Replies to the Anonymous Referee 2

We would like to thank the referee for the valuable comments. Please find below our responses (in black) after the referee comments (in blue). Changes in the revised manuscript are written in *italics.*

This paper is a nice overview of the changing role of ammonia in the European atmosphere. I think it is generally well written, and my only major criticism is that a number of important uncertainties which might affect the conclusions are not discussed or addressed.

Major comments
The major areas of uncertainty that I missed include:
1. Bi-directionality. It is well established that ammonia can be emitted as well as deposited as a result of the equilibria between atmospheric and surface concentrations. It displays a so-called compensation point (Nemitz et al., 2001; Flechard et al., 1999, 2013), and this can affect the deposition close to source areas and long-range transport in general (Bash et al., 2013; Wichink Kruit et al., 2012).

Bi-directionality of ammonia is of course very important for the air concentration and dry deposition of ammonia. Its treatment in the Zhang dry deposition algorithm was improved in the latest version of CAMx, which was released this year. We added the following statements in the new Section (2.2 Deposition Scheme):

P4, L111
Dry and wet deposition of species were calculated using the Zhang scheme (Zhang et al., 2003; Ramboll, 2018). Although bi-directional air-surface exchange of NH_3 has been observed over a variety of land surfaces, most of the chemical transport models (CTMs) treat this exchange only as dry deposition that might lead to an underestimation of daytime NH_3 concentration because of overestimated dry deposition (Zhang et al., 2010). Winchink Kruit et al. (2012) reported that the inclusion of a stomatal compensation point led to increased modelled ammonia concentrations in agricultural areas in the Netherlands. Since stomatal compensation points are affected by the canopy type, temperature, growth stage, meteorological conditions, nitrogen status and cutting practices, it is very difficult to implement it in CTMs due to imprecise knowledge about the sub-grid variations in concentration, vegetation type and fertilizer applications (Huijsmans et al., 2018; Skjoth et al., 2011). Although the introduction of such a compensation point improves the model performance, the modelling of ammonia remains challenging due to temporal and spatial variations of emissions and grid resolution (Sutton et al., 2013). The bi-directional ammonia algorithm of Zhang et al. (2010) has been added recently as an option to the original Zhang deposition algorithm in the latest version of CAMx (v7.00). Default landuse-dependent emission potentials control ammonia compensation points along the surface-air transport circuit. When the atmospheric ammonia concentration exceeds the compensation point, the net flux is from air to surface; in the opposite case, the net flux is from surface to air. Although the Zhang dry deposition algorithm in the previous version of the CAMx (v6.50) model used in this study did not include compensation points, it did treat bi-directionality indirectly by using a deposition parameter that strongly influenced ammonia deposition via surface resistance.

2. This study seems to ignore the impacts of co-deposition, in which the acidity of the surface (affected by both SO2 and NH3 emissions, and their trends) changes. The impacts of this process on trends have been explored in for example Wichink Kruit et al. (2017).

The CAMx dry deposition model considers these effects. We added the following text in the revised manuscript:

P5, L129

3. A similar issue with trends, also not mentioned, is changing pH of rainwater (Banzhaf et al., 2012).

The pH-dependent parameterizations are incorporated and cloud water pH is calculated by the aqueous-phase chemistry algorithms in the CAMx model. We added this information in the text as follows:

P5, L138

Wet deposition is the predominant removal process for fine particles. Particles act as cloud condensation nuclei and the resulting cloud droplets grow into precipitation. The CAMx wet deposition model employs a scavenging approach using the 3-dimensional cloud/rain input from the meteorological model. Banzaf et al. (2012) reported that droplet pH variation within atmospheric ranges affects modelled air concentrations and wet deposition fluxes significantly. The pH-dependent parameterizations are incorporated and cloud water pH is calculated by the aqueous-phase chemistry algorithms in the CAMx model.

4. Meteorological variability. The current study mainly uses meteorology from just two years, 1990 and 2010, but Wichink Kruit et al. (2017) showed that meteorology can also account for a significant contribution to NH3 trends.

