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A new assessment of global and regional budgets, fluxes, and lifetimes of atmospheric reactive N and S gases and aerosols

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S1.1 Model aerosol scheme

The model aerosol scheme is the Equilibrium Simplified Aerosol Model V4 (EQSAM4clim), which efficiently parameterises the aerosol water uptake and full gas-liquid-solid partitioning of mixtures of semi-volatile and non-volatile compounds. For environments with low NH_3 concentrations, sulfuric acid occurs in aerosol phase as H_2SO_4. When NH_3 is present, this dissolves irreversibly in the sulfate aerosol either totally, if limited by NH_3, or until titration of acidity (R1, R2, and R3), if limited by H_2SO_4. When H_2SO_4 is fully neutralised, residual NH_3 equilibrates with HNO_3 to form NH_4NO_3 aerosol (R4). Concentrations of NH_3 that exceed this full titration remain in the gas phase. Ammonium sulfates are considered thermally stable but the volatilisation of NH_3 and HNO_3 from NH_4NO_3 is a function of temperature and relative humidity. Both ammonium sulfate (from R1-R3) and ammonium nitrate (from R4) are classified as fine mode aerosol.

$$NH_3 + H_2SO_4 \rightarrow (NH_4)HSO_4 \qquad (R1)$$

$$3NH_3 + 2H_2SO_4 \rightarrow (NH_4)_3H(SO_4)_2 \qquad (R2)$$

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4 \qquad (R3)$$

$$NH_3 + HNO_3 \rightleftharpoons NH_4NO_3 \qquad (R4)$$

The HNO_3 also reacts with coarse mode sea salt and dust particles to produce coarse nitrate (R5 and R6).

$$HNO_3 + \ seasalt \rightarrow NO_3^-\text{\_c} \qquad (R5)$$

$$HNO_3 + \ dust \rightarrow NO_3^-\text{\_c} \qquad (R6)$$

Table S1: Definition of RDN, OXN and OXS chemical groups.

Groups	Chemical species		
RDN	NH_3, aerosol-phase NH_4^+		
OXN	HNO_3		
	NO_x	NO, NO_2	
	aerosol-phase NO_3^-	NO_3^-_f, NO_3^-_c	
	Rest OXN	N_2O_5, HONO	
		Other OXN species	HO_2NO_2, $SC_4H_9NO_3$, PAN, MPAN, ISON, NALD
OXS	SO_2, aerosol-phase SO_4^{2-} (latter includes H_2SO_4, NH_4HSO_4, $(NH_4)_3H(SO_4)_2$ and $(NH_4)_2SO_4$)		

In the chemical group of 'Other OXN species', PAN is peroxyacetyl nitrate, MPAN is peroxymethacryloyl nitrate, ISON is a lumped species representing first-generation nitrates from isoprene degradation, and NALD is used as a representative species for second- and subsequent-generation nitrates from isoprene degradation. The suffices '_f' and '_c' denote fine and coarse particle size fractions, respectively.

Table S2: The allocation of IPCC reference regions (Iturbide et al., 2020) to the 10 world regions used in this study.

World regions in this paper	IPCC region numbers (0-57)
Southeast Asia	38
East Asia	35
South Asia	37
Rest of Asia	28, 29, 30, 31, 32, 33, 34, 36
Euro_Medi	16, 17, 18, 19
North America	3, 4, 5, 6, 7, 8
South America	9, 10, 11, 12, 13, 14, 15
Africa	20, 21, 22, 23, 24, 25, 26, 27
Oceania	39, 40, 41, 42, 43
Rest of world	0, 1, 2, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57

