

Guidance documents on measurements and
modelling of novel air quality pollutants:

Ammonia (NH_3)

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Research Infrastructures Services Reinforcing Air Quality Monitoring Capacities in European Urban & Industrial Areas (RI-URBANS)

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Table of Contents

ABBREVIATIONS.....	I
CHEMICAL SPECIES.....	II
1. ABOUT THIS DOCUMENT	1
2. AMMONIA IN AMBIENT AIR	2
2.1. FORMATION OF SECONDARY PM	2
2.2. EFFECTS ON ECOSYSTEMS	3
2.3. AMMONIA EMISSIONS.....	3
3. METHODS AND QUALITY CONTROL OF AMMONIA MEASUREMENTS	5
3.1. INTRODUCTION TO OFF-LINE METHODS	5
3.2. INTRODUCTION TO ON-LINE METHODS	6
3.3. PROS AND CONS OF THE METHODS	7
3.4. STATE OF HARMONISATION	8
3.5. DESCRIPTION OF METHODS FOR THE DETERMINATION OF AMMONIA	9
3.5.1. <i>Offline methods</i>	9
3.5.1.1. Passive samplers (CEN method).....	9
3.5.1.2. Denuder method (EMEP)	10
3.5.1.3. Filter pack method (EMEP)	11
3.5.2. <i>Real-time and near real-time methods</i>	11
3.5.2.1. Near real-time techniques	12
3.5.2.2. Real-time techniques	13
3.6. QUALITY CONTROL, QUALITY ASSURANCE AND MEASUREMENT UNCERTAINTY.....	16
3.7. DATA MANAGEMENT	17
4. PAN-EUROPEAN OVERVIEW OF AMMONIA CONCENTRATIONS ACROSS URBAN ENVIRONMENTS.....	18
4.1. INTRODUCTION.....	18
4.2. METHODOLOGY.....	18
4.2.1. <i>NH₃ data compilation</i>	18
4.2.2. <i>Interannual trends of urban and regional NH₃ in Europe</i>	21
4.3. LEVELS OF NH ₃	21
4.3.1. <i>Spatial variability of concentrations</i>	21
4.3.1.1. Concentrations of NH ₃ out of the farming/agricultural hotspots (non-FAHs)	21
4.3.1.2. Concentrations of NH ₃ in the farming/agricultural hotspots (FAHs).....	22
4.3.2. <i>Diel and seasonal patterns</i>	24
4.3.3. <i>Inter-annual trends</i>	25
5. RECOMMENDATIONS AND MAIN FINDINGS	28
5.1. RECOMMENDATIONS ON MEASUREMENTS, QUALITY CONTROL AND DATA MANAGEMENT	28
5.1.1. <i>Sampling system</i>	28
5.1.2. <i>NH₃ measurements</i>	30
5.2. INSTRUMENT PERFORMANCE, MAINTENANCE AND QUALITY CONTROL.....	31
5.3. CALIBRATION INFRASTRUCTURES	32
5.4. DATA MANAGEMENT	33
5.5. MAIN FINDINGS FOR NH ₃ IN URBAN EUROPE	33
5.5.1. <i>Instrument and data management</i>	33
5.5.2. <i>Concentrations of NH₃</i>	33
5.5.3. <i>Inter-annual concentration trends</i>	35
6. REFERENCES	35

Abbreviations

ACTRIS	Aerosols, Clouds and Trace gases Research InfraStructure
AMOR	Ammonia monitor
AQ	Air quality
BC	Black carbon
BrC	Brown carbon
CEN	European Committee for Standardization
CLD	Chemiluminescence Detector
CLe	Critical levels
CRDS	Cavity ring-down spectroscopy
DOAS	Differential optical absorption spectroscopy
EBAS	A database infrastructure developed and operated by Norwegian Institute for Air
EEA	European Environmental Agency
EMEP	European Monitoring and Evaluation Programme
EN	European Standard
EU	European Union
EURO	European emission standards
FAH	Farming/agricultural NH ₃ hotspots
FIA	Flow injection analysis
FTIR	Open-path Fourier transform infrared systems
GC-MS	Gas chromatography mass spectrometry
HFOC	High-finesse optical cavity
IC	Ion chromatography
IND	Industry
LOD	Limit of detection
NRT	Near real-time
OA-ICOS	Off-axis cavity output spectrometer
OF-CEAS	Optical-feedback cavity-enhanced absorption spectrometers
OP	Oxidative potential
PM	Particulate matter
PM_{2.5}	Mass concentration of particles <2.5 µm in diameter
PPWD	Parallel plate wet denuder
QA/QC	Quality assurance and quality control
QCLAS	Quantum cascade laser absorption spectrometers
RB	Regional background
RBCH	Regional background station close to hotspots
RI-URBANS	Research Infrastructures Services Reinforcing Air Quality Monitoring Capacities in
RT	Real-time
SCR	Selective catalytic reduction
SIA	Secondary inorganic aerosols
SUB	Sub-urban background
TR	Traffic
UFP	Ultrafine particles
UNECE	United Nations Economic Commission for Europe
VOC	Volatile organic compound
WHO	World Health Organization

Chemical species

CO₂	Carbon Dioxide
EC	Elemental carbon
H₂SO₄	Sulfuric acid
HNO₃	Nitric acid
N	Nitrogen
NH₃	Ammonia
NH₄	Ammonium
NH₄NO₃	Ammonium nitrate
(NH₄)₂SO₄	Ammonium sulphate
NO₂	Nitrogen dioxide
NO₃⁻	Nitrate
NO_x	Nitrogen oxides (NO+NO ₂)
SO₂	Sulphur dioxide
SO₄²⁻	Sulphate

1. ABOUT THIS DOCUMENT

This document was prepared as part of the "Research Infrastructures Services Reinforcing Air Quality (AQ) Monitoring Capacities in European Urban & Industrial AreaS" (RI-URBANS) EU-project that connects the atmospheric observation expertise from the Aerosols, Clouds and Trace gases Research InfraStructure (ACTRIS) with the urban air quality observation capacities of the regulatory air quality monitoring networks. This document summarises the guidance for ammonia measurements, and it is specifically connected to the European AQ Directive (AQD) 2024/2881/EC published on 20th November 2024.