We would like to emphasize that our aim in this study was not to calculate trends for which continuous, long-term simulations are required (continuous simulation of 21 years between 1990 and 2010), as already done in the EDT project (Colette et al., 2017; Ciarelli et al., 2019). In this study, however, we performed the simulations for the 3 base years in the past 1990, 2000 and 2010 using the meteorology of each of those 3 years. We used the meteorology of 2010 only for the future scenarios and discussed the potential effects of different future meteorology in the text. The effect of meteorology on ammonia is well known. Both emissions and chemistry (particulate nitrate formation) are affected by meteorological conditions – mainly temperature. Backes et al. (2016) and Hendriks et al., (2016) showed that the modelling of ammonia concentrations can be improved when ammonia emissions are modulated by local meteorological conditions. The trends calculated by several models for the full 21 years between 1990-2010 were analyzed and compared to the observed trends during the Eurodelta-Trends project (Ciarelli et al., 2019). Therefore, the models in the EDT study were able to take into account the effect of meteorology on chemistry, but not the effect of temperature on ammonia emissions; these were based on static emission profiles. We expanded the section 3.1 as follows:

P6, L188

Atmospheric concentrations of ammonia are not well characterized due to relatively small number of monitoring sites, the short lifetime of NH3 in the air and the difficulty

of measuring non-point source emissions such as agricultural fields. Most of the measurement sites used in this study are located in the north; only very few stations are in the other parts of Europe (Fig. 1). The detailed information about the measurements (location, methods, temporal resolution) at each site is given in Table S1. Most of the measurements are daily concentrations, except for some sites in the Netherlands (hourly), Spain and Italy (weekly), Switzerland (bi-weekly) and UK (monthly). Measurement methods also differ; most of the stations use filter-pack sampling, while the passive samplers were used at 2 sites in Spain and the denuder systems were adopted at sites in the Netherlands, Great Britain and Switzerland. One should keep in mind that sampling artefacts due to the volatile nature of ammonium nitrate and the possible interaction with strong acids make separation of gases and particles by simple aerosol filters less reliable as indicated by EMEP (Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of the Air Pollutants in Europe), (https://projects.nilu.no/ccc/reports/cccr1-2019_Data_Report_2017.pdf). Modelled ammonia concentrations are similar to the measured ones at the few sites in the south while one site in eastern Europe shows an underestimation (Fig. 1). On the other hand, ammonia is overestimated at several sites such as in the UK, and in high emission areas around the Netherlands and Denmark. The mean fractional bias at all sites is 37.9% (Table S2). Overestimation might originate from either overestimated emissions or underestimated removal (deposition, particle formation). There are still large uncertainties about ammonia emissions. Recent studies show that better agreement between models and measurements can be achieved when ammonia emissions are modulated with local meteorological conditions (Backes et al., 2016; Hendriks et al., 2016). Most models, however rely on the static ammonia emission profiles provided in the emission inventories (Ciarelli et al., 2019).

5. Ship-plumes. It is well known that models tend to mis-represent HNO3 production from NO emitted from ships into clean marine environments (von Glasow et al., 2003; Vinken et al., 2011, 2014). This could potentially have been handled with the CAMx model'splume-in-grid approach, but this doesn't seem to have been used. However, some of the comments made about HNO3 (e.g. L187 onwards) may be impacted by this issue.

The Plume-in-Grid (PiG) sub-model in CAMx addresses the size and chemical evolution of point source plumes and is used for stationary sources such as power plants. Using PiG for ship emissions would require modelling the plumes from each of different, individual emission sources, which would be computationally impossible. The main obstacle, however, arises from the fact that these sources (ships) are moving. As Vinken et al. (2011) showed, accounting for in-plume chemistry is most relevant for pristine marine environments. We believe that the effect of plume-in-grid non-linear chemistry is very small in polluted areas with heavy ship traffic along the European coastal areas and other uncertainties coming mainly from emissions are more important. In this study, the ship emissions were not injected into the first model layer as ground emissions, but into the second layer. We added the following paragraph in the Methods Section:

P5, L157

The anthropogenic emissions were distributed to various vertical layers depending on their sources using the vertical profile given by Bieser et al. (2011). The ship emissions

over the sea were injected into the second model layer. All the biogenic emissions were released into the surface layer.

