Rapid declines in UK PM2.5 reflect coordinated reductions in regional nitrate and continental influence

Daniel J. Bryant[1], John Halfacre[1], Massimo Vieno[2], Eiko Nemitz[2], Lucy V. Brown[1], Shona E. Wilde[3], Alastair Lewis[4], Sarah Moller[4]

[1] Department of Chemistry, Wolfson Atmospheric Chemistry Laboratories, University of York, United Kingdom of Great Britain and Northern Ireland
[2] UK Centre for Ecology & Hydrology, Bush Estate, Penicuik, EH26 0QB, United Kingdom of Great Britain and Northern Ireland
[3] Energy and Emissions Research Laboratory, Department of Mechanical and Aerospace Engineering, Carleton University, Ottawa, Ontario K1S 5B6, Canada
[4] National Centre for Atmospheric Science, University of York, Heslington, York YO10 5DD, UK

Corresponding author: Daniel J. Bryant – daniel.bryant@york.ac.uk

John Halfacre - john.halfacre@york.ac.uk
Massimo Vieno - mvi@ceh.ac.uk
Eiko Nemitz - en@ceh.ac.uk
Lucy V. Brown - lucy.v.brown@york.ac.uk
Shona E. Wilde- shonawilde@cunet.carleton.ca
Alastair Lewis - ally.lewis@york.ac.uk
Sarah Moller - sarah.moller@york.ac.uk

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Abstract

Fine particulate matter ($PM_{2.5}$) is a major environmental risk factor for premature mortality globally. Although $PM_{2.5}$ concentrations have declined across Europe since the 1990s, recent progress has shown signs of slowing, raising concerns over the achievability of increasingly stringent ambient air quality targets. Ambient $PM_{2.5}$ concentrations across the UK underwent a rapid and sustained decline beginning in 2019-2020, with annual mean concentrations decreasing by approximately 2.4 μg m^{-3} (23.8 %) and remaining persistently lower through to 2024. Using long-term observations of aerosol chemical composition, we demonstrate that these reductions were primarily due to a reduction in ammonium nitrate, a major component part of ambient $PM_{2.5}$. Atmospheric transport pathways analysis and source attribution modelling show that the locations and periods with the largest $PM_{2.5}$ improvements in the UK were those influenced by air masses that had been substantially influenced by continental European emissions. There was an estimated absolute reduction in transboundary $PM_{2.5}$ of 0.9 [IQR: 0.65-1.15] μg m^{-3}, equivalent to approximately 43% of the national $PM_{2.5}$ decline. Aerosol thermodynamic analysis indicates that nitrate formation across the UK is predominantly nitric acid limited. Regional reductions in the precursor nitrogen oxide (NOx) emissions effectively suppresses nitrate aerosol formation in the UK's ammonia-rich atmosphere. Whilst NO_x emission reduction policies across Europe have been motivated to reduce ambient NO_2 concentrations, they have also delivered substantial co-benefits for $PM_{2.5}$ that may have been underappreciated. The preferential selection of future non-combustion decarbonisation pathways (e.g. electrification over biofuels) with lower NO_x emissions, has substantial potential to further reduce $PM_{2.5}$ across Europe and create additional health co-benefits across large geographic areas.

Introduction

Fine particulate matter ($PM_{2.5}$) has been linked to impacts on almost every organ in the human body, affecting people throughout their lives.(1,2) Across the UK and Europe, $PM_{2.5}$ concentrations have declined substantially since the 1990's, following reductions in primary emissions and precursors such as sulfur dioxide, enabled by improvements in industrial and vehicle emission controls and reductions in fuel sulfur content. However, improvements in ambient $PM_{2.5}$ air quality had slowed across much of Europe since ~2014, raising concerns over the feasibility of attainment of increasingly stringent air quality standards. (3–5)

In response to growing evidence of health impacts, governments across Europe have adopted increasingly stringent targets for ambient $PM_{2.5}$ concentrations. Directive (EU) 2024/2881 requires EU member states to achieve an annual mean $PM_{2.5}$ limit value of 10 μg m^{-3} by 2030. (6) In England, the Environmental Targets (Fine Particulate Matter) Regulations 2023 establish legally binding targets to reduce annual mean $PM_{2.5}$ concentrations to 10 μg m^{-3} by 2040 and to reduce population exposure by at least 35 % over the same period, relative to a 2016-2018 baseline.(7) However, recent observations indicate an acceleration in the decline of ambient $PM_{2.5}$ concentrations, such that by 2024 all but one monitoring site in England already recorded annual mean concentrations at or below the 10 μg m^{-3} limit set for 2040. (8)

The drivers of this accelerated improvement are not yet understood, particularly given an absence of any substantial step changes in estimated national primary $PM_{2.5}$ emissions corresponding to the observed step change in concentrations.(9)

Since the 1990s, nitrogen oxide (NO_x = NO + NO_2) emissions and concentrations have decreased significantly across the UK and Western Europe, largely due to tightening vehicle emissions standards, fleet turnover, low-emission zones, and broader decarbonisation policies associated with electricity generation.(5,10) NO_x abatement technologies have historically been introduced to reduce direct population exposure to nitrogen dioxide (NO_2), and to reduce the secondary formation of photochemical ozone on regional scales. However, NO_x also influences the formation of secondary inorganic aerosol (SIA), a major component of $PM_{2.5}$ across the UK and Europe, through nonlinear oxidation and gas-particle partitioning processes. (11,12)

SIA is formed through atmospheric oxidation of gaseous precursors followed by neutralisation with ammonia (NH_3). NO_x is oxidised to nitric acid (HNO_3), which reacts reversibly with NH_3 to form particulate ammonium nitrate (NH_4NO_3), while SO_2 is oxidised to sulfuric acid (H_2SO_4), which is neutralised by NH_3 to form ammonium sulfate. The partitioning of ammonium nitrate between the gas and particle phases is strongly dependent on temperature, relative humidity and the availability of NH_3 and HNO_3, whereas ammonium sulfate is substantially less volatile.(13)

Across Western Europe however, declining sulfur dioxide emissions and persistently high agricultural ammonia emissions have shifted aerosol composition toward nitrate dominance.(11,12,14) As less NH_3 is consumed in neutralising sulfuric acid, a greater proportion remains available to react with HNO_3. Under these increasingly ammonia-rich conditions, ammonium nitrate formation therefore becomes progressively more sensitive to the availability of HNO_3, and ultimately to its NO_x precursor emissions.(14–16) Historically, the atmospheric lifetime of particulate nitrate of up to ~ 1 week enables its transport over hundreds of kilometres. (17,18) Because ammonium nitrate exists in a thermodynamic equilibrium with gas phase ammonia and nitric acid, the exact lifetime depends on concentrations encountered during transport. As a result, under certain weather conditions UK $PM_{2.5}$ concentrations are sensitive to precursor emissions across continental Europe, and vice versa. Declining European NO_x emissions may therefore influence UK $PM_{2.5}$ through reductions in transboundary nitrate.

Here, we combine long-term observations of $PM_{2.5}$ and NO_x concentrations, aerosol chemical composition measurements, thermodynamic modelling and atmospheric transport analysis, to explore the causes of rapid $PM_{2.5}$ reductions across the UK. We show that $PM_{2.5}$ concentrations underwent a sustained step-change reduction beginning in 2019-2020, driven primarily by a decline in ammonium nitrate and transboundary pollution from continental Europe. Further, $PM_{2.5}$ formation across the UK is increasingly sensitive to the availability of NO_x under ammonia-rich condition. As such, continued decarbonisation and electrification across Europe, which frequently leads to lower NOx emissions, may deliver increasing $PM_{2.5}$ and health co-benefits over coming decades.

Methods

UK $PM_{2.5}$, NO_2 and Inorganic gas and aerosol observations

Hourly $PM_{2.5}$ and NO_2 observations from the UK Automatic Urban and Rural Network (AURN) (19) were accessed via the *importAURN* function within the openair R package (version: 3.1.0).(20) Urban traffic, urban background and rural background sites measuring $PM_{2.5}$ that were operational by 1 January 2019 and provided data during 2015–2024 were included (Table S1; Figure S1). Sites in Northern Ireland were excluded. Only sites with ≥85% data availability from their operational start date were retained, and annual network statistics were calculated from site-level annual means.

Inorganic gas and aerosol observations were obtained from the UK Acid Gas and Aerosol Network (AGANET), National Ammonia Monitoring Network (NAMN), and Monitor for Aerosols and Gases in Ambient Air (MARGA) instruments at Auchencorth Moss and Chilbolton Observatory (Table S2; Figure S2).(12,21–24) Further details of instrumentation and data treatment are provided in the Supplementary Information.

European observations

Ambient $PM_{2.5}$ and NO_2 observations for the Netherlands, Germany and Belgium were downloaded using the *euroaq* R package (version: 0.2.0.(25) Only measurements flagged as valid and fully verified were retained. To maintain consistency with the UK analysis, only urban traffic, urban background and rural background sites with ≥85% data availability across 2015–2024 were included (Table S1; Figure S1). Particulate nitrate, sulfate and ammonium measurements were obtained from the European Environment Agency for available sites in Germany, the Netherlands and Poland (Table S2; Figure S2).

Air-mass trajectory and transboundary analysis

Seventy-two-hour HYSPLIT back trajectories (version 5.4.2) were calculated every 3 h for 14 UK monitoring sites using the 1° GDAS archive meteorology (Figure S3). Trajectory-associated source regions were evaluated using Simplified Quantitative Transport Bias Analysis (SQTBA) in *openair*, which links measured receptor $PM_{2.5}$ concentrations to the probability of trajectories passing through each grid cell. (26) European-influenced air masses were defined as trajectories containing at least one hourly location within the predefined continental European domain; trajectories with no locations within this domain were classified as non-European. The transboundary $PM_{2.5}$ increment was estimated as the difference between the mean concentration across all air masses and that associated with non-European air masses. Full trajectory-processing and SQTBA methods are given in the Supplementary Information.