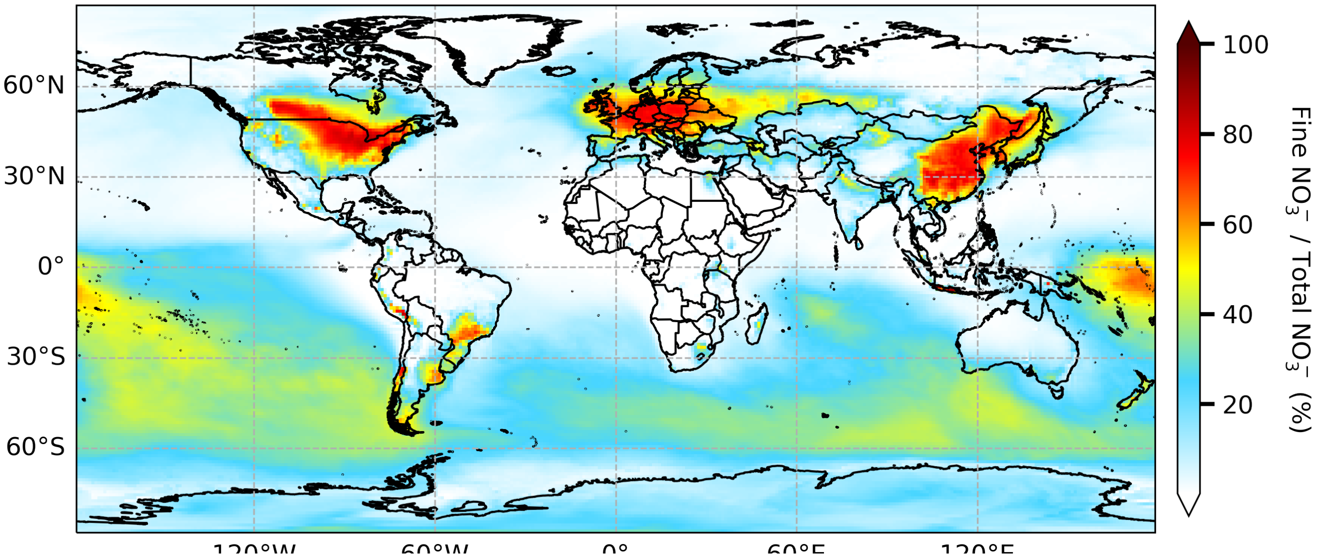

Figure S1: The % contribution of fine NO_3^- to total NO_3^- (fine + coarse).