6. In the introduction, I missed some discussion of trend studies on land-based emissions and concentration/deposition trends which have already been done, e.g. Fowler et al.(2007); Fagerli and Aas (2008) or Wichink Kruit et al. (2017). How does the current study add to these? (Page 3 gives a lot of information given on the impacts of shipping, but not much about land.)

We extended the part about the emission reductions in the Introduction as follows:

P3, L48
European anthropogenic emissions have decreased substantially since the 1990s as a result of large emission reductions following the Gothenburg Protocol (GP) (UNECE, 1999), revised Gothenburg Protocol (revised on 4 May 2012, https://www.unece.org/env/lrtap/multi_h1.html) and EU Directives (https://www.eea.europa.eu/data-and-maps/indicators/main-anthropogenic-air-pollutant-emissions/assessment-6). Several studies investigated the effects of reduced land emissions on the air quality in various parts of Europe (Guerreiro et al., 2014, Aksoyoglu et al., 2014; Wichink Kruik et al., 2017; van Zanten et al., 2017; Theobald et al., 2019; Ciarelli et al., 2019). The largest decrease was in SO_2 emissions (by more than 90% in 2017 compared to 1990), followed by NO_x and NMVOC (non-methane volatile organic compounds) emission reductions (more than 50%), while ammonia emissions decreased less – approximately 23% on average in the EU-28 countries. Ammonia emissions have been increasing again since 2014, however, posing problems for Europe (NEC, 2019). This is mainly due to the difficulty in implementing additional emission reductions in the agriculture sector, especially in the housing of animals and the storage and application of animal manures. The large decrease in sulfur emissions over the last few decades has changed the aerosol composition: particulate nitrogen was dominated by sulfates in the 1990s while today nitrate predominates (Colette et al., 2016).

Smaller comments
1. L36. The Maas & Grennfelt reference is not peer-reviewed. There are plenty of peer-reviewed publications on this subject.
We replaced the reference by Fowler et al., (2009; 2015) in P2, L37.

2. L37. The authors only mention ammonium sulfate here, but bi-sulfate is an important component of European aerosol too.

We modified the relevant paragraph as:

P2, L38
Ammonia reacts very rapidly with sulfuric acid (H_2SO_4), which is formed from the oxidation of SO_2 by OH in the gas phase and by O_3, hydrogen peroxide (H_2O_2) and other oxidants in the aqueous phase, to form ammonium sulfate ($(NH_4)_2SO_4$) or ammonium bisulfate (NH_4HSO_4) (Seinfeld and Pandis, 2012). If there is enough ammonia available after the neutralization of H_2SO_4, it reacts with nitric acid (HNO_3) to produce ammonium nitrate. These secondary inorganic aerosols (SIA) contribute

most to the fine particulate matter ($PM_{2.5}$) in Europe (Ciarelli et al., 2016; 2019; Aksoyoglu et al, 2017).

3. L42. The Dentener ref is 14 years old now; find something more

Dentener et al., (2006) was replaced by Jones et al. (2014) in P2, L45

4. L53. Are you sure it is ammonium sulfate, and not bisulfate?

A series of compounds may exist in the aerosol phase like $(NH_4)_3H(SO_4)_2$, $(NH_4)_2SO_4$ and NH_4HSO_4 depending on the availability of ammonia, sulfuric acid, temperature and relative humidity. Bisulfate exists in acidic atmospheres with low ammonia availability. The ISORROPIA model in CAMx deals with the inorganic aerosol thermodynamics/partitioning. In order to avoid confusion, we rephrased the sentence in the text as:

P3, L59
The large decrease in sulfur emissions over the last few decades has changed the aerosol composition: particulate nitrogen was dominated by sulfates in the 1990s while today nitrate predominates (Colette et al., 2016).