Aerosol thermodynamic analysis

Aerosol thermodynamic properties at Auchencorth Moss and Chilbolton Observatory were calculated using ISORROPIA-II (version 2.3) in forward, metastable mode from measured temperature, relative humidity, gas-phase NH_3, HNO_3 and HCl, and particulate NH_4^+, NO_3^-,

SO_4^{2-}, Cl^-, Na^+, K^+, Ca^{2+} and Mg^{2+}. Aerosol pH was calculated from modelled H^+ and aerosol liquid water content. Sensitivity of ammonium nitrate formation to NH_3 and HNO_3 was classified following the thermodynamic framework of Nenes et al. (2020).(27) Full model configuration and classification criteria are provided in the Supplementary Information.

EMEP4UK modelling

The EMEP4UK chemical transport model was used to quantify changes in $PM_{2.5}$ sensitivity to NO_x and NH_3 emissions under 2015 and 2022 atmospheric conditions. (11,28–32) Separate simulations applied 30% reductions to UK land-based NO_x or NH_3 emissions, excluding offshore sources, and the resulting $PM_{2.5}$ responses were normalised per kilogram of nitrogen abated. UK emissions were derived from the National Atmospheric Emissions Inventory, non-UK European emissions from EMEP inventories, and Republic of Ireland emissions from MapEIre. Full model configuration, meteorology and emissions processing are described in the Supplementary Information.

Results

Rapid reductions in $PM_{2.5}$ and NO_2 concentrations

Annual mean $PM_{2.5}$ concentrations across the UK monitoring network observed a significant and sustained decline beginning in 2019-2020 (Figure 1), with median annual concentrations decreasing from approximately 10.1 µg m^{-3} (IQR: 8.89-11.15) over the period 2015-2019 to 7.7 µg m^{-3} (IQR: 6.99-8.57) for the period 2020-2024, representing a reduction of 23.8 %. This large decline occurred mainly across 2020 and persisted through 2024 and was observed consistently across urban and rural sites. By 2024, approximately 99 % of UK monitoring sites were below the 2040 annual mean $PM_{2.5}$ target of 10 µg m^{-3}, compared with only 58 % of sites in 2015. While this indicates that current concentrations are already substantially below those anticipated when the 2040 target was established, future attainment will remain sensitive to interannual meteorological variability and associated changes in transboundary pollution. Similar, but temporally earlier, reductions in $PM_{2.5}$ were observed across Belgium, the Netherlands and Germany (Figure 1), where a pronounced decrease occurred after 2018, preceding the main UK decline in 2019-2020. This temporal sequence is consistent with a broader change in continental European atmospheric composition contributing to subsequent reductions in UK $PM_{2.5}$, rather than the UK decline arising solely from changes in domestic emissions.

Ambient NO_2 concentrations exhibited similar long-term behaviour. Median annual concentrations decreased from approximately 23.6 µg m^{-3} (IQR: 17.87-29.82) over the period 2015-2019 to 16.8 µg m^{-3} (IQR: 12.70-20.38) over 2020-2024, representing a reduction of 28.8% across the UK. Similar declines were observed across Belgium, the Netherlands and Germany (Figure 1), with particularly pronounced decreases between 2018 and 2020; the relative reduction over this period was greater at some continental European sites, notably in Belgium, than across the UK. NO_2 concentrations fell sharply between 2019 and 2020 in all selected countries in association with reduced activity during the COVID-19 pandemic but did not subsequently return to pre-pandemic levels following the removal of restrictions. The broadly coincident reductions in $PM_{2.5}$ and NO_2 across multiple European

regions therefore suggest either a common underlying driver or a chemical linkage between declining NO_x and secondary $PM_{2.5}$ formation.

Changes in national emissions inventories provide further insight into the drivers of these trends (Table S3).(33) Between 2015-2019 and 2020-2024, NO_x emissions declined consistently across European countries, decreasing by 29.4 % in the UK, 28.4 % in Germany, 27.5 % in Belgium and 22.8 % in the Netherlands (Figure 1). In contrast, ammonia (NH_3) emissions were estimated to have comparatively modest reductions, ranging from 4.2 % in the UK to 19.2 % in Germany. Primary $PM_{2.5}$ emissions also declined across all countries, with reductions of approximately 15-16.5 %. Although these reductions in primary $PM_{2.5}$ emissions will have contributed to lower ambient concentrations, primary $PM_{2.5}$ represents only a fraction of total ambient $PM_{2.5}$. As such, even if ambient primary $PM_{2.5}$ responded proportionally to emissions, a 15-16.5% reduction in primary emissions would produce a substantially smaller relative reduction in total $PM_{2.5}$ concentrations. The observed decline in $PM_{2.5}$ therefore requires a substantial reduction in secondary $PM_{2.5}$, with the relative decrease in the secondary fraction likely greater than that observed for total $PM_{2.5}$. The similar temporal behaviour across countries, together with the strong coupling between $PM_{2.5}$ and NO_2 trends, therefore, points to changes in secondary aerosol formation as an important driver of the observed reductions.

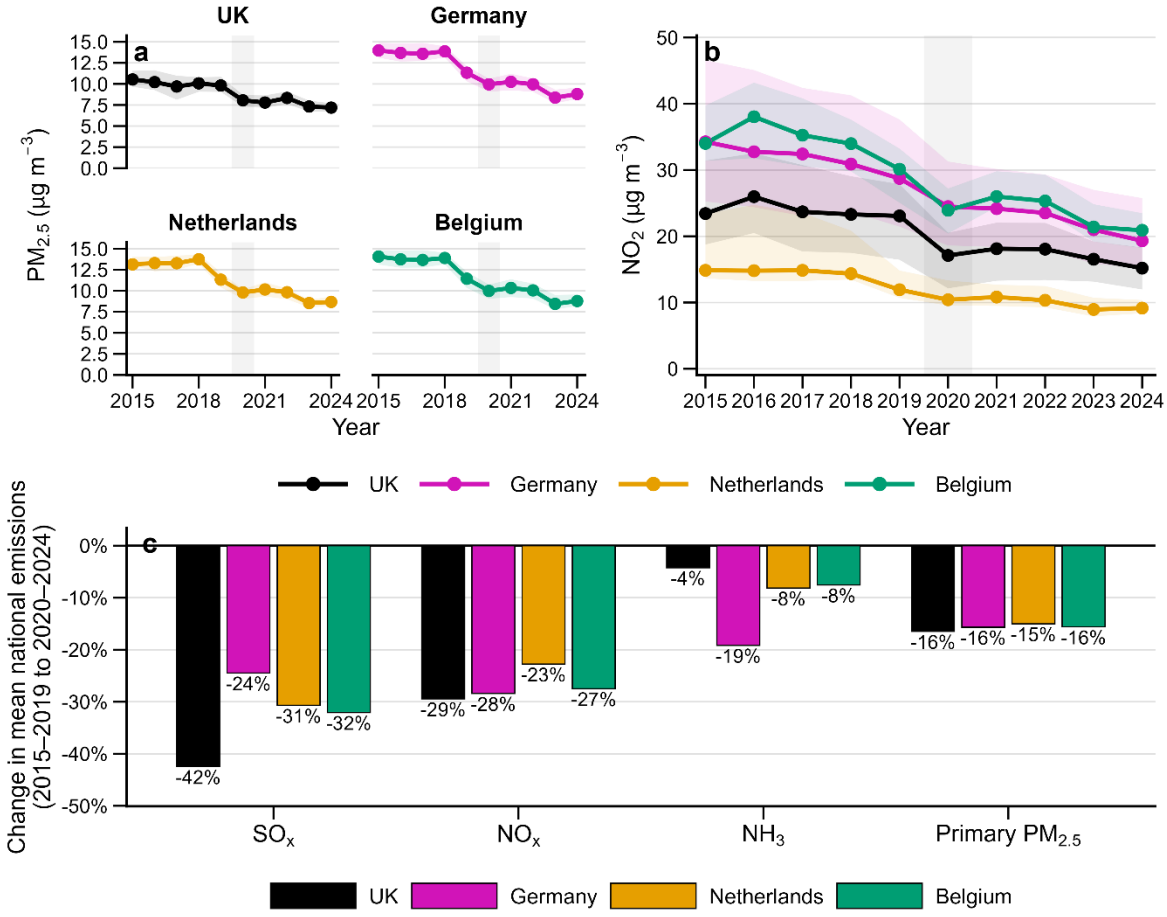

Figure 1. Changes in ambient $PM_{2.5}$ and NO_2 concentrations and national air pollutant emissions across the UK and neighbouring European countries. (a,b) Country level trends in $PM_{2.5}$ and NO_2 concentrations between 2015 and 2024. Lines and points show the median of site-level annual mean concentrations, with the shaded ribbons indicating the interquartile range across available sites. The grey shading represents 6 months pre and post 1st January 2020. (c) Percentage reduction in mean national emissions of SO_x, NO_x, NH_3 and primary $PM_{2.5}$ between 2015-2019 and 2020-2024.

Secondary inorganic aerosol compositional changes

Temporal trends in SIA components were assessed across the UK using data from the UK National Ammonia Monitoring Network (NAMN) and Acid Gas and Aerosol Network (AGA-Net), which provide monthly-averaged measurements. These were complemented by hourly measurements from MARGA instruments installed at two rural supersites: Auchencorth Moss, Scotland, and Chilbolton Observatory, Southern England.

Across the rural sites, nitrate concentrations declined substantially across the UK networks between 2017-2024, from 1.47 ± 0.74 to 0.84 ± 0.44 μg m^{-3} across the rural network, equivalent to a reduction of 43.2 %. Comparable reductions occurred at the two supersites, where nitrate declined from 1.0 to 0.64 μg m^{-3} at Auchencorth Moss and from 2.78 to 1.54 μg m^{-3} at Chilbolton Observatory between 2017 and 2024. Similar percentage reductions were observed for ammonium across the same sites (34-44 %), but smaller reductions were observed for sulfate (4-31 %). Even so, nitrate was consistently the dominant acid ion in this period, representing 43-53 % of mean total SIA mass, with sulfate and ammonium contributing 23-34% and 21.5-23.4 % respectively (Figure 2).