It is important that pollutants of emerging concern, such as ultrafine particles (UFP), black carbon (BC) and elemental carbon (EC), as well as ammonia (NH₃) and the oxidative potential (OP) of particulate matter (PM), be monitored to support scientific understanding of their effects on health and the environment.

To ensure that the information collected on air pollution is sufficiently representative and comparable across the European Union, it is important that standardised measurement techniques and common criteria for the number and location of measuring stations are used for the assessment of ambient air quality.

In the EU AQ Directive 2024/2881/EC, measurements of NH₃ are requested for rural supersites, and measurements at urban supersites are only recommended. However, in the urban pollution hotspots measurements of NH₃ are very relevant to evaluate possible effects of AQ policy actions to abate fine particulate matter (PM_{2.5}), since this pollutant has a key role in the generation of secondary PM.

This is a RI-URBANS guidance for this specific service tool (measurements of ammonia) that is part of the RI-URBANS deliverable D46 (D6.1, containing guidance for all service tools provided in the project) with the support for publication from AXA Research Fund to build up the final dissemination D55 (D7.6). Any dissemination of results must indicate that it reflects only the authors' view and that the European Commission is not responsible for any use that may be made of the information it contains.

2. AMMONIA IN AMBIENT AIR

Ammonia (NH_3) is an alkaline gaseous pollutant of high relevance for AQ. Ammonia affects AQ negatively by increasing the formation of secondary PM and by negatively impacting on sensitive ecosystems.

2.1. Formation of secondary PM

In the urban background areas of European cities, 70% of the $\text{PM}_{2.5}$ arise from secondary inorganic (SIA) and secondary organic aerosols (SOA) (Amato et al., 2016). Emitted sulphur dioxide (SO_2) and nitrogen oxides (NO_x) undergo atmospheric oxidation reactions that generate gaseous sulphuric (H_2SO_4) and nitric acid (HNO_3). Once formed, these react with NH_3 to generate ammonium sulphate (NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$) and ammonium nitrate (NH_4NO_3), two major components of $\text{PM}_{2.5}$ (Figure 1). $\text{PM}_{2.5}$ reduction can become challenging with increasing (or stable) NH_3 concentrations, in situations where NH_3 availability is the limiting factor in SIA formation (i.e. HNO_3 is in excess). Furthermore, NH_3 might interact with volatile organic compounds (VOCs) and SOA to produce NH_4^+ -bearing SOA (Hao et al., 2020, and references therein), which contributes to increase the aerosol radiative forcing (brown carbon, BrC; Bones et al., 2010) and to stabilize SOA in PM (Paciga et al., 2014). It has been demonstrated the abating NH_3 emissions is a cost-effective measure for mitigating $\text{PM}_{2.5}$ (Gu et al., 2021). Furthermore, Lelieveld et al. (2015) attributed premature mortality to NH_3 -derived SIA in Europe, Russia and East Asia, assuming all particles are of equal toxicity. Although in some cases, $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 in $\text{PM}_{2.5}$ are considered as the PM components with the lowest potential for health effects, WHO (2013) stated that there is no evidence to exclude health effects for these components.

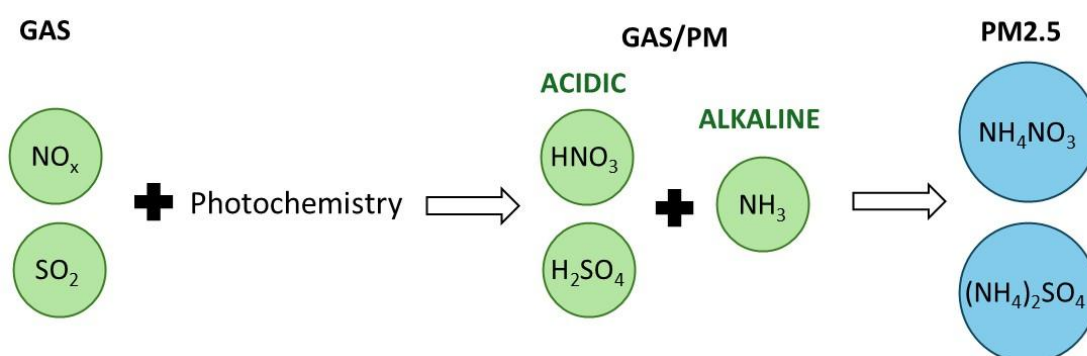


Figure 1: Atmospheric processes yielding to the formation of secondary inorganic $\text{PM}_{2.5}$.

2.2. Effects on ecosystems

According to Krupa (2003), acute exposures to high concentrations of NH_3 can lead to foliar injury on vegetation, when the rate of foliar uptake of NH_3 is greater than the rate and capacity for in vivo detoxification by the plants. The sensitivity of these effects follows native vegetation > forests > agricultural crops. According to the same review, adverse effects of NH_3 on higher plants include alterations in growth and productivity, tissue content of nutrients and toxic elements, drought and frost tolerance, responses to insect pests and disease-causing microorganisms (pathogens), development of beneficial root symbiotic or mycorrhizal associations and inter species competition or biodiversity, in addition to direct injuries.

Nitrogen (N) deposition, including NH_3 and counterpart aerosol species ($(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3), are known to result in negative effects to sensitive ecosystems (e.g. eutrophication). To abate these, critical loads are set defined as “a quantitative estimate of exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present day knowledge” and are used to inform policy makers to identify where exceedances occur in our natural environment (Nilsson and Grennfelt, 1988). For N critical loads, both dry (gas, aerosol) and wet (precipitation, fog, snow) deposition of all atmospheric N species are included, with NH_3 dry deposition often being a major component (Bobbink et al., 2022; Hettelingh et al., 2017).