5. L54. The Colette et al 2016 reference seems to be some grey literature, with no address and no url. What is this? And surely there are some peer-reviewed papers that be cited to support this statement?
It is an EMEP Report. We added the complete citation: EMEP: CCCP Report 1/2016, https://projects.nilu.no/ccc/reports/cccr1-2016.pdf, NILU, Oslo, 2016

6. L65-17. The SECA's came into effect at the start of 2015
SECAs were introduced in Europe in July 2010 with sulfur limit of 1.0% and then it was further reduced to 0.1% in January 2015. We modified the sentence as follows:

P3, L73
For example, in Europe, the North Sea and Baltic Sea areas were defined as SECAs (sulfur emission control areas), where the limits were restricted to 1.0% in July 2010 and further reduced to 0.1% in 1 January 2015. New global sulfur emission regulations, which reduce limits from 3.5% to 0.5% came into force on 1 January 2020 (https://www.imo.org/en/MediaCentre/HotTopics/Pages/Sulphur-2020.aspx, last access on 23.10.2020).

7. L80-84. It is unclear where the cited 1-14% PM2.5 applies. This number sounds very different to those cited for Karl et al., and so this paragraph is a little confusing. Are the Karl et al results similar to, or very different from those cited from Viana et al.?
Viana et al. is a literature review of past studies (until 2012) where different calculation methods were used at different locations. The numbers given in that paper therefore, vary depending on location in Europe and the time period the studies were performed. On the other hand, Karl et al. is a model intercomparison study for 2012 only for the Baltic Sea. To avoid confusion, we modified the paragraph as follows:

P3, L84

Viana et al. (2014) reviewed a series of studies performed before 2012 dealing with the impact of shipping emissions on air quality in the European coastal areas and reported that contribution of ship emissions to $PM_{2.5}$ and to NO_2 vary between 1-14% and 7-24%, respectively, depending on location and time. In a recent model-intercomparison study, Karl et al. (2019) evaluated the contribution of ship emissions to air quality in the Baltic Sea region in 2012 to investigate the differences among model predictions and showed that variations in ship-related $PM_{2:5}$ were mainly due to differences in the models' schemes for inorganic aerosol formation.

8. L100-102 How is the coarse-mode aerosol (e.g. for nitrate) handled in this model system?

The coarse-mode nitrate is treated in the coarse fraction (PM10-PM2.5) in CAMx. In this study, we only investigated the fine aerosol (PM2.5).

9. L103. Be explicit with a reference to the Zhang scheme (not just the cited CAMx user's guide). And whether co-deposition is included or not?

We included the original reference Zhang et al. (2003) in the revised manuscript (Section 2.2) for the Zhang scheme (P4, L112)

10. L134 on. Brief details on the measurement networks underlying EDT work should be given.

We added some information about the measurement networks used for model evaluation in Section 3.1:

P6, L179

The model results for 1990, 2000 and 2010 were compared with the measurements available at the EDT project database which is based on EMEP datasets (https://wiki.met.no/emep/emep-experts/tfmmtrendstations). The number of available measurement stations varies between 15 and 64 depending on the year and species. For ozone, only measurements at the background-rural stations were used to reduce uncertainties due to the model resolution. Model performance for SO_2, NO_2, PM_{10}, $PM_{2.5}$ and hourly O_3 was discussed in detail in Jiang et al. (2020).