Across both supersites, $PM_{2.5}$ concentrations were strongly correlated with total SIA (sulfate, nitrate, ammonium) concentrations (r^2 = 0.68 at Auchencorth Moss; r^2 = 0.71 at Chilbolton Observatory). As such, declines in total SIA closely tracked reductions in $PM_{2.5}$ at both supersites on annual and seasonal timescales. As above, nitrate accounted for the largest absolute reduction in SIA mass, providing further evidence that declining SIA, and in particular nitrate, contributed substantially to the observed reduction in bulk $PM_{2.5}$. Previous analyses have shown that ammonium nitrate is the main contributor to $PM_{2.5}$ during high concentration episodes.(23)

To determine whether the decline in nitrate and more broadly SIA represented a wider regional change, measurements of particulate nitrate, sulfate and ammonium from available monitoring sites across the Netherlands (n = 1), Germany (n = 7) and Poland (n = 5) were analysed. Particulate nitrate concentrations fell significantly across all three countries across 2018-2020. The coordinated decline in particulate nitrate across the UK and continental Europe suggests a regional reduction in ammonium nitrate formation.

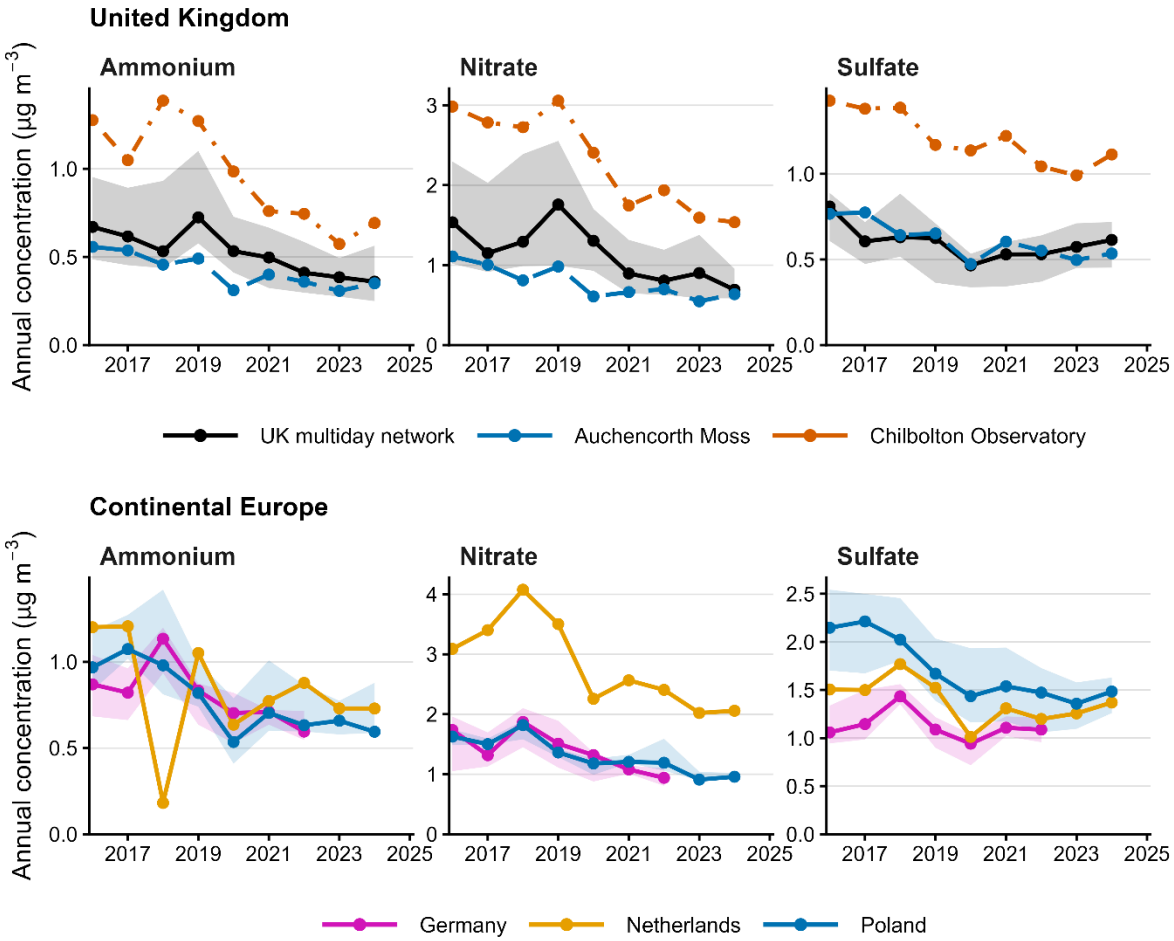

Figure 2. Annual mean concentrations of particulate ammonium, nitrate and sulfate across UK and available continental European sites during 2016-2024. The upper panel shows the median of the site level annual means across the UK multiday monitoring networks, with shading indicating the interquartile range between sites, alongside annual means from MARGA measurements at Auchencorth Moss and Chilbolton Observatory. The lower panels show the annual country level concentrations for available sites across Germany, the Netherlands and Poland. Note: no sites were available in Belgium. Lines for Germany and Poland represent the median of station level annual means, with shading representing the interquartile range between stations. The line for the Netherlands represents a single monitoring station.

Secondary Inorganic aerosol system sensitivities

To identify which precursor most strongly constrained ammonium nitrate formation at the two UK rural supersites, we combined ISORROPIA-II-derived aerosol pH and liquid water content with the thermodynamic sensitivity framework of Nenes et al. (2020).(27) Across all valid observations, ammonium nitrate formation was classified as HNO_3-acid-limited for 88.3% of observations at Chilbolton and 86.0% at Auchencorth Moss (Figure S4). This regime indicates that particulate nitrate responds strongly to changes in HNO_3 availability but is

comparatively insensitive to NH_3, consistent with ammonia being largely in excess during the observation period.

Similar nitric-acid sensitivity has also been observed at Cabauw (2012-2013), a rural site in the Netherlands(27), indicating that the sensitivity regimes observed at the UK supersites are consistent with those found elsewhere in the ammonia-rich atmosphere of northwestern Europe. This Benelux region is particularly relevant because it encompasses many of the continental transport pathways associated with European-influenced air masses reaching the UK (Figure S5). However, these observations indicate that reductions in nitric acid availability can efficiently suppress ammonium nitrate formation under the ammonia-rich conditions characteristic of the UK and northwestern Europe. The UK supersites and Cabauw represent individual locations and cannot establish a uniform sensitivity regime across the whole of northwestern Europe.

Nitric acid is produced primarily through atmospheric oxidation of NO_x, although gas phase nitric acid can also be regenerated through reversible evaporation of particulate ammonium-nitrate to nitric acid and ammonia. IN HNO_3-sensitive regions, the availability of oxidised nitrogen therefore provides a control on ammonium nitrate formation. However, the relationship between NO_x emissions and HNO_3 availability is nonlinear, reflecting interactions between NO_x chemistry, atmospheric oxidant availability and reversible gas-particle partitioning. To investigate whether the effectiveness of NO_x and ammonia controls has changed as emissions have declined, we calculated the $PM_{2.5}$ response to 30% reductions in UK land based NO_x and ammonia emissions using the EMEP4UK atmospheric chemistry transport model under 2015 and 2022 emission conditions (Figure 3). Offshore emissions, including those from the North Sea, were not included in these perturbations. Responses were normalised per kilogram of nitrogen abated to compare the efficiency of NO_x and ammonia reductions on a common molar basis.

Under 2015 emission conditions and meteorology, $PM_{2.5}$ concentrations across the UK were more sensitive to ammonia reductions than NO_x reductions on a per-unit nitrogen basis, consistent with the higher NO_x to NH3 ratio at the time (Table S3). Under 2022 emission conditions, the system has shifted substantially toward NO_x sensitivity across nearly all UK regions, except some areas with high population densities and associated NOx emissions. This change is consistent with a declining NO_x-to-ammonia precursor ratio: as NO_x emissions decrease while ammonia remains comparatively abundant, nitric acid becomes increasingly limiting and further NO_x reductions become more effective at suppressing ammonium nitrate formation. These results demonstrate that the PM2.5 benefit associated with UK NO_x abatement has increased as the atmospheric precursor environment has evolved. It should be noted that in terms of concentration analysis the EMEP4UK model predicts similar sensitivities to NH_3 vs HNO_3 as indicated by the analysis of the measurements.

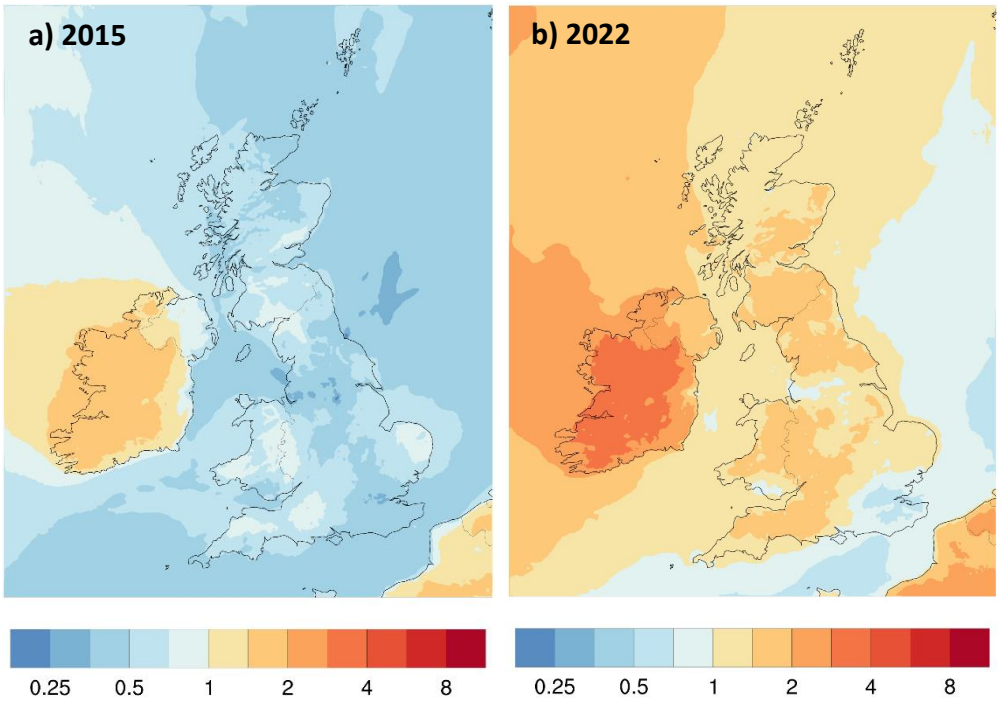

Figure 3. Sensitivity ratio of $PM_{2.5}$ to changes in NO_x vs NH_3 emissions, normalised to kg of N emission abated by 30% emission reductions in the UK for 2015 and 2022 emission levels. Warm colours indicate areas there the $PM_{2.5}$ concentrations respond more to UK wide NO_x-N emission reductions than to UK wide NH_3-N emission reductions, whilst cold colours indicate a higher sensitivity to NH_3-N changes.