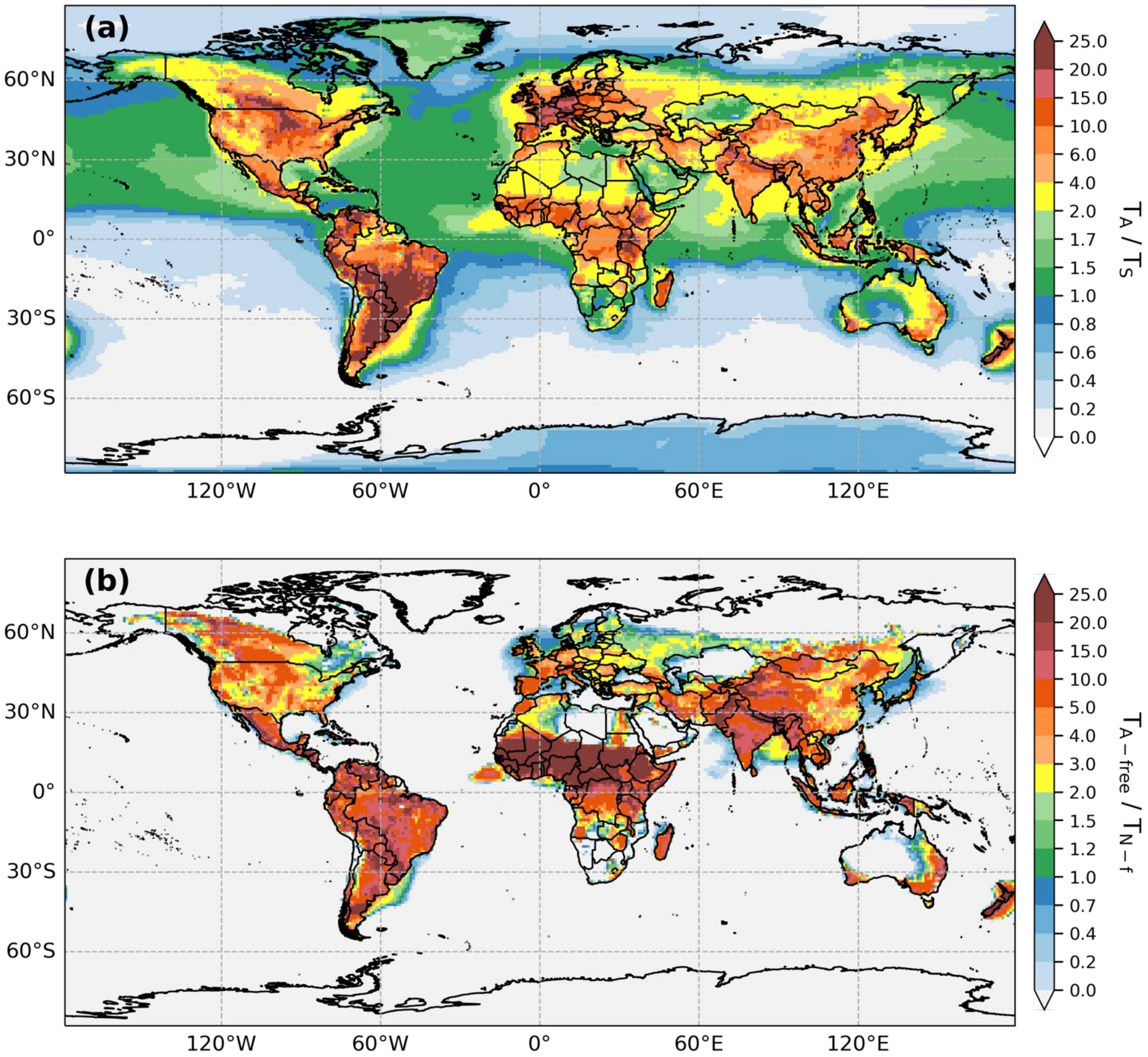

Figure S2: Maps of (a) the ratio of annual surface total ammonia T_A (= $[NH_3]$ + $[NH_4^+]$) to total sulfate T_S (= $[SO_4^{2-}]$) molar concentrations; (b) the ratio of free ammonia $T_{A\text{-}free}$ (= $T_A - (2 \times T_S)$) to total nitrate (fine) $T_{N\text{-}f}$ (= $[HNO_3]$ + $[NO_3^-\_f]$). These maps provide the quantitative species ratios that underpin the categorisation into the four chemical domains shown in Fig. 3 of the main paper. In panel (a), wherever $\frac{T_A}{T_S} > 2$ all sulfate is fully neutralised to $(NH_4)_2(SO_4)_2$. Locations where $1 < \frac{T_A}{T_S} < 2$ are characterised as 'SO_4^{2-} rich', and locations where $\frac{T_A}{T_S} < 1$ are characterised as 'SO_4^{2-} very rich'. In panel (b) there are coloured areas only where $\frac{T_A}{T_S} > 2$ in panel (a), i.e. the grey colour in panel (b) shows locations where the sulfate is not fully neutralised with ammonia and no free ammonia exists. Locations in panel (b) where $0 < \frac{T_{A-free}}{T_{N-f}} < 1$ indicate where NH_3 is the limiting factor for NH_4NO_3 formation and are characterised as 'NO_3^- rich.' Locations in panel (b) where $\frac{T_{A-free}}{T_{N-f}} > 1$ are characterised as 'NH_3 very rich', and are where it is availability of nitrate rather than NH_3 that limits NH_4NO_3 formation. See main paper for further description.

Table S3: Maximum, median, and mean $\frac{T_{A-free}}{T_{N-f}}$ ratios in the 10 world regions defined in Figure 1 of the main paper. The max and median values refer to an individual model grid within that region, while the mean ratio is calculated using the full-region area-weighted T_{A-free} divided by the full-region area-weighted T_{N-f}.

	Maximum	Median	Mean
Southeast Asia	56	0.0	1.9
East Asia	17	2.4	3.0
South Asia	87	9.9	9.6
Rest of Asia	93	-2.6	4.1
Euro_Medi	18	1.3	2.5
North America	68	2.0	3.1
South America	57	7.4	8.6
Africa	730	2.8	7.2
Oceania	138	-1.5	0.7
Rest of world	31	-7.7	-2.8