Unlike the air quality criteria pollutants, NH_3 does not have Air Quality Standards in Europe. However, recommended thresholds have been proposed (Bobbink et al., 2022; UNECE, 2007; Cape et al., 2009), and a number of Member States adopted thresholds for the protection of vegetation. Thus, UNECE long-term Critical Levels (CLE) have been set to $1 \mu\text{g}/\text{m}^3$ for lichens and bryophytes, and $3 \mu\text{g}/\text{m}^3$ for higher plants, above which an ecosystem is at risk of potential harmful effects. Furthermore, it has been suggested by Franzaring and Köstler (2022) that the protective effect of this long-term UNECE CLE cannot be assumed for long periods of more than 20 to 30 years, and a maximum monthly value of $12 \mu\text{g}/\text{m}^3$ should be also applied.

2.3. Ammonia emissions

In the European Union 27 nations (EU-27), agriculture is the major source contributing to the EU-27 NH_3 emission inventory, with 94% of the total NH_3 emissions in 2020, while other sources such as

industry, road transportation, and solid waste management contribute with around 1% each (EEA, 2022). However, in urban and industrial areas, where SO₂ and NO_x emissions are high, high NH₃ concentrations from local sources might contribute to the increase of PM_{2.5} at local scale. Relevant urban sources of NH₃ are waste management, traffic and fugitive emissions from sewerage systems (Reche et al., 2012, 2015; Pandolfi et al., 2012).

Van Damme et al. (2018) evidenced very large and intense NH₃ pollution hotspots in Europe using remote sensing. These were in locations such as the Po Valley in northern Italy, eastern and central Spain, Netherlands and Germany, and these were attributed to agricultural emissions. Van Damme et al. (2021) estimated roughly a 13% rise in global NH₃ concentrations between 2008 and 2018. However, Tichý et al. (2023) found that NH₃ emissions peaked over Eastern Europe (industrial activity) and over Spain (pig farming). Their calculations show that these emissions decreased by 26 % from 2013 to 2020. These decreasing emissions are not reflected in ambient NH₃ concentrations. Aas et al. (2024) interpreted that the increase in ambient NH₃ background concentrations in Europe during the last decade, which was opposite to the slight downward trend of NH₃ emissions, was due to a progressive decrease in the atmospheric NH₃ sink to generate (NH₄)₂SO₄ and NH₄NO₃ due to the marked decreases in the emissions of SO₂ and NO_x. While the EU-27 emissions of PM_{2.5} and PM₁₀ declined from 2005 to 2020 by 30% and 32%, respectively (according to inventories), NH₃ only underwent a modest reduction of only 8% (EEA, 2022). Furthermore, in the EMEP domain as a whole, NH₃ emissions have increased by 12% since 2000 (Aas et al., 2024). As discussed by Tichý et al. (2023), the discrepancies in trends in NH₃ concentrations arise from differences between top-down and bottom-up methodologies. This clearly underlines the need of establishing and maintaining harmonized gas phase ammonia measurements in Europe.

In urban areas, the contribution of NH₃ derived from traffic sources could increase due to the widespread implementation of selective catalytic reduction (SCR) NO_x-controls in the new EURO 6/VI diesel vehicles (Hopke and Querol, 2022), which uses urea or NH₃ as catalysts to reduce NO₂ tail-pipe emissions. In fact, Reche et al. (2022) reported increases in roadside NH₃ concentrations in Barcelona in 2011–2020 attributed to the increase of emissions from traffic and waste management.

3. METHODS AND QUALITY CONTROL OF AMMONIA MEASUREMENTS

Measurements of NH₃ concentrations are severely limited, with most measurements taking place in rural background sites. Measurements at NH₃ hotspot regions, and in urban areas, are relatively scarce. Measurements fall into two categories, offline measurement methods and online measurement methods. For now, there is no standardised method available for online monitoring methods, but several techniques are routinely being used to quantify NH₃ concentrations.

3.1. Introduction to off-line methods

Passive samplers are based on trapping NH₃ by passive (without pumping) sampling onto a media, to collect an integrated NH₃ amount over a chosen sampling time. As there is no active sampling, this approach requires a longer sampling time to achieve a sufficient NH₃ mass to be successfully detected by the analytical method; however, the exposure time varies as it is dependent on sampler design, ambient air concentration and detection limit of the analytical method. There is a European standard method (CEN) available: EN 17346:2020, Ambient air – Standard method for the determination of the concentration of ammonia using diffusive samplers (CEN, 2020).

In addition to passive samplers, active sampling methods have been routinely used for decades to report time integrated average concentrations of NH₃ in monitoring networks. The European Monitoring and Evaluation Programme (EMEP) recommends using denuders for NH₃ measurement and describes the method in the EMEP Manual (EMEP, 2014). In the United States, a US EPA measurement protocol for NH₃ using daily sampling with denuders is available (US EPA, 1999). In both methods, a known air volume is drawn through denuders chemically impregnated to trap NH₃. In EMEP there is also an alternative method described, which reports the sum of ammonia and ammonium (NH₃+NH₄⁺) by using chemically coated filters. A recent EMEP report on measurements (EMEP, 2023) shows that in 2021 at rural stations, denuders were only used by two countries, whereas the filter pack approach is by far the most common method used (16 countries). In a few cases, passive samplers, Differential Optical Absorption Spectroscopy (DOAS) and online ion chromatography were also used in EMEP.

The active and passive sampling with offline analysis, depending on the integrating time, can involve high labour costs for sampling and analysis (e.g. when daily changes are undertaken). Also, the low time resolution from several hours to week(s) limits the scope of the data. These approaches,

however, are often very useful for monitoring inter-annual and long-term trends. In the case of passive samplers, their relative lower cost offers also a good possibility to obtain detailed spatial variations of NH₃ concentrations.