Transboundary contributions to UK $PM_{2.5}$

Several analyses were used to examine the influence of transboundary sources on the observed reduction in UK $PM_{2.5}$ concentrations. The geographical pattern of the $PM_{2.5}$ decline was examined using local wind sector analysis at the observational network level (Figure S6). Reductions in $PM_{2.5}$ occurred under all wind directions, but the largest decreases were consistently associated with easterly and south easterly wind vectors. As easterly and south-easterly winds frequently transport polluted air masses from continental Europe towards the UK, this suggests that part of the observed decline in $PM_{2.5}$ is due to changes in regional sources.

To investigate the geographical origin of this change in greater detail, Simplified Quantitative Transport Bias Analysis (SQBTA) was applied to $PM_{2.5}$ observations and back trajectories for 2015-2019 and 2020-2024 at a combined subset of 14 sites, distributed across the UK (Figure S3). In SQTBA, the value assigned to each grid cell represents the $PM_{2.5}$ concentration measured at the receptor site, weighted by the frequency and probability of trajectories passing through that grid cell. Therefore, higher values indicate source regions more strongly associated with elevated $PM_{2.5}$ at the UK monitoring sites. Independently, both periods show elevated $PM_{2.5}$ concentrations associated with trajectories passing across continental Europe,

particularly the Benelux region, Germany and Poland (Figure 4a,b). In the later period, the receptor concentrations associated with trajectories passing through these regions were substantially lower. The difference field (2020–2024 minus 2015–2019; Figure 4c) shows widespread negative values across continental Europe, indicating that air masses from these regions were associated with lower $PM_{2.5}$ concentrations upon arrival in the UK than during 2015-2019. This reduction may reflect lower particulate matter carried directly within the air masses and/or lower precursor loading and subsequent secondary aerosol formation during transport. The SQTBA results therefore provide geographical support for the wind-sector analysis: the largest measured reductions in $PM_{2.5}$ occurred under easterly and south-easterly flow, while the trajectory analysis identifies declining $PM_{2.5}$ associated with air masses passing over central and western continental Europe (Figure 4d).

To quantify the contribution of transboundary sources to this UK reduction, annual $PM_{2.5}$ concentrations were calculated with and without European influenced air masses. Across the same subset of 14 sites, the transboundary contribution to UK $PM_{2.5}$, estimated as the concentration difference between non-European air masses and the annual site concentrations, declined from approximately 1.86 [IQR: 1.45-2.04] μg m^{-3} during 2015-2019 to 0.87 ± 0.5 μg m^{-3} during 2020-2024, with median reductions across the sites of approximately 0.9 [IQR: 0.65-1.15] μg m^{-3}. This indicates that the transboundary concentrations of $PM_{2.5}$ approximately halved over the study period.

Across the subset of 14 UK measurement sites, mean $PM_{2.5}$ concentrations declined by 2.04 μg m^{-3} between 2015-19 and 2020-24, while the estimated transboundary increment declined by 0.87 μg m^{-3}. The reduction in the transboundary increment was therefore equivalent to approximately 43 % of the mean observed decline in $PM_{2.5}$. Reducing pollution associated with mainland European emissions reductions of NO_x were therefore responsible for a large fraction of the recent improvement in UK $PM_{2.5}$ air quality, Changes in regional atmospheric composition have been a major contributor to recent UK air-quality improvements.

The reduction in $PM_{2.5}$ was not explained by a change in airmass transport frequency or geographical coverage (Figure S5). The annual number of European-influenced air masses did not change between 2015-19 and 2020-24 with the mean number of European influenced airmasses varying from 765 ± 297 to 767 ± 296 respectively. The comparatively small change in airmass transport frequency, relative to the large decline in associated $PM_{2.5}$ concentrations, suggests that European-influenced air masses became substantially less polluted rather than simply becoming less frequent. This interpretation is supported by the coordinated decline in $PM_{2.5}$ concentrations and particulate nitrate observed across the UK and neighbouring European countries. This suggests that reductions in regional precursor emissions and secondary inorganic aerosol formation have reduced the $PM_{2.5}$ transported into the UK during continental flow.

Nitric acid has a relatively short atmospheric lifetime because of rapid deposition to surfaces, but in the presence of ammonia it partitions into the particle phase as ammonium nitrate, increasing the distance over which reactive nitrogen can be transported. At Auchencorth Moss and Chilbolton Observatory, higher $PM_{2.5}$ concentrations were accompanied by lower gas-phase fractions of nitric acid and ammonia and higher particulate nitrate and ammonium fractions (Figure S7/8), consistent with enhanced gas-to-particle partitioning leading to these

elevated aerosol loadings.(27,34) These observations indicate that ammonium nitrate formation contributes substantially to the development of high concentration $PM_{2.5}$ air masses(23) and provides a mechanism through which reductions in nitric acid availability can suppress regional particulate pollution. Taken together, the decline in continental European nitrate, the reduction in European-associated $PM_{2.5}$ reaching the UK and the observed gas-to-particle partitioning behaviour are consistent with reduced regional ammonium nitrate formation as NO_x emissions have declined. European NO_x reductions are likely to impact on ammonium nitrate production and its persistence in the particle phase before air masses reach the UK, while concurrent UK NO_x reductions may further limit the amount of nitric acid available for additional aerosol production during airmass passage over the UK.

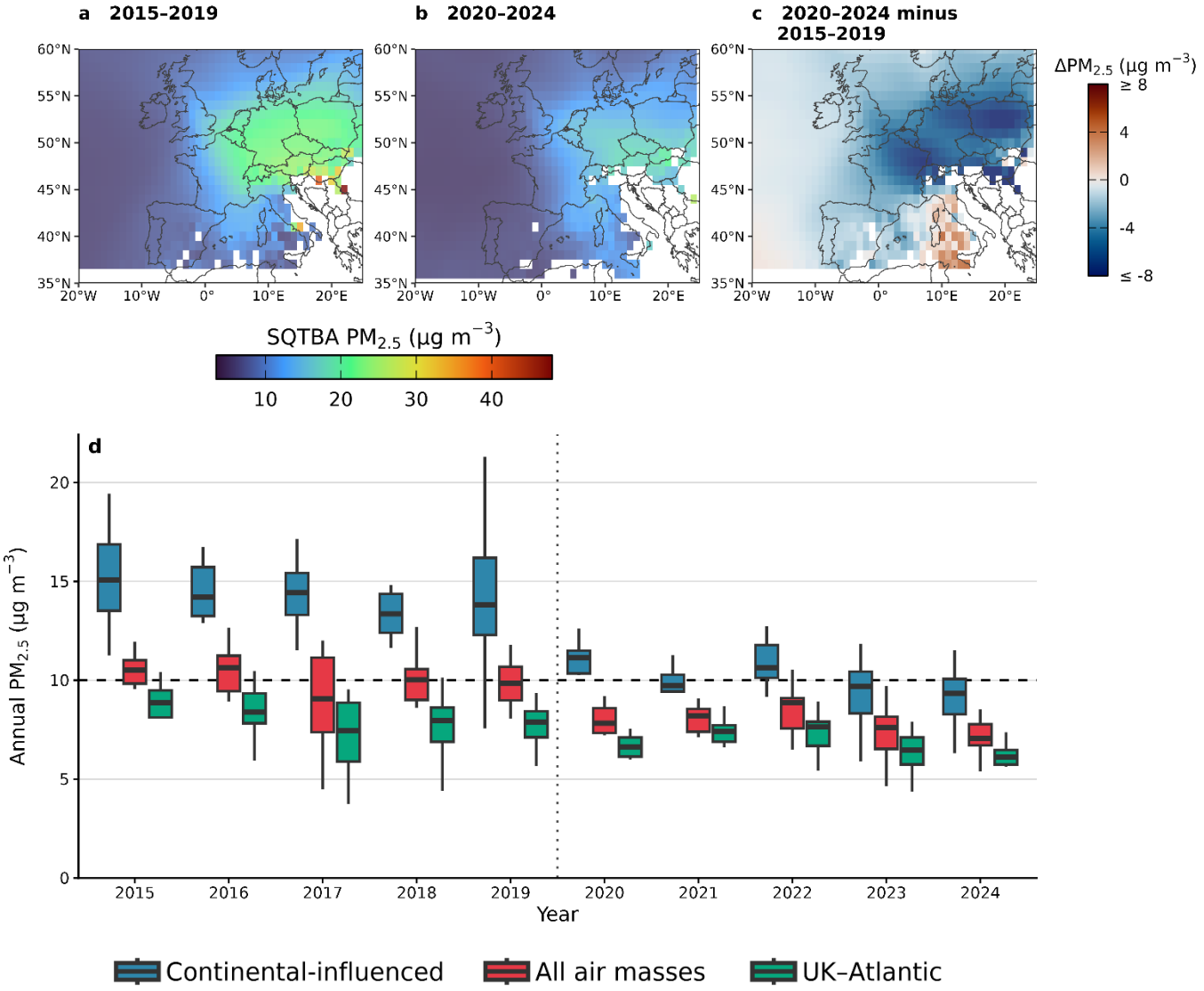

Figure 4. Changes in trajectory-origin and transboundary influenced $PM_{2.5}$ concentrations arriving over the UK and surrounding regions between 2015-2019 and 2020-2024. SQBTA predicted grids are shown for a) 2015-2019 and b) 2020-2024 from 14 sites across the UK. C) Difference in SQBTA $PM_{2.5}$ between the two periods, calculated as 2020-2024 minus 2015-2019 for grid cells represented in both periods (n >=5). Negative values indicate lower trajectory-associated $PM_{2.5}$ during 2020-2024. d) Annual distribution of site level mean $PM_{2.5}$ concentrations for trajectories classified as continental influenced, all air masses and UK-Atlantic dominated. Boxes show the median and interquartile range across the 14 sites, with whiskers extending to 1.5 times the interquartile range, outliers are not displayed. The vertical dotted line divides the time series into the two periods in a and b, the horizontal line represents the UK's 2040 target of 10 µg m^{-3}.