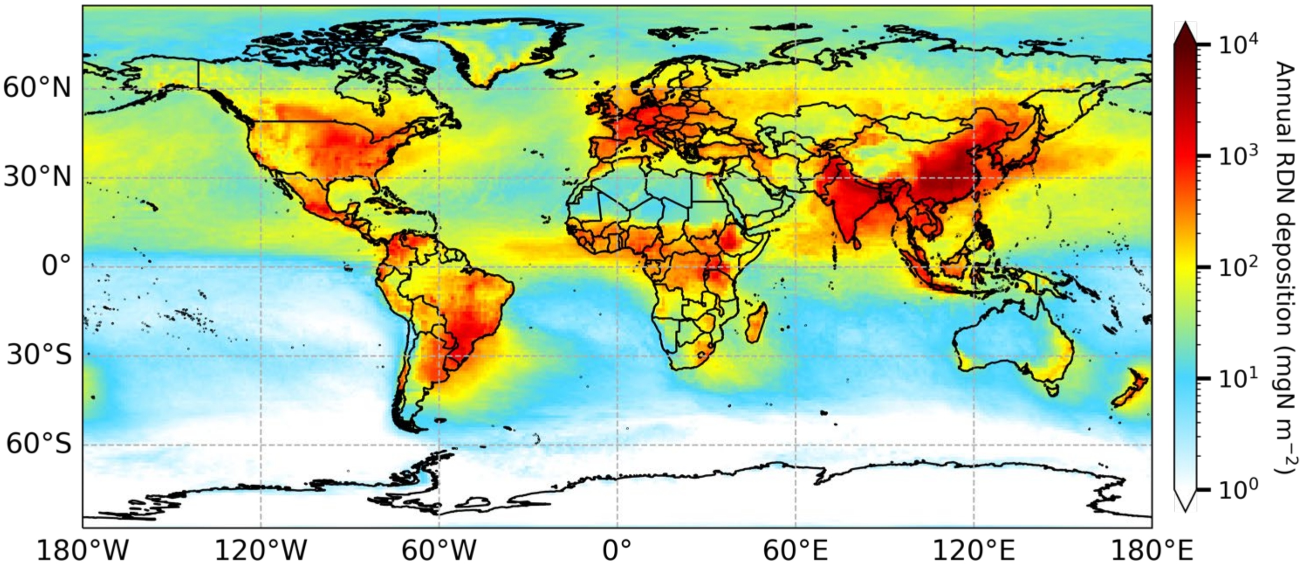

Figure S3: Annual total deposition (wet + dry) of RDN for 2015. Note the logarithmic scale.

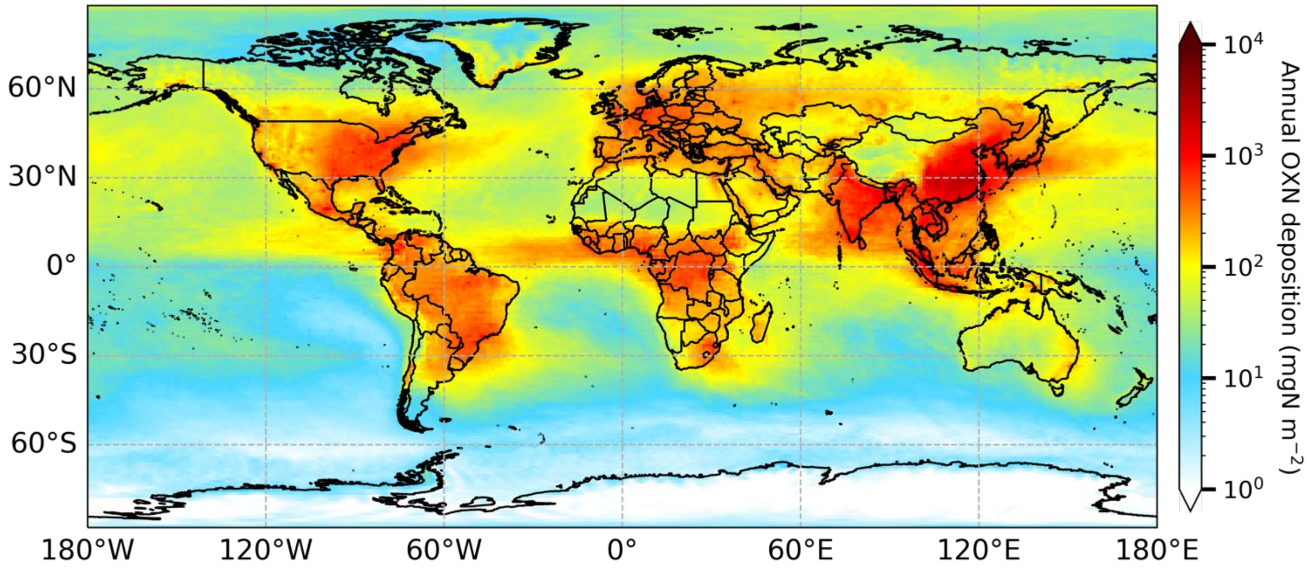

Figure S4: Annual total deposition (wet + dry) of OXN for 2015. Note the logarithmic scale.