3.2. Introduction to on-line methods

To obtain higher time resolution, there were important developments in the measurements of NH₃. Earlier near-real-time (NRT) monitoring methods were based on continuous collection in aqueous solution and in situ online analysis. According to Twigg et al. (2022), NRT wet chemistry approaches require specialist operators and are labour intensive; however, calibration and quality assurance are accurate and simple, as they employ, e.g., traceable liquid calibration standards and control sample solutions that are routinely used by laboratories. The challenge is for elevated concentrations, as all NH₃ might not be captured by the sampler, and some interferences (for example, volatile amines in flow injection analysis, Wyers et al., 1993) in the method system might affect measurements.

In the last two decades important advances have been made in spectroscopic methods, reporting concentrations in real time (RT). These include the following methods (Twigg et al., 2022; Franzaring and Köstler, 2022; and references therein):

- Differential Optical Absorption Spectroscopy (DOAS)
- Quantum Cascade Laser Absorption Spectroscopy (QCLAS)
- Cavity Ring-Down Spectroscopy (CRDS)
- Off-axis integrated cavity output spectroscopy (OA-ICOS)
- Optical-Feedback Cavity-Enhanced Absorption Spectroscopy (OF-CEAS)
- Open-Path Fourier Transform Infrared Systems (FTIR)
- Photoacoustic spectroscopy (PAS)
- Chemiluminescence spectroscopy (CLD)

At this stage, none of the methods might be recommended, all of them having their advantages and disadvantages.

Out of the above-mentioned methods, CRDS systems have been introduced in the last decade in a number of sites for routine air quality measurements in France, supported by French metrology institutes for instrument calibration (Macé et al., 2022). There are also other methods available that have been used at other sites in Europe, as summarized by a recent overview (Liu et al., 2024).

3.3. Pros and cons of the methods

Figure 2 shows a classification of the NH₃ measurement methods as a function of the Real Time (RT), or Near-Real Time (NRT) vs. offline approaches, and pre-concentration vs. no pre-concentration, but also considering the analytical procedure, the passive or active sampling and the type of sampling and sorbent.

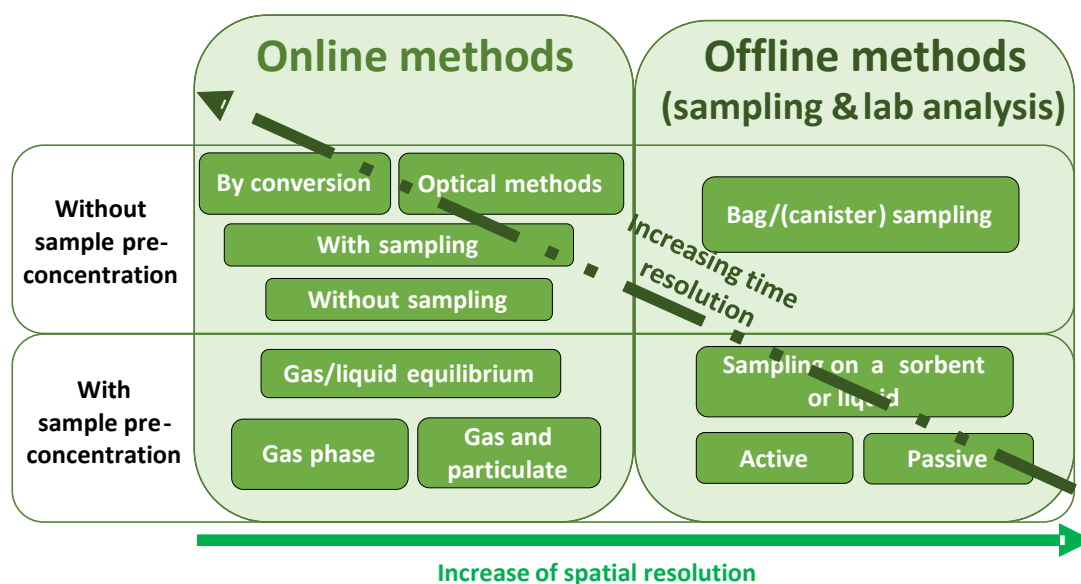


Figure 2: Classification of methodologies for measuring NH₃ concentrations (modified from Crunaire, 2024). Bag and canister samples are not used in AQ monitoring but may be suitable for other applications.

Offline measurements tend to be cheaper, and more sampling sites might be included in the NH₃ monitoring network. Thus, passive sampling followed by offline analyses tend to be used to evaluate spatial gradients and long-term trends, while the NRT and RT approaches are usually selected when high time resolution are required, e.g. for source apportionment and especially to supply atmospheric process information for models (Franzaring and Kössler, 2022; Twigg et al., 2022).

An international initiative comparing different active and passive analysers was set up within the European MetNH₃ (Metrology for NH₃ in ambient air) project. One of the work packages of the MetNH₃ project evaluated NH₃ passive samplers. Samplers were tested in the UK's National Physical Laboratory's (NPL) controlled atmosphere test facility (CATFAC) and at the Scottish Whim Bog Experimental site. The inter-comparisons between different sampler types have been presented by Braban et al. (2018) and Martin et al. (2019). Expanded uncertainty of the passive samplers tested varied between 11 and 23 % at the reference concentration of 1 µg/m³, i.e. a concentration

representative for the lower critical level. A specific passive sampler proved to be the best suited for the lower concentration ranges with an exposure time of ~28 days, whereas other samplers were typically designed to be used to for shorter exposure periods. The passive sampler in question is also used in short term studies but for the purpose of the uncertainty work by Martin et al. (2019) was only exposed for 28 days. At higher concentrations it is suggested a shorter exposure period not to saturate the sampler.