Discussion

$PM_{2.5}$ concentrations across the UK underwent a rapid and sustained decline beginning around 2019-2020 observed to be driven broadly by reductions in particulate ammonium nitrate. Ammonium nitrate is an important component of $PM_{2.5}$ across Europe (14) and previous modelling has demonstrated that it is a substantial contribution of long-range transport to UK $PM_{2.5}$.(30) The timing and similarity of trends in $PM_{2.5}$ across the UK and neighbouring European countries suggests that this decline is not a result solely from changes in local/domestic primary $PM_{2.5}$ emissions.

Thermodynamic analysis indicates that ammonium nitrate formation at two rural UK supersites is predominantly HNO_3-sensitive, consistent with observations in the ammonia rich atmosphere of the Netherlands. (27,35) Under these conditions, declining NO_x which reduces HNO_3 availability supresses ammonium nitrate formation. EMEP4UK simulations further show that this sensitivity has evolved over time. NH_3 abatement was shown to produce a greater $PM_{2.5}$ response per unit of nitrogen reduced in 2015, but NO_x abatement was more effective across most of the UK under 2022 conditions. This shift is consistent with European modelling predicting increasing NO_x sensitivity as NO_x declines relative to NH_3. (15,36)

It should be noted that shipping represents a substantial source of NO_x along transport pathways between continental Europe and the UK. Maritime NO_x emissions have shown no decline during the study period, while satellite observations indicate much larger reductions in NO_2 over north-western continental Europe.(37,38) This difference suggests that the reduction in $PM_{2.5}$ associated with continental air masses was more likely driven by declining land-based precursor emissions than by changes in shipping.

This mechanism is likely to remain important as NO_x and NH_3 emissions continue to diverge in their reductions. The UK NO_x-N:NH_3-N emission ratio declined from approximately 1.34 in 2015 to 0.8 in 2024, and is projected to reach ~ 0.5 by 2040, with similar changes expected elsewhere in Europe. (5,39) These bulk emission ratios do not determine aerosol sensitivity directly but are consistent with an increasingly ammonia-rich chemical environment. This shift towards NOx sensitivity is happening because ambition to reduce NH_3 emissions is lacking. Whilst it is not the topic of this paper it should be noted that NH_3 dominates the nitrogen deposition into sensitive UK ecosystems and will continue to do so in the future. Thus, for reducing nitrogen impacts the additional control of NH_3 is vital.

This changing precursor balance has important implications for energy and NO_x abatement policies. The justification for NO_x emission control is commonly framed around achieving compliance with national ambient NO_2 standards and long-term tropospheric ozone objectives. Once NO_2 concentrations are below limit values, the perceived policy benefit of further NO_x interventions may appear superficially modest. However, further reduction in NO_x would continue to lower ammonium nitrate and $PM_{2.5}$ bringing air quality benefits, even when NO_2 concentrations themselves followed regulatory requirements. Since $PM_{2.5}$ is associated with substantial health impacts, these secondary air quality benefits represent an additional health co-benefit of NO_x policy that may not be fully captured in current economic assessments. The regional nature of ammonium nitrate means that these benefits extend beyond national borders in Europe. As shown here, EU NO_x mitigation can reduce UK

population exposure to $PM_{2.5}$, while UK NO_x control will provide reciprocal benefits.(11) The importance of air pollution exported by the UK was recognised in the 1980s when it significantly contributed to the acid deposition problems in Scandinavia. Coordinated regional action may therefore generate larger aggregate health benefits than policies assessed solely based on changes in domestic NO_2 concentrations.

These sensitivities are important to consider from the perspective of future decarbonisation investments and net zero decision-making. Some low-carbon energy pathways retain combustion and the associated NO_x emissions, including applications of biofuels, sustainable aviation fuels (SAF), hydrogen and ammonia. Direct electrification avoids combustion-related NO_x emissions at the point of use and could therefore deliver additional $PM_{2.5}$ and health benefits alongside greenhouse-gas reductions.

Conclusion

UK $PM_{2.5}$ concentrations underwent a sustained step change reduction beginning around 2019-2020, driven largely by declining ammonium nitrate and reduced continental European influence. Across the 14-site trajectory subset, the reduction in transboundary $PM_{2.5}$ was equivalent to approximately 43 % of the observed decline. Thermodynamic and chemical transport modelling further show that ammonium nitrate formation has become increasingly sensitive to HNO_3 availability as NO_x declines relative to NH_3. Continued NO_x abatement, particularly through non combustion decarbonisation may therefore deliver increasingly $PM_{2.5}$ benefits across the UK and wider Europe.

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Supplementary Information

UK air-quality observations

Hourly $PM_{2.5}$ and NO_2 measurements were obtained from the UK Automatic Urban and Rural Network (AURN) using the importAURN function in the *openair* R package (version 3.1.0). (1,2) Sites classified as urban traffic, urban background or rural background were considered. To ensure coverage of the period surrounding the identified 2019-2020 change in $PM_{2.5}$, sites were required to have commenced operation by 1 January 2019 and to provide observations during the 2015-2024 analysis period. Sites in Northern Ireland were excluded. Individual sites were retained where valid observations represented at least 85% of the expected measurements from the site's operational start date. Annual mean concentrations were calculated separately for each site before calculating network-level summary statistics.

Inorganic gas and aerosol measurements were obtained from the Acid Gas and Aerosol Network (AGANET) and National Ammonia Monitoring Network (NAMN) through the UK Department for Environment, Food and Rural Affairs data service. These networks provide integrated measurements, typically at approximately monthly resolution. AGANET uses a DELTA denuder-filter system to separate gas- and aerosol-phase species and has an effective aerosol size cut-off of approximately 4.5 µm. Higher-time-resolution inorganic composition measurements were obtained from Monitor for Aerosols and Gases in Ambient Air (MARGA) instruments at the rural supersites at Auchencorth Moss, Scotland, and Chilbolton Observatory, southern England. Hourly measurements included gas-phase NH_3 and HNO_3 and particulate NH_4^+, NO_3^- and SO_4^{2-}. Site locations and periods of availability are summarised in Table S2 and Figure S2. (3–7)

European air-quality observations

Ambient $PM_{2.5}$ and NO_2 observations for Germany, Belgium and the Netherlands were downloaded using the *euroaq* R package (version 0.2.0), which accesses European air-quality monitoring services. (8) Measurements were restricted to observations flagged as valid (Validity = 1) and fully verified (Verification = 1). Only urban traffic, urban background and rural background sites were retained, and sites were required to provide at least 85% data availability over 2015–2024.

Particulate NO_3^-, SO_4^{2-} and NH_4^+ measurements were obtained from the European Environment Agency air-quality data service for available monitoring sites in Germany, the Netherlands and Poland. No suitable measurements were available for Belgium. Site numbers, measurement periods and methods are provided in Table S2.

HYSPLIT trajectory calculations and SQTBA

Air-mass transport to the UK was investigated using the NOAA Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model, version 5.4.2. Seventy-two-hour backward trajectories were initiated every 3 h from a subset of 14 monitoring sites selected to provide broad geographical coverage of the UK while retaining sufficient PM2.5 data availability (Figure S3). Meteorological fields were taken from the National Centers for Environmental Prediction 1° Global Data Assimilation System archive.

Source regions associated with receptor $PM_{2.5}$ concentrations were evaluated using Simplified Quantitative Transport Bias Analysis (SQTBA) implemented in openair.(2) Each trajectory location is represented as a two-dimensional Gaussian probability distribution to account for increasing positional uncertainty and atmospheric dispersion with back-trajectory age. For each trajectory l, a time-averaged trajectory probability field $\bar{T}_l(x \mid x')$is calculated to represent the likelihood that an air mass arriving at receptor x'passed through location x. This field is weighted by the pollutant concentration $c_l$measured at the receptor at the trajectory arrival time to give:

$$\tilde{T}(x \mid x') = \sum_{l=1}^{L} \bar{T}_l\,(x|x')c_l$$

The final SQTBA field is then calculated as

$$SQBTA(x|x') = \frac{\tilde{T}(x|x')}{\sum_{l=1}^{L} \bar{T}_l(x|x')}$$

Higher SQTBA values therefore indicate grid cells more strongly associated with elevated $PM_{2.5}$ concentrations measured at the receptor.

Separate SQTBA fields were calculated for 2015–2019 and 2020–2024. Difference fields were calculated as 2020–2024 minus 2015–2019 for grid cells represented in both periods, with cells represented by fewer than five trajectories excluded.

ISORROPIA-II thermodynamic modelling

Aerosol thermodynamic properties were calculated from MARGA observations at Auchencorth Moss and Chilbolton Observatory using ISORROPIA-II version 2.3. The model was run in forward mode under metastable conditions using measured temperature and relative humidity. The full-ion configuration included gas-phase NH_3, HNO_3 and HCl together with particulate NH_4^+, NO_3^-, SO_4^{2-}, Cl^-, Na^+, K^+, Ca^{2+} and Mg^{2+} within the measured $PM_{2.5}$ fraction.

Aerosol pH was calculated from modelled hydrogen ion concentration and aerosol liquid water content according to

$$pH = -\log_{10}(a_{H^+})$$

with H^+ activity derived from the modelled aqueous hydrogen ion concentration and aerosol liquid water.