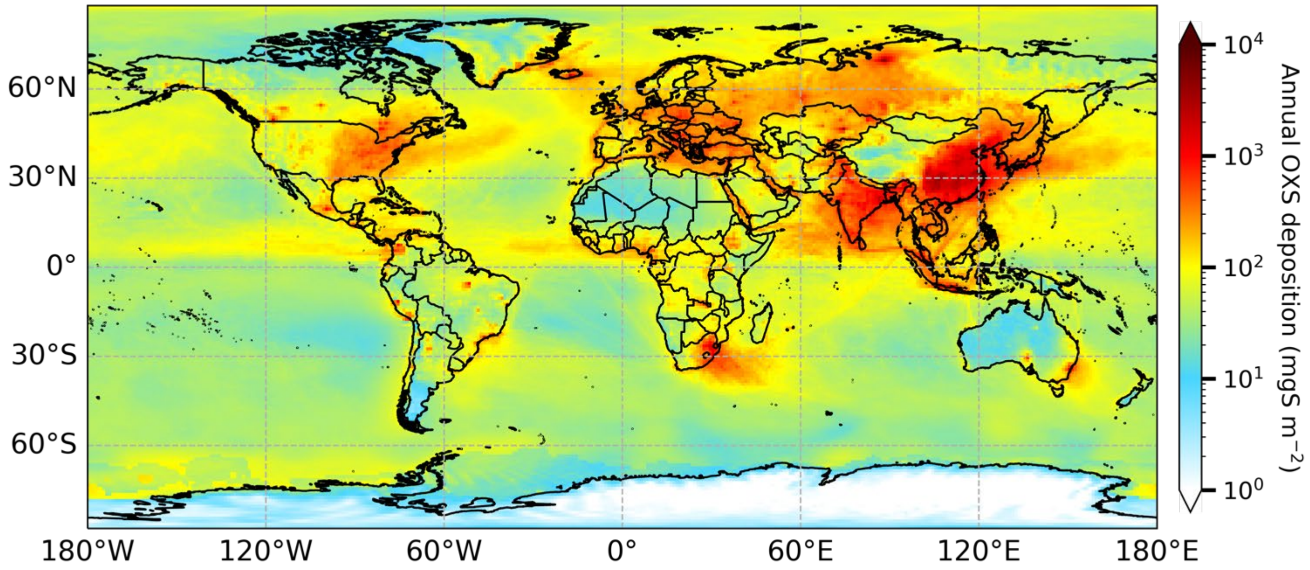

Figure S5: Annual total deposition (wet + dry) of OXS for 2015. Note the logarithmic scale.

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Table S4: Annual global deposition of gaseous and aerosol-phase RDN, OXN, and OXS species. DDEP represents dry deposition, and WDEP represents wet deposition. The 'Amount' represents the absolute value of deposition of one component, while the 'Proportion' represents the contribution of that component to global total RDN/OXN/OXS deposition.

(TgN/TgS yr^{-1})	Gaseous DDEP		Aerosol DDEP		Gaseous WDEP		Aerosol WDEP	
	Amount	Proportion	Amount	Proportion	Amount	Proportion	Amount	Proportion
RDN	22.4	40%	5.02	9%	12.2	22%	15.8	28%
OXN	16.0	28%	8.71	15%	10.5	18%	22.7	39%
OXS	17.9	35%	5.24	10%	5.44	11%	22.0	44%

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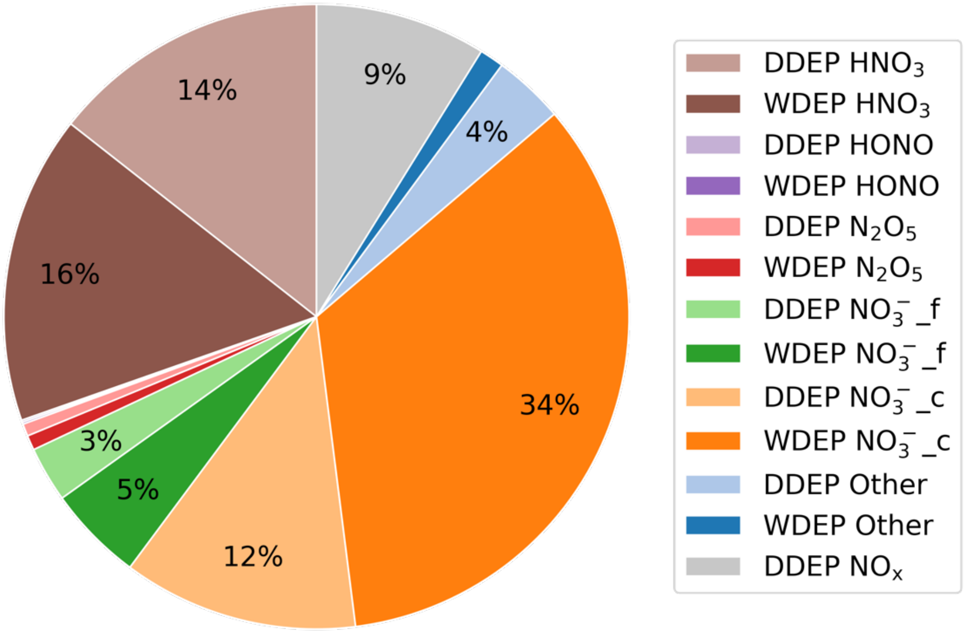

Figure S6: Relative contributions to annual global OXN deposition. Labels for individual contributions <2% are omitted to aid clarity. The darker shade colours collectively indicate wet deposition (WDEP), whilst the lighter shade colours collectively indicate dry deposition (DDEP). The 'Other' OXN species is predominantly PAN (full compositional details in Table S1).