The overview of NH₃ measurement protocols and comparisons of their performance recently supplied by Twigg et al. (2022) is the basis of the following sections on NRT and RT measurements. The current reference protocols were first developed >20 years ago, but important instrumental developments have taken place since then. Twigg et al. (2022) inter-compared 13 instruments in a field study in Scotland including passive samplers, near-real-time and real-time analysers. They found a relatively good agreement for high concentrations (up to near 200 µg/m³ NH₃), but the comparability decreased for concentrations <7 µg/m³. This was the case even for duplicate instruments, and this highlights the impact of the setup, inlet design, and operation (external pump, inlet length, maintenance, filter ageing) on the reported concentrations. Accordingly, instrument set-ups that do not need to use an (active) sampling inlet or inlet filter have an advantage. They also found that the use of reference standards for calibration is limited by losses of NH₃ to the surfaces of the inlet and the instrument. They recommended regular calibrations as well as zero and span checks to be undertaken at a frequency determined by the operational need in the location of the measurements as part of routine QA/QC for any short- or long-term deployment. Thus, if high PM and NH₃ are expected, higher frequency for maintenance and cleaning inlets will be needed. Twigg et al. (2022) concluded that even though instrumentation for ambient air NH₃ measurements have greatly progressed in measurement precision, further work is still required to improve accuracy and therefore the equivalency of NH₃ instruments under field conditions.

3.4. State of harmonisation

The EU legislation does not describe a reference method for the measurement of NH₃. However, guidance is given by the EMEP Programme for sampling and subsequent offline analysis of active sampling methods. These methods are commonly used at a number of air quality monitoring sites around the world but are usually applied at regional background sites.

Furthermore, a CEN standard exists only for passive sampling of NH₃ (EN 17346:2020); however, as various protocols exist for measuring NH₃ using passive samplers, the CEN standard is not always followed when conducting these measurements.

No standardised protocols are available for NRT or RT NH₃ measurement methods, covering both sampling, instrument operations and data handling to ensure high quality data is achieved. There are several European initiatives, including the aforementioned MetNH₃ project (ENV MetNH₃, 2017), QuantiAgremi project (EMRP, 2024) and the AMICA project (Chelin et al., 2024), that are working towards improving the accuracy and precision of the NRT and RT methods. These include the development of calibration techniques of RT analysers by national metrology institutes (LNE, France, and METAS, Switzerland, Macé et al., 2022; NPL, UK, Martin et al., 2016), guidance for passive sampler and CRDS automatic analysers (LCSQA, 2022; Martin et al., 2016, 2019), and inter-comparison in the laboratory (LCSQA, 2021) or in the field (Martin et al., 2019; Twigg et al., 2022; Chelin et al., 2024).

3.5. Description of methods for the determination of ammonia

3.5.1. Offline methods

For offline analyses of NH₃, passive samplers and denuders are suitable sampling methods. Also, impregnated filters are used for semi-quantitative NH₃ measurements. The passive sampling method is described in detail in EN 17346 (CEN, 2020), while the denuder and filter methods are described in the EMEP Manual (EMEP, 2014).

3.5.1.1. *Passive samplers (CEN method)*

There are different types of passive samplers available that collect NH₃ quantitatively. In this chapter, the description is limited to the CEN method (EN 17346:2020), which already describes several sampler types.

This technique is based on diffusion, where the sampler is exposed to ambient air for a defined time period enabling gaseous NH₃ to migrate through the sampler along a diffusion path of defined dimensions and to be collected by reaction onto an acid sorbent. It is essential to determine the sampling rate, and this can be done experimentally. Typically, manufacturers provide this information and there is literature available (Martin et al., 2019), but it is good practice to calculate a locally applicable sampling rate.

The different types of samplers include tube-type, badge-type, and radial samplers that have different dimensions. A common feature for these is the acidic sorbent and the analytical technique. The sorbent may be citric, phosphoric, phosphorous, sulphuric or tartaric acid, depending on the sampler and climate. Possible analytical techniques include ion chromatography (IC), spectrophotometry and flow injection analysis (FIA).

Passive samplers are typically deployed for one to several weeks, and thus a major drawback of the method is the limited time resolution. However, they are small, relatively inexpensive and do not need electricity which makes them an attractive choice when long term trends are to be monitored. The technique requires laboratory facilities for sample analysis and careful control of the blank levels.

3.5.1.2. *Denuder method (EMEP)*

The EMEP Manual (EMEP, 2014) describes the denuder method, which quantitatively collects NH_3 . Before sampling, the thoroughly cleaned denuder tube is coated with an acidic sorbent (citric acid, oxalic acid, or phosphorous acid) in the laboratory. During sampling, the air sample is drawn through the denuder with a known sampling volume and the gaseous NH_3 is absorbed onto the denuder coating. The denuder is made of glass and is capped before and after sampling to ensure the integrity of the sample. In the laboratory, the denuder is extracted with a known volume of solution and the extract is analysed for NH_4^+ content by an analytical method. The recommended analytical techniques include ion chromatography and spectrophotometry (e.g., with the indophenol blue method).

In the EMEP method, the sampling system composes of three denuders in series with a filter pack at the back of the system (refer to section 3.5.1.3 below) to collect other compounds of interest in addition to NH_3 . In this system, the first two denuders are used for the collection of acid gases (HNO_3 and SO_2), and the third one for NH_3 , while the filter pack is used for the measurement of chemical composition of PM, including the counterpart particulate species of the reactive gases measured (including NH_4^+).

With this method, the recommended sampling frequency is daily. However, this technique is labour intensive due to the sampling frequency and therefore can be expensive to operate. The quality control procedures need to be rigorous to control especially the blank level. A less expensive

denuder method tuned for monthly sampling is also available (Tang and Sutton, 2007), and it is endorsed by the EMEP Programme.