The thermodynamic sensitivity of ammonium nitrate formation to NH_3 and HNO_3 was classified using the framework of Nenes et al. (2020).(9) This framework combines aerosol pH, liquid water content and temperature to determine whether particulate nitrate is primarily sensitive to changes in NH_3, HNO_3, both precursors, or neither. Characteristic pH

thresholds for nitrate and ammonium partitioning were calculated using the temperature-dependent thermodynamic relationships described by Nenes et al. (2020), using partitioning thresholds of $\alpha = \beta = 0.1$. Observations were subsequently assigned to the HNO_3-sensitive, NH_3-sensitive, dual-sensitive or insensitive regime.

Aerosol sensitivity to NH_3 and HNO_3 was classified following the thermodynamic framework of Nenes et al. (2020), using ISORROPIA-II-derived aerosol pH, aerosol liquid water content (W_i) and temperature. The framework defines characteristic pH thresholds for nitrate (pH') and ammonium (pH'') partitioning as functions of W_i and temperature. Following Nenes et al. (2020), partitioning thresholds of $\alpha = \beta = 0.1$ were used, corresponding to the assumption that aerosol becomes sensitive to a precursor when at least 10% of the total available nitrate or ammonia can partition to the particle phase. Observations were classified into four regimes: (1) insensitive to both NH_3 and HNO_3, where $pH > pH''$and $pH < pH'$; (2) HNO_3-sensitive, where $pH > pH''$and $pH > pH'$; (3) sensitive to both NH_3 and HNO_3, where $pH < pH''$and $pH > pH'$; and (4) NH_3-sensitive, where $pH < pH''$and $pH < pH'$ as defined below where $\Psi$and $\Phi$are temperature-dependent thermodynamic terms.

$$pH' = -\log(9\Psi W_i)$$

$$pH'' = \log(9\Phi W_i)$$

EMEP4UK model configuration and sensitivity simulations

The EMEP-WRF model is a regional and global application of the EMEP Meteorological Synthesizing Centre-West (MSC-W) chemical transport model(28), with subsequent updates documented in the annual EMEP Status Reports published by MSC-W (https://www.emep.int/mscw/mscw_publications.html) freely available at https://github.com/metno/emep-ctm. The EMEP-WRF model has been widely used for applications at both the UK and regional scale.(29–31) The meteorology used for the EMEP-WRF model simulations is derived from the Weather Research and Forecast model (WRF, http://www.wrf-model.org) version 4.4.2.(32) Here, WRF was forced by meteorological fields from the numerical weather prediction model meteorological reanalysis from is fifth-generation European Centre for Medium-Range Weather Forecasts atmospheric reanalysis of the global climate (ERA5) using grid nudging (four-dimensional data assimilation) of large-scale meteorological variables, including wind components, temperature.(33) This maintains consistency with the driving meteorological analyses while allowing the development of regional-scale features. The non-UK European emissions were derived from the EMEP emission inventories (https://www.ceip.at/webdab-emission-database/emissions-as-used-in-emep-models). The UK emissions were derived from the UK The National Atmospheric Emissions Inventory (NAEI) that calculates and reports on the UK quantity of pollutants that are emitted to air (https://naei.energysecurity.gov.uk/). The Republic of Ireland national emissions inventory (MapEIre - https://www.epa.ie/publications/research/air/research-317-mapeire-national-mapping-of-greenhouse-gas-and-non-greenhouse-gas-emissions-sources-project.php) was used for the Republic of Ireland.

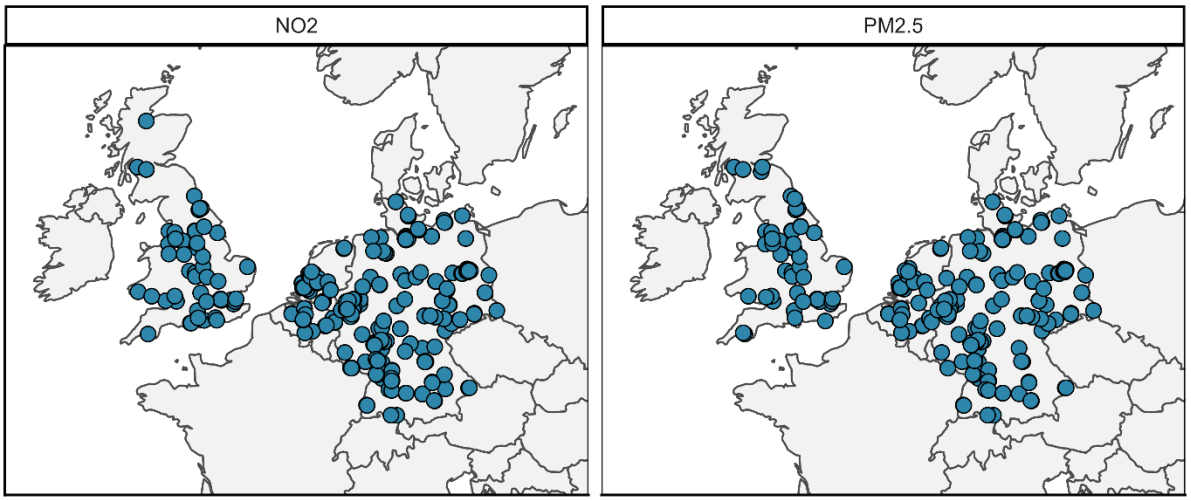

Figure S1. Map of NO2 and PM2.5 monitoring sites across the UK and Europe.

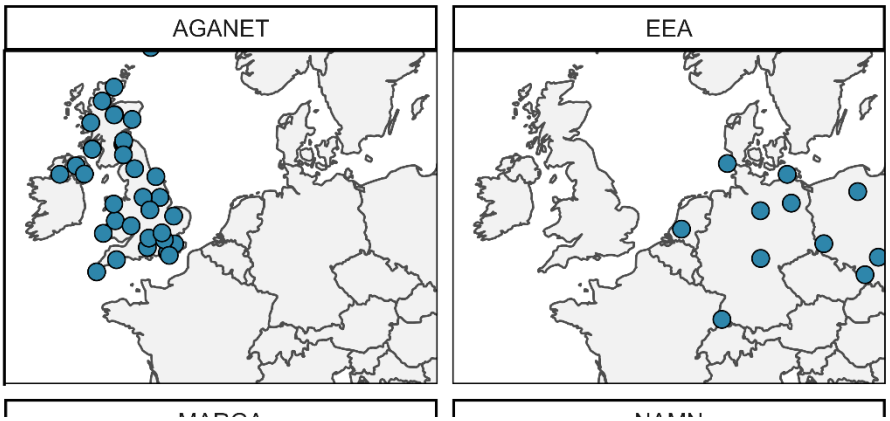

Figure S2. Map of aerosol compositional network sites across the UK and Europe.

Figure S3 – Map of UK sites used in HYSPLIT analysis.

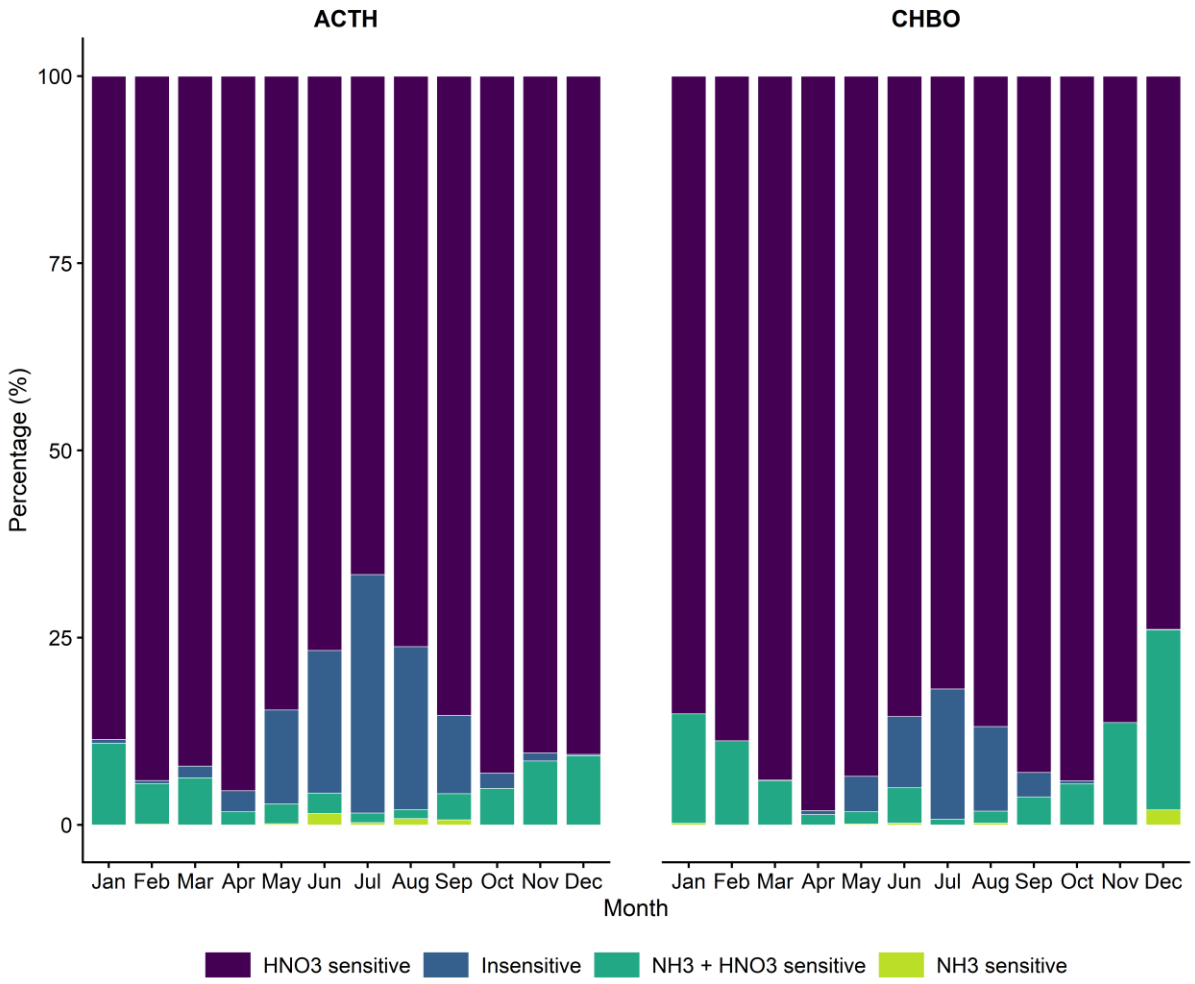

Figure S4. Monthly distribution of ISORROPIA-II thermodynamic sensitivity regimes at Auchencorth Moss and Chilbolton Observatory. Stacked bars show the percentage of modelled observations assigned to each thermodynamic regime within each calendar month, illustrating the seasonal variation in aerosol sensitivity to precursor availability at the two rural supersites.