11. L140 I won't repeat Ref #1's comments, but agree with them.

We provided detailed information about the measurements in a new table in the Supplementary (Table S1) and added the following statements in Section 3.1.:

P6, L188

Atmospheric concentrations of ammonia are not well characterized due to relatively small number of monitoring sites, the short lifetime of NH_3 in the air and the difficulty of measuring non-point source emissions such as agricultural fields. Most of the measurement sites used in this study are located in the north; only very few stations are in the other parts of Europe (Fig. 1). The detailed information about the measurements (location, methods, temporal resolution) at each site is given in Table S1. Most of the measurements are daily concentrations, except for some sites in the Netherlands (hourly), Spain and Italy (weekly), Switzerland (bi-weekly) and UK (monthly). Measurement methods also differ; most of the stations use filter-pack sampling, while the passive samplers were used at 2 sites in Spain and the denuder

systems were adopted at sites in the Netherlands, Great Britain and Switzerland. One should keep in mind that sampling artefacts due to the volatile nature of ammonium nitrate and the possible interaction with strong acids make separation of gases and particles by simple aerosol filters less reliable as indicated by EMEP (Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of the Air Pollutants in Europe), (https://projects.nilu.no/ccc/reports/cccr1-2019_Data_Report_2017.pdf). Modelled ammonia concentrations are similar to the measured ones at the few sites in the south while one site in eastern Europe shows an underestimation (Fig. 1). On the other hand, ammonia is overestimated at several sites such as in the UK, and in high emission areas around the Netherlands and Denmark. The mean fractional bias at all sites is 37.9% (Table S2). Overestimation might originate from either overestimated emissions or underestimated removal (deposition, particle formation). There are still large uncertainties about ammonia emissions. Recent studies show that better agreement between models and measurements can be achieved when ammonia emissions are modulated with local meteorological conditions (Backes et al., 2016; Hendriks et al., 2016). Most models, however rely on the static ammonia emission profiles provided in the emission inventories (Ciarelli et al., 2019).

12. L145. As noted above, many processes not discussed in this manuscript might also contribute to model-measurement bias. Another issues is scale, which is very briefly mentioned on L156, but which can be a very important factor for NH3 (Theobald et al.,2016; Denby et al., 2020).

There are of course several factors which could contribute to the bias. The most important one, however, is the large uncertainty in the quantity as well as temporal variation of ammonia emissions.

13. Notation. Better to use pNH4, pNO3, pSO4 than PNH4 etc, to avoid mixing chemical and atmospheric nomenclature.

The aerosol components are defined with capital “P” in the model and used in all the publications in the same way. We prefer to keep them as they are in order to be consistent with our previous publications.

14. L242 states that the amount of precipitation is crucial, but no figures are given on this here; please expand.

Precipitation is calculated by the meteorological model. In this study, the meteorological input was obtained from the Eurodelta-Trends project as described in Jiang et al. (2020). The performance evaluation of the seasonal and annual accumulated precipitation used in the Eurodelta-Trends exercise is discussed in detail in Theobald et al. (2019). We expanded this part in Section 3.3.2:

P10, L317

The performance evaluation of the accumulated precipitation used in the Eurodelta-Trends exercise is discussed in detail in Theobald et al. (2019). The model biases are very small for accumulated annual precipitation for the meteorological model used in this study; there is an underestimation of 4%-8%.

15. Many of the figure legends and colors need to be re-done. For example, in Fig2c reds are used for positive values and blues for negative, which is great, but in Figs. 2d

and 2e the color-scale shows white for levels both above and below certain thresholds! Later Figures also show such strange behaviors. I suggest using the same color-scale for all subplots, and do not have the same color for different values.

The reviewer probably means Fig.2b versus Figs. 2c and 2d, since there is no Fig. 2e in the manuscript. In all the difference plots (change between years), the same color scheme was used, i.e. no change (around zero) is always white, positive values (increase) are always red and negative values (decrease) are always blue. Since the scales are very different for different species (more than a factor of 10), it is not possible to use the same color for the same number. We did, however, keep the same scale for the same species in different time periods (e.g. always from -6 to +3 ppb for NH_3 in Fig2b-d (left panels) and always from -0.1 to +0.4 ppb for HNO_3 in Fig2b-d (right panels).

16. Fig. S2 - which measurements? Be explicit.

The description of the measurements used for model evaluation is given in Section 3.1. We added the relevant information in the caption of FigS2 as follows:

Measurements are from the EMEP network (see Section 3.1 in the main text).

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