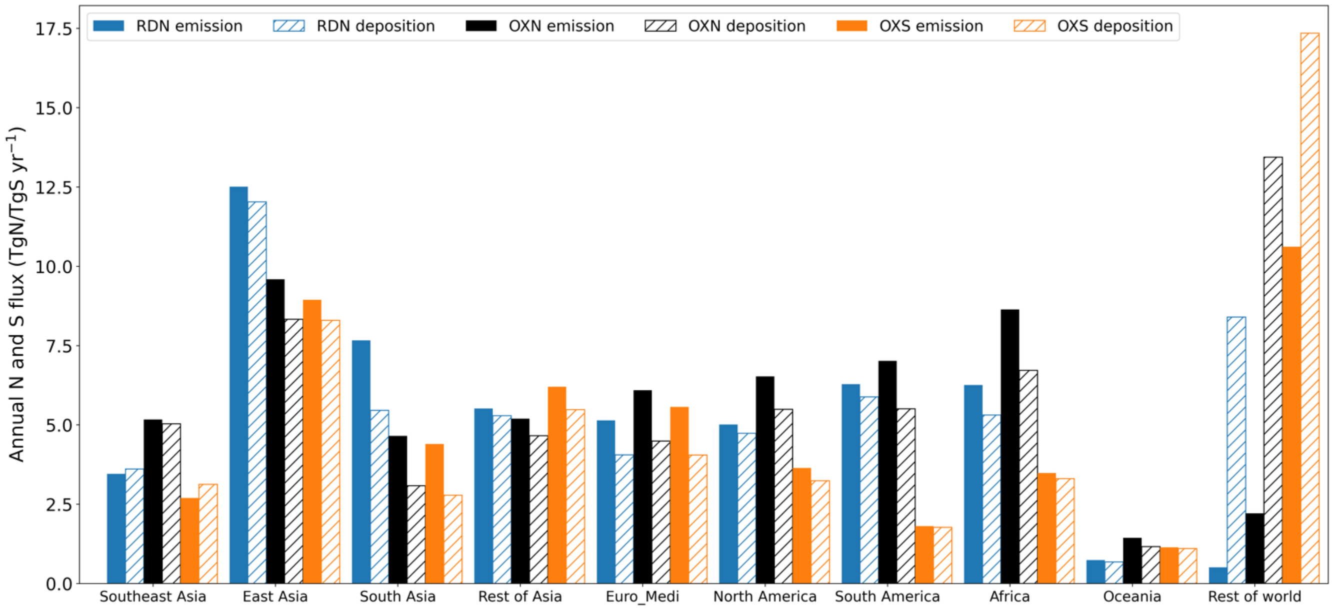

Figure S7: Emission and deposition fluxes of RDN (TgN yr^{-1}), OXN (TgN yr^{-1}), and OXS (TgS yr^{-1}) for the 10 world regions defined in Fig. 1. The constituents of RDN, OXN and OXS are listed in Table S1.