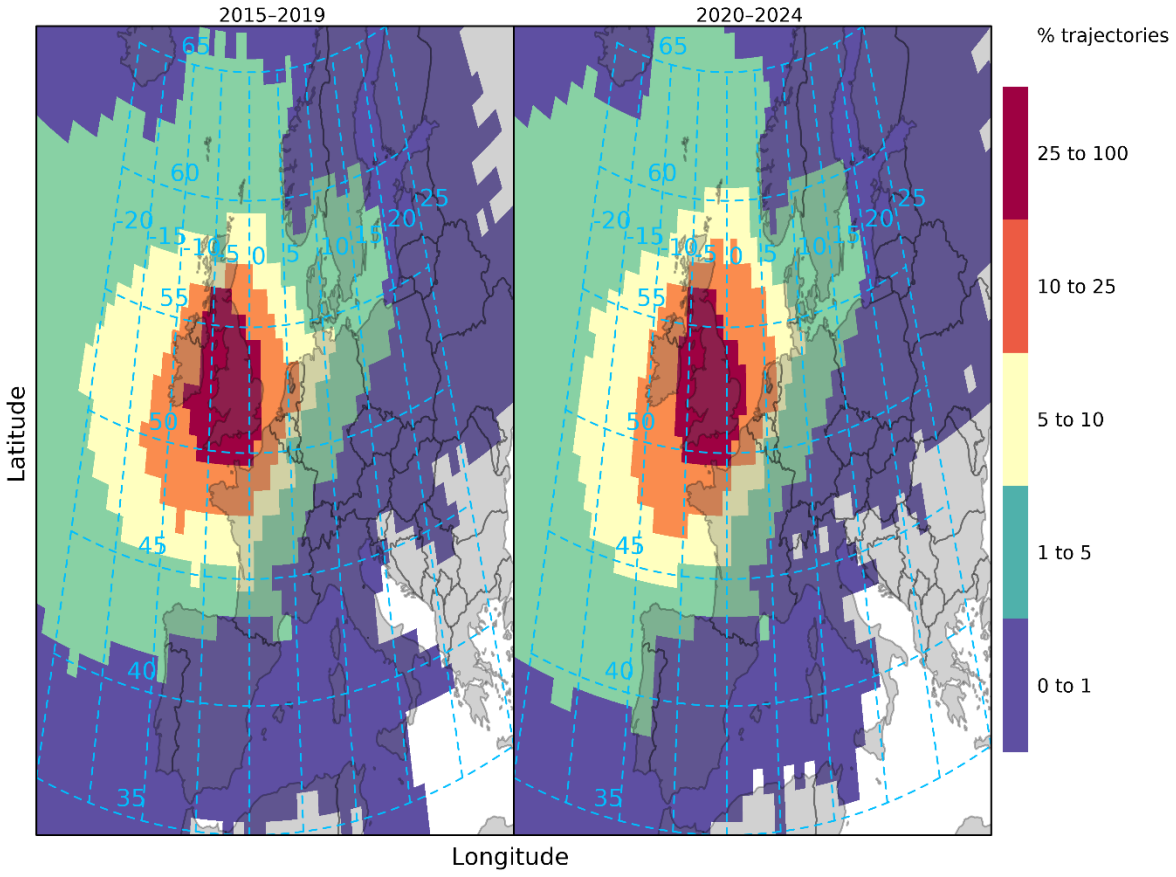

Figure S5. Spatial distribution of trajectory frequency for air masses arriving at the 14 UK PM2.5 monitoring sites during **(a)** 2015-2019 and **(b)** 2020-2024. Back trajectories from all sites were combined and mapped onto a common spatial grid, with colour indicating the frequency with which trajectories passed through each grid cell. The two periods are shown using a common colour scale to allow direct comparison of transport pathways and geographical coverage before and after 2020.

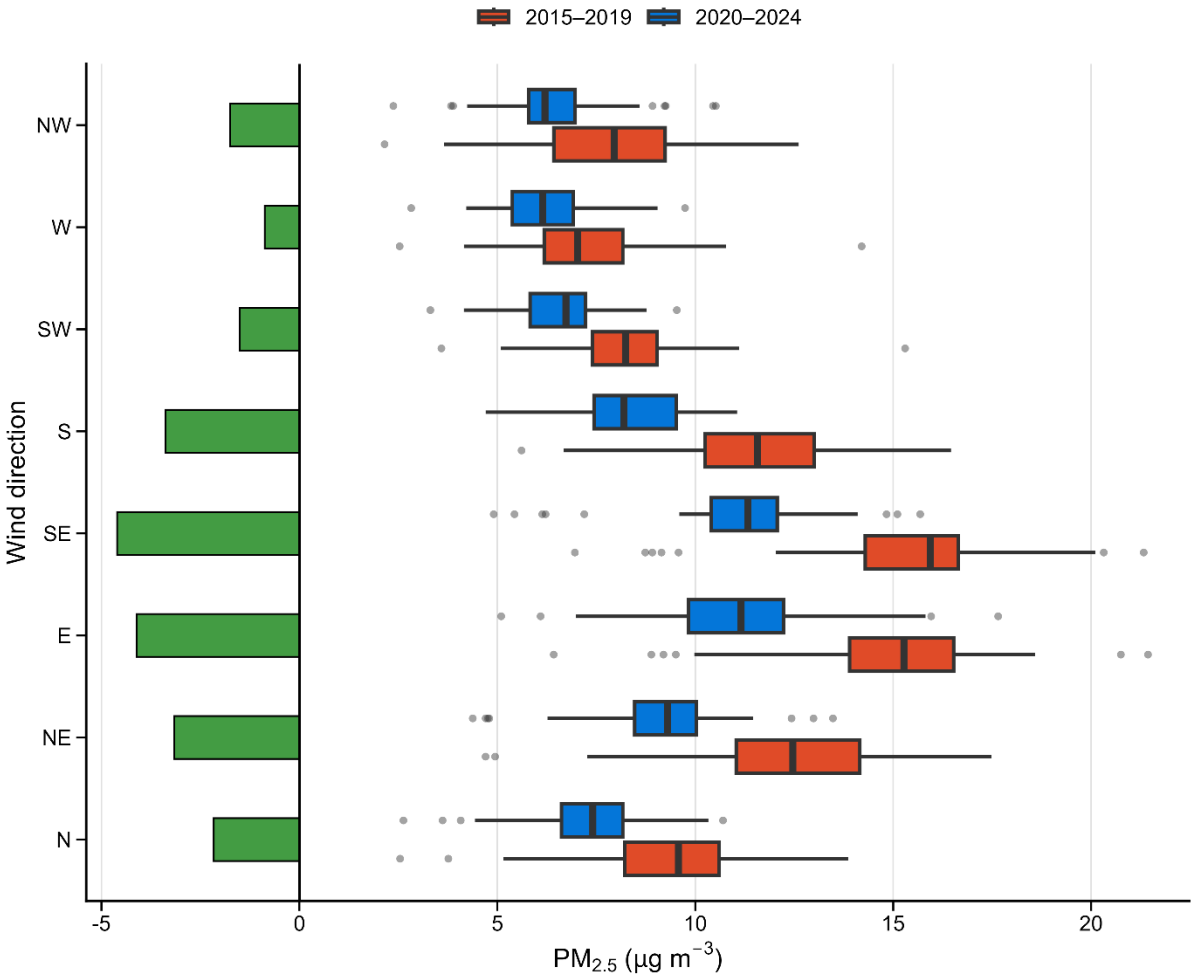

Figure S6. Distribution of site-level mean PM2.5 concentrations by wind direction for 2015-2019 and 2020-2024 across the UK monitoring network. Boxplots show the distribution of mean PM2.5 concentrations across sites within each wind-direction sector. Green bars show the change in the median site-level PM2.5 concentration between the two periods, calculated as 2020-2024 minus 2015-2019; negative values therefore indicate lower PM2.5 concentrations in the later period.

