aerosol effect by nitrate is even to increase. The only reason for this can be a more efficient activation of partly organic aerosol particles compared to a case without any activation modification by nitrate. This underlines the potential importance of aerosol nitrate, but does not increase the indirect effect; only the disturbance by nitric acid becomes more significant.

Intensification of the nitric acid effect when the aerosol number concentrations decrease can take place because the same fractional increase in the CDNC causes a larger increase of cloud albedo at lower aerosol concentration. We agree that the future simulations need to be carried out much more realistically to obtain reliable numbers. At the same time we believe that our simple exercise is useful in pointing out that the nitric acid effect may partially offset the future decrease of cloud albedos due to diminishing sulfate emissions, and that this is an issue that deserves attention. There are numerous studies investigating the nitrate forcing, but so far they have been lacking the mechanism studied here.

Consequently, even though the study is performed well with respect to simulation setup and scientific question investigated, I cannot recommend publication due the severe weaknesses in the methodology. In my opinion the scientific answers obtained from this study are flawed by the strong limitations of effects being included with the presented approach. Since this study is one of the first actually providing quantifying numbers of the indirect aerosol effect of nitrate, wrong assumptions and strong limitations will substantially influence follow-up studies. The presented approach leaves out too many effects to actually quantify the indirect aerosol effect of nitric acid properly. Therefore, the answers provided by this study are a quantification of the indirect aerosol with heavy restrictions, such that the obtained values are not representing the realistic state of the atmosphere. As the authors state themselves in their conclusions such a study should be performed with a coupled aerosol chemistry climate model, treating aerosol nitrate explicitly.

We will make it clear in the revised manuscript that we are not trying to quantify the indirect effect of nitrate but the enhancement of aerosol activation by gaseous nitric acid.

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