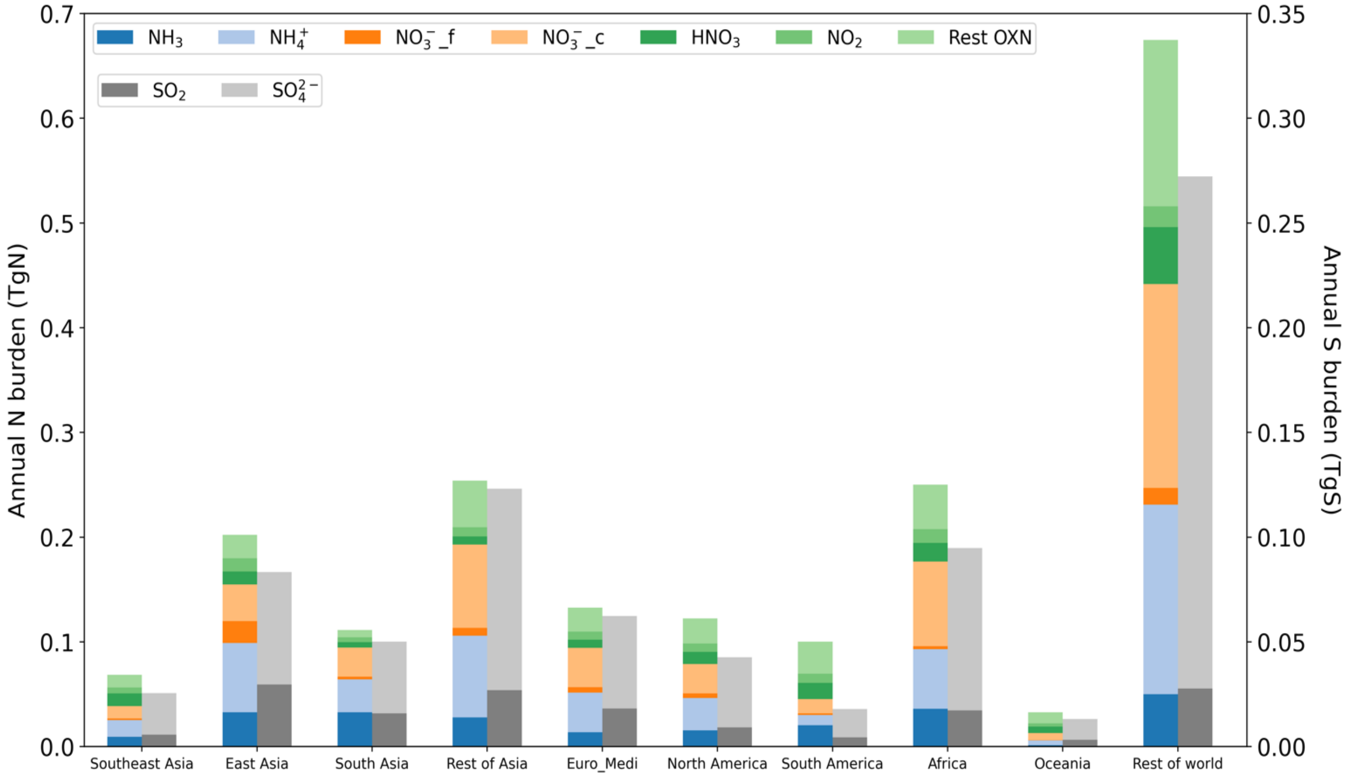

Figure S8: Compositions of the tropospheric burdens in 2015 of total N (RDN + OXN) and total S (OXS) for the 10 world regions defined in Fig. 1. 'Rest OXN' includes HONO, N_2O_5 and other OXN species (full listing given in Table S1). Note the different scales for the N and S burdens.

S1.2 Calculation of atmospheric burdens and lifetimes for N_r and S_r quantities

The calculation of annual average atmospheric burdens utilises the EMEP model's annual column output and gridded area output. For a given species:

$$Q(species) = \sum \frac{Col(species) \times Area}{6.022 \times 10^{23}} \times MW(species)$$

where $Q(species)$ is the annual average burden (TgN or TgS), $Col(species)$ is the model column output of this species for each grid (molecules cm^{-2}), $Area$ is the surface area of the same grid (km^2), 6.022×10^{23} is the Avogadro constant, and $MW(species)$ is the molar weight of this species.

The atmospheric lifetime of NH_3 is derived from both production and removal pathways. The only source of NH_3 is its emissions, whilst sinks of NH_3 include its dry and wet deposition, chemical conversion to ammonium, and the flux loss from the model domain to the upper atmosphere (details in next paragraph), as illustrated in Fig. S9. The formation of ammonium sulfate is a permanent chemical loss. Although the formation of ammonium nitrate is a reversible reaction, the production rate of NH_4NO_3 is larger than its decomposition rate on an annual scale, otherwise fine nitrate NO_3^-_f would not exist. In other words, the annual net direction of this equilibrium is from HNO_3 and NH_3 to NH_4NO_3, and therefore the formation of ammonium nitrate is considered as a permanent sink of NH_3 as well. Chemical production is the only source of NH_4^+, equal to NH_3 chemical loss rate, and the only removal pathway for NH_4^+ is wet and dry deposition besides the flux loss from the upper domain boundary.

For each species in the EMEP model, there are model outputs of initial mass (at the beginning of the model simulation), final mass (at the end of model simulation), Flux out (from the top of the model domain), and Flux in (from the top of the model domain). The rate of mass change (final mass - initial mass) thus represents the difference between sources and sinks of NH_4^+, which can then be used to calculate the production rate (TgN yr^{-1}) of NH_4^+. The flux losses and rate of mass change are generally one or two orders of magnitude smaller than the deposition and emission/chemical production quantities. We use the following equations to estimate the production and removal rates (TgN yr^{-1}) of NH_4^+, and removal rate of NH_3.