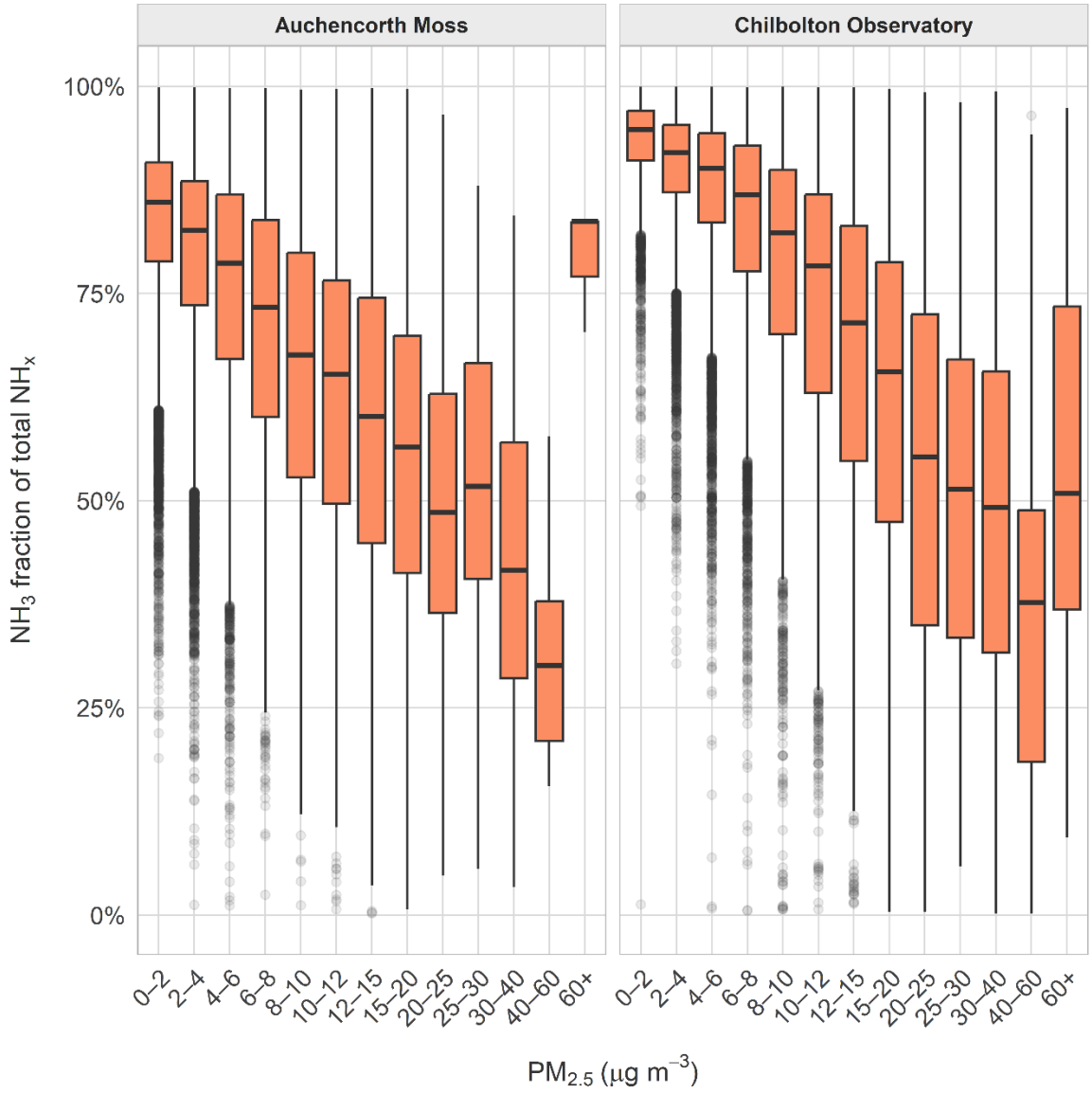

Figure S7. Relationship between the gas-phase fraction of total reduced nitrogen (NHx) and PM2.5 concentration at Auchencorth Moss and Chilbolton Observatory between 2016 and 2024. The NH_3 fraction is calculated as NH3/(NH3 + NH_4^+), representing the fraction of total NHx present in the gas phase. Lower values therefore indicate a greater proportion of reduced nitrogen partitioned to particulate ammonium.

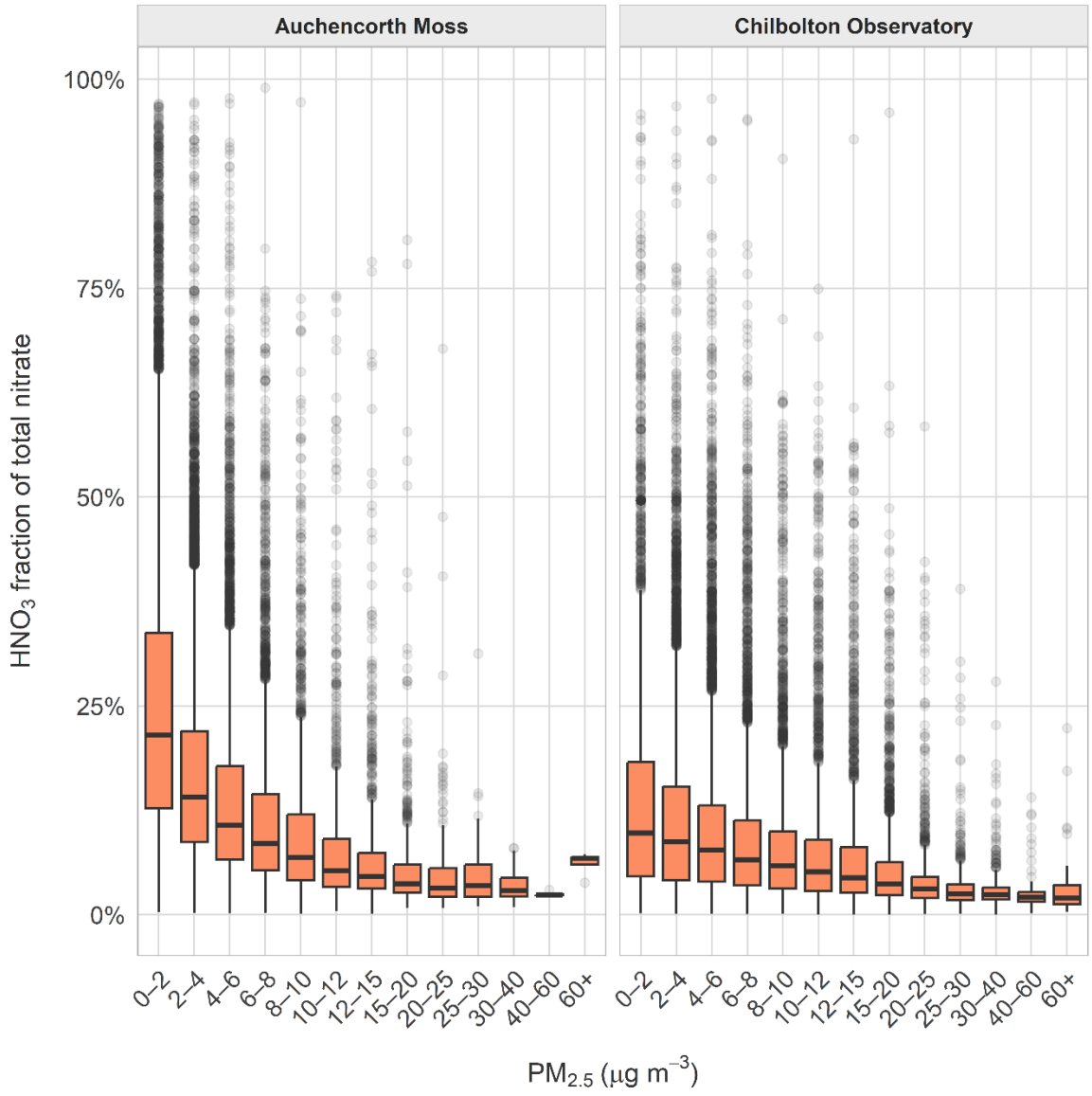

Figure S8. Relationship between the gas-phase fraction of total nitrate and PM2.5 concentration at Auchencorth Moss and Chilbolton Observatory between 2016 and 2024. The HNO_3 fraction is calculated as $HNO_3/(HNO_3 + NO_3^-)$, representing the fraction of total nitrate present in the gas phase. Lower values therefore indicate a greater proportion of total nitrate partitioned to particulate nitrate.

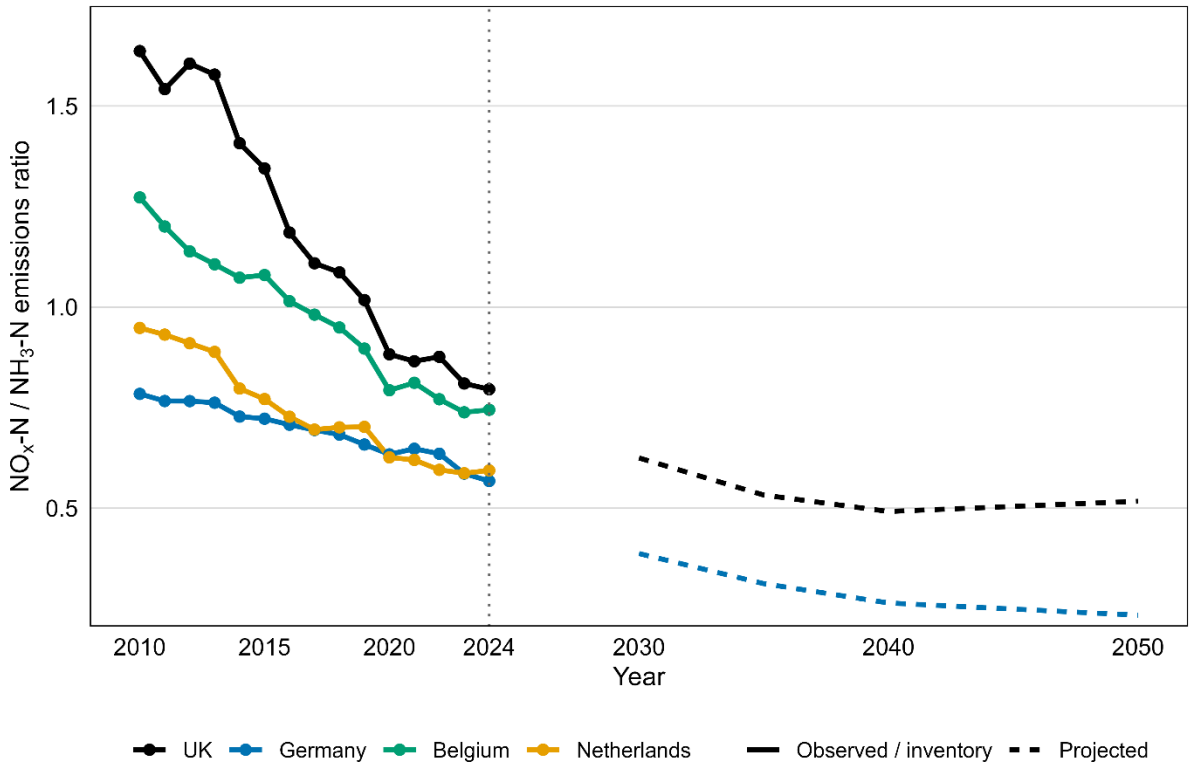

Figure S9. Temporal evolution of the NOX-N to NH3-N emissions ratio in the UK, Germany, the Netherlands and Belgium. Reported NOx and NH_3 emissions were converted to equivalent nitrogen mass before calculating the ratio (NO_x-N/NH_3-N). Lower ratios indicate a declining abundance of oxidised nitrogen emissions relative to reduced nitrogen emissions. Solid lines show historical inventory estimates and dashed lines show projected emissions.