3.5.1.3. *Filter pack method (EMEP)*

In the EMEP Programme, concentrations of gaseous NH_3 , and of NH_4^+ in PM, are typically measured with the filter pack method where the filter is impregnated with either oxalic or citric acid, which will trap the gaseous NH_3 on the filter when a known air volume is drawn through the filter pack. With this method, other gaseous and PM pollutants are commonly measured at the same time including, e.g., SO_2 , SO_4^{2-} , and NO_3^- , using a filter pack system composing of 2–3 filters in line. When a three-stage filter pack is used, the first filter is used to collect particles, the second filter impregnated with potassium hydroxide to collect HNO_3 and SO_2 , and the third one is for collecting NH_3 . If a 1-stage filter pack is used for NH_3 sampling using the impregnated filter, it will collect both NH_3 and NH_4^+ together with other PM components; thus, it is suggested to use a multistage filter pack including a particulate filter in front of the NH_3 filter. The recommended sampling time is 24 h.

After sampling, the filter packs are sent to the laboratory for analysis. First, acid-impregnated filters are extracted with dilute HNO_3 , and the extract is analysed for NH_4^+ content (including both the collected NH_3 and the part of NH_4^+ in PM that has vaporised from the first filter). The recommended analysis techniques include ion chromatography and spectrophotometry (e.g., the indophenol blue method).

The method is fairly simple, and sampling parts and components are commercially available. The drawback of the method is that the method cannot fully separate NH_3 and NH_4^+ , even when a three-stage filter pack is used. This is due to the sampling artefact that originates from the volatile nature of NH_4NO_3 especially in warm temperatures when the NH_4^+ in PM evaporates from the first filter and is collected as NH_3 on the impregnated filter. Thus, only the sum of NH_3 and NH_4^+ is quantitatively collected. However, sometimes the filter pack data can explain the partition between the gaseous and PM relatively well. According to the EMEP manual, this may be valid in situations, e.g., where the concentration of gaseous NH_3 is usually high, or where the concentration of NH_3 is so low, that the partial pressure for NH_4NO_3 to be present is not reached.

3.5.2. Real-time and near real-time methods

There are a number of online methods for monitoring NH_3 concentrations, which can be split into either real-time (RT) and near real-time (NRT) measurements. For NRT, samples are collected over

a short period (minutes to 1 hour) and then analysed online by an analytical method resulting in a slight delay in the reported concentration (~15 minutes to 1 hour). For RT methods, the rate at which concentrations are reported are continuous at higher reporting frequency of 10 Hz to 1 min⁻¹ typically. There are a number of NRT and RT methods available. Below, the methods that have been identified as being applicable in routine monitoring of NH₃ concentrations are summarised.

3.5.2.1. *Near real-time techniques*

Near real-time methods use wet-chemistry approaches for the quantification of NH₃ in air. The basic approach is that NH₃ is collected in a solution as NH₄⁺ for a defined time period. The NH₄⁺ content is analysed, typically with either ion chromatography (IC) or flow injection analysis (FIA).

The online ion chromatography method is typically used for simultaneous monitoring of chemical composition of PM (e.g., sulphate, nitrate, ammonium, chloride, calcium, magnesium, potassium, and sodium) and specific water-soluble gases (e.g., ammonia, sulphur dioxide, nitric acid, and nitrous acid). First, water soluble gases are collected using either a wet rotating annular denuder (WRD) or a parallel plate wet denuder (PPWD), through which ambient air is drawn through, and any water-soluble gases passing are absorbed into the liquid. The remaining air stream is drawn through into a chamber containing steam, where hydrophilic aerosol particles undergo rapid growth (supersaturation) and are mechanically separated out with a cyclone. Both the gas and aerosols fractions are continuously collected and then sent to an IC for analysis. Typically, the systems are configured to have a one-hour sampling resolution. As one set of samples is collected, another set is analysed in turn by ion chromatography (typically both anion and cations simultaneously) in both the particulate and gas phases. This technique of online IC has been used by several networks in Europe and elsewhere for monitoring NH₃ (Makkonen et al., 2012; Markovic et al., 2012; Rumsey et al., 2014; Makkonen et al., 2014; Stieger et al., 2018).

The online flow injection analysis (FIA) method is typically used specifically to quantify NH₃. As with online IC methods, these systems either use a WRD (Wyers et al., 1993) or a selective diffusion membrane to capture NH₃ as NH₄⁺ in an absorbing solution (Erisman, 2001). The sample is then mixed with a sodium hydroxide solution, which converts the NH₄⁺ back to gas phase NH₃ to allow it to diffuse across a Teflon membrane into ultra-pure water. The conductivity of the sample is then measured and temperature corrected concentration of NH₄⁺ can be derived, from which the ambient NH₃ concentration can be calculated.

The advantage of both approaches is that calibrations are simple, as they can be undertaken with liquid standards. In some online IC systems, each sample is analysed with an internal standard, whereas in FIA and other online ICs, the system is regularly calibrated using a series of liquid NH_4^+ standards to produce a calibration curve.

The disadvantage to the wet chemistry approaches is that there is potential at elevated concentrations that not all NH_3 will be captured by the sampling system. In the FIA system, the approach is not ion specific and therefore it can potentially suffer interferences from other gas phase compounds such as amines (Wyers et al., 1993). To the authors knowledge there are no longer commercial suppliers of the FIA method.

3.5.2.2. *Real-time techniques*

There are several RT methods available on the market for routine monitoring of NH_3 concentrations. Below we briefly summarise the major RT techniques currently available. They can be divided into categories, i) open path systems, where the measurements are done directly in the atmosphere and ii) closed path systems where atmospheric samples are drawn into sampling system consisting typically of an inlet and detecting instrument, with an air pump downstream.

Open path systems:

Differential Optical Absorption Spectroscopy (DOAS) derives the concentration of NH_3 based on the absorption fingerprint of NH_3 in the ultraviolet. The basic system consists of a light source which sends a beam to a reflector (typically 20 m away), which sends the light back to the instrument containing a detector. The advantage of this approach is a contact free measurement, which therefore does not suffer losses of NH_3 to surfaces, on top of being highly sensitive and molecule specific. The disadvantage is that the calibration and the zeroing of the system can be challenging. It requires specialist operators to set-up the system with a clear line of sight between the source and reflector, to ensure accurate measurements. The approach has been successfully used for long term monitoring in Europe in rural sites (Berkhout et al., 2017) and has recently been applied in urban environment, too (Viatte et al., 2023).