Assuming steady-state condition:

$$F_{out-in}(species) = Flux_{out}(species) - Flux_{in}(species)$$

$$\Delta M(species) = M_{final}(species) - M_{initial}(species)$$

$$R(NH_4^+) = DEP(NH_4^+) + F_{out-in}(NH_4^+)$$

$$P(NH_4^+) = \Delta M(NH_4^+) + R(NH_4^+)$$

$$R(NH_3) = DEP(NH_3) + P(NH_4^+) + F_{out-in}(NH_3)$$

where F_{out-in} $(species)$, $\Delta M(species)$, $R(species)$, $DEP(species)$, and $P(species)$ represent the flux loss, mass change, removal rate, total deposition, and production rate for each species respectively.

Similarly, for HNO_3, NO_3^-_f and NO_3^-_c:

$$R\left(NO_{3\ f}^{-}\right) = DEP\left(NO_{3\ f}^{-}\right) + F_{out-in}(NO_{3\ f}^{-})$$

$$R\left(NO_{3\ c}^{-}\right) = DEP\left(NO_{3\ c}^{-}\right) + F_{out-in}(NO_{3\ c}^{-})$$

$$P\left(NO_{3\ f}^{-}\right) = \Delta M\left(NO_{3\ f}^{-}\right) + R\left(NO_{3\ f}^{-}\right)$$

$$P\left(NO_{3\ c}^{-}\right) = \Delta M\left(NO_{3\ c}^{-}\right) + R\left(NO_{3\ c}^{-}\right)$$

$$R(HNO_3) = DEP(HNO_3) + P\left(NO_{3\ f}^{-}\right) + P\left(NO_{3\ c}^{-}\right) + F_{out-in}(HNO_3)$$

$$P(HNO_3) = \Delta M(HNO_3) + R(HNO_3)$$

Once the annual average atmospheric burden, production and removal rates are obtained, the annual-mean atmospheric lifetime τ (days) for a given species is calculated in the following two pathways.

Lifetime against sources:

$$\tau = \frac{Q(species)}{P(species)} \times 365$$

Lifetime against sinks:

$$\tau = \frac{Q(species)}{R(species)} \times 365$$

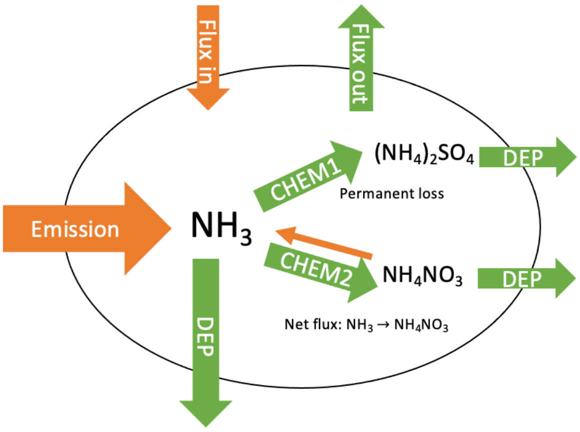

Figure S9. Basic chemical and physical behaviour of NH_3 in the atmosphere. DEP represents total deposition. CHEM1 and CHEM2 represent chemical production of ammonium sulfate and ammonium nitrate respectively.

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Table S5: Regional atmospheric lifetimes for RDN, OXN and OXS calculated using either total emission or deposition fluxes. *Q* is the burden, *P* is the production pathway (i.e., emissions), *R* is the removal pathway (i.e., depositions), and τ is atmospheric lifetime. These regional lifetimes are not fully accurate because they do not take into account the net transport of RDN, OXN or OXS across the boundary of the region, but these are relatively small for all regions except Rest of world.

(days)	Southeast Asia	East Asia	South Asia	Rest of Asia	Euro_Medi	North America	South America	Africa	Oceania	Rest of world
RDN										
$\tau = \frac{Q}{P}$	2.7	2.9	3.1	7.0	3.7	3.4	1.8	5.4	2.9	164
$\tau = \frac{Q}{R}$	2.6	3.0	4.3	7.3	4.6	3.6	1.9	6.4	3.2	10
OXN										
$\tau = \frac{Q}{P}$	3.1	3.9	3.7	10	4.8	4.2	3.6	6.6	6.8	73
$\tau = \frac{Q}{R}$	3.1	4.5	5.6	12	6.6	5.0	4.6	8.5	8.4	12
OXS										
$\tau = \frac{Q}{P}$	3.4	3.4	4.2	7.2	4.1	4.3	3.6	9.9	4.2	9.4
$\tau = \frac{Q}{R}$	3.0	3.7	6.6	8.2	5.6	4.8	3.7	10	4.4	5.7

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