Open-Path Fourier Transform Infrared Systems (FTIR) is another open path method, based on NH_3 molecular absorption in the infrared. The system basically operates in a similar manner as a DOAS in that there is a light source, and a reflector to send the beam back to the system detector. It has been utilized to quantify emissions from vehicles (Gieshaskiel and Clairotte, 2021).

Closed path systems:

Quantum Cascade Laser Absorption Spectrometers (QCLAS) derive concentrations of NH_3 by quantifying the unique absorption fingerprint of NH_3 within a specific region of the mid-infrared. Air is continuously drawn through a sampling cell which is under reduced pressure (typically 30 to 70 Torr). A monochromatic infrared light is produced using a quantum cascade laser. This light enters the cell and is reflected multiple times (McManus et al., 1995), prior to leaving the cell to reach a detector. The system produces an absorption spectrum, which is directly related to the path length of the light travelled and the concentration of NH_3 , based on Beer-Lambert law. The QCLAS has been implemented for atmospheric NH_3 measurements (Whitehead et al., 2007). The main advantage of this method is that it has a fast time response (up to 10 Hz, e.g. Whitehead et al., 2008), however it tends to require specialist operators and there is a large capital investment required to purchase these systems. Therefore, they tend not to be favoured for long term monitoring of NH_3 concentrations.

Off-axis integrated cavity output spectrometer (OA-ICOS) is similar to the QCLAS method, in that it determines the absorption spectrum of NH_3 within the infrared spectral region but there are differences in the spectral region used, design of the sample cavity and detection method. Air is drawn into a pressure-controlled cavity (100 Torr), with a laser directed into the inlet of the cavity and a detector on the gas outlet of the cavity. On each pass within the cavity, light will “leak”, allowing collection of a resolved, continuously scanned absorption spectrum. Details on the method can be found, e.g. in Baer et al. (2002) and Baer et al. (2012).

Optical-Feedback Cavity-Enhanced Absorption Spectrometers (OF-CEAS) again uses the principle of absorption spectroscopy utilising a laser that operates in the near infrared. The difference in this method is the design of the cavity. It contains three highly reflective mirrors within the sample cell (cavity), in order for the light to be reflected back and forth within the cavity. Details of this method can be found in Morville et al. (2005).

Cavity Ring-Down Systems (CRDS) like QCLAS derives concentrations by utilising the absorption of NH_3 molecule in the infrared region, however the IR region typically used by commercial models is different from QCLAS systems. In CRDS, the air is drawn through a cell but this time instead of the absorption of spectrum being produced, the concentration of NH_3 is quantified by allowing the light that enter the cell reflect multiple times on mirrors with the cavity to decay by periodically switching

off the laser. When NH_3 is in the cell, the time it takes the beam to decay decreases, as NH_3 absorbs the light, resulting in a ring-down time, which is the time taken for light to decay to $1/e$ of its original intensity. There are now a number of instruments on the market that have been used for monitoring of NH_3 based on this method (e.g. Lemes et al., 2023). The advantage of this method is that it is highly sensitive and easy to use, however it is an expensive to purchase.

Photoacoustic spectroscopy (PAS) utilises the absorption of NH_3 molecules in the infrared spectrum but instead of quantifying the absorbed light. Using a microphone, it measures the change in acoustic signal occurs when the molecules absorb the light and become excited, resulting in a change of pressure (von Bobrutzki et al., 2010; Twigg et al., 2022). Recent studies at agriculture sites, however, have presented evidence that it can suffer from interference of volatile organic compounds such as acetic acid (Liu et al., 2020). It is however noted that the concentration range studied by Liu et al. (2020) was much higher, as it was specifically investigating sources of NH_3 (in parts per million, ppm range).

The above methods all use absorption spectroscopy. The main advantage to these methods, in theory, is that they are calibration free methods as concentrations can be determined based on Beer-Lamberts law. They tend to be highly sensitive, molecule specific, and have low detection limit (Twigg et al., 2022; Ellis et al., 2010). There is evidence in the literature that depending on the infrared region used, there is a possibility of cross interferences from other atmospheric species such as water (H_2O), carbon dioxide (CO_2) and volatile organic compounds (VOCs) (Martin et al., 2016; Benedict et al., 2017; Kamp et al., 2019; Liu et al., 2020). In addition, there is some evidence that instruments can suffer from drift, which can impact the accuracy of the reported concentration (Twigg et al., 2022; Misselbrook et al., 2016).

Chemiluminescence detector (CLD) determines the concentration of NH_3 by first converting NH_3 to NO by passing air over a stainless-steel convertor. NO then undergoes a chemical reaction with ozone (O_3) resulting in the emission of light. The system typically calculates the NO concentration in one mode, then NO_2 in another mode. The system then calculates the NH_3 by subtracting the NO and NO_2 contributions. The advantage of this method is the capital costs tends to be lower than some spectroscopic methods above. The disadvantage is the conversion of NH_3 is not molecule specific and therefore there is a potential for other species to be reported as NH_3 (Fehsenfeld et al., 2002). Caution is recommended if this method is considered as it is not a direct measurement and there are potential artefacts in the reported concentration.

3.6. Quality control, quality assurance and measurement uncertainty

Since the methods for measuring NH_3 significantly differ, quality assurance and quality control (QA/QC) procedures also differ accordingly.

For the passive samplers, denuders and filter packs, the main QA/QC procedures include visual checks of the samplers, different type of blank samples (field, transport and laboratory blanks) as well as calibration and quality control in the laboratory (see EN 17346:2020 and EMEP 2014 Manual for details). Written instructions and documentation of work tasks in the field/laboratory in logbooks are essential to ascertain harmonized sampling in the field and analysis in the laboratory. Replicate sampling is recommended. For passive samplers, also the accuracy of the sampling rate of the diffusive sampler is crucial for the accuracy of the NH_3 measurement. For the denuders and filter packs, regular determination of the sample flow rate in the field with calibrated flowmeters is as important.

For the NRT methods, the main QA/QC procedures include regular blanks, internal standards and calibrations. An internal standard (e.g. LiBr) is used in some ion chromatography systems to calculate the concentration of NH_4^+ based on their specific conductivity (Van Os et al., 1984), as well as to check for drift in the detector response. For some online IC systems and FIAs, calibration can be conducted either manually or automatically (depending on the instrument capabilities) by using a set of ammonium standard solutions. In addition, monitoring the liquid sample and air sample flow rates is also essential to obtain accurate ambient air concentrations.

For RT methods, regular blanks and calibrations are essential, alongside routine maintenance protocols (Twigg et al., 2022). There are however no standard operating protocols, and the application of blanks, calibrations and maintenance protocol appears to vary across networks.

The calculation of measurement uncertainty is described in EN 17346:2020 for passive samplers. The EMEP Manual gives also guidance for determination of accuracy and precision of the denuder and filter pack methods. Generally, the measurement uncertainty using the offline methods is (or should be) calculated by the individual networks and is usually considered acceptable if the EN standard or the EMEP Manual is carefully followed.

The uncertainty of NRT methods is controlled by several factors including LOD, repeatability (accuracy), fluctuations of air flow rate, liquid sample volume and internal standard quality. Espina-Martin et al. (2022) outline the method to calculate uncertainty for NRT methods. The study by

Espina-Martin et al. (2022) however does not quantify the uncertainty introduced by the inlet, which tends to vary between set-ups.

The uncertainty of RT methods also requires quantification, however at the time of writing to authors knowledge there has been no assessment of uncertainty of the methods. For closed path instruments both the method and inlet set-up need to be quantified, whereas for open path methods only the uncertainty of the method is required. Further development in protocols both in quality assurance procedures and determination of measurement uncertainty are therefore required.

3.7. Data management

Concerning the data reporting, it is recommended to report data on the EBAS database following the EBAS protocol (<https://ebas-submit.nilu.no/>).

In the absence of harmonized protocol in Europe for NH₃ measurements and data management, a high diversity of protocols has been adopted by the scientific community and air quality monitoring networks. RI-URBANS has collected NH₃ data from 69 sites with a large panel of online and offline instruments and methods used (see part 4.2.1).

Nevertheless, there was no specific EBAS template for reporting NH₃ data. Therefore, an adaptation of the Non-Methane Volatile Organic Compounds (NMVOC) EBAS format was made to address the NH₃ issue in RI-URBANS. These NH₃ data are available at the EBAS data access site (<https://ebas-data.nilu.no/>). By examining the NH₃ data available from the RI-URBANS framework, new NH₃ submitters can use a template to aid them in the data submission process.

For NH₃, there are two defined data levels in EBAS. Level 0 contains raw concentration data with calibration data at the instrument's native temporal resolution, and Level 2 contains concentrations data validated after QA/QC checks.

4. PAN-EUROPEAN OVERVIEW OF AMMONIA CONCENTRATIONS ACROSS URBAN ENVIRONMENTS

4.1. Introduction

Long term ambient air measurements of NH₃ are scarce in Europe. The AQ Directive 2024/2881/EC is requiring NH₃ measurements in rural supersites in Europe. In addition, it recommends NH₃ measurements in urban background supersites. Hotspots of NH₃ in urban environments and in the farming/agricultural areas were identified by Van Damme et al. (2018) using remote sensing. Indeed, the need for monitoring has raised due to high proportion of NH₃ emissions from the agriculture/farming sector in the EU-27 emission inventory (EEA, 2022), and because of the relevance of regional background NH₃ concentrations for the formation of SIA as NH₃ is an important component of PM_{2.5}. However, in addition to farming/agricultural emissions, relevant sources of NH₃ are present at urban scale including mainly traffic, waste management and sewage systems. These are probably not properly reported in the emission inventories, and they may have a relevant impact in the generation of SIA, especially of NH₄NO₃ at metropolitan scales. It is for these reasons and for monitoring the trends of urban and hotspot NH₃ concentrations that RI-URBANS recommends measuring NH₃ in these pollution hotspots.

Within RI-URBANS, Liu et al. (2024) compiled a large number of datasets of NH₃ concentrations of different duration from urban Europe and from farming/agricultural hotspots for a joint evaluation according to (i) the instrumental and methodological approaches implemented; (ii) the comparison of urban and hotspot concentrations across Europe; and (iii) the evaluation of inter-annual trends. The results from this RI-URBANS study are summarised below (Sections 4.2–4.3). It has to be pointed out that the lack of harmonisation of measurement protocols for NH₃ might hinder an accurate comparison of the data.

4.2. Methodology

4.2.1. NH₃ data compilation

In the framework of RI-URBANS, Liu et al. (2024) compiled 69 datasets of NH₃ concentrations from European regional, suburban and urban background (RB, SUB and UB, respectively), industrial (IND) and traffic sites (TR), see Figure 3 and Table 1. These included 36 sites from Spain, 15 from France, 12 from Italy, five from UK and one from Finland. Most of the data was from non-rural sites (UB, 15; SUB, 12; TR, 12; IND, 5), but although the focus was on urban and Farming / Agricultural Hotspots

(FAH), 15 RB datasets were also collected to better interpret NH₃ spatial and temporal variability. Table 1 shows the sites, the cities and countries, and the instruments used for measuring NH₃ concentrations.

Remote sensing data (Van Damme et al., 2018) was used to identify the spatial extension of farming/agricultural NH₃ hotspots (FAHs). Furthermore, arbitrarily, RB sites reaching average concentration >1.5 µg/m³ were also classified as FAHs, and these were named Regional Background sites Close to Hotspot (RBCH). The FAHs are identified in Figure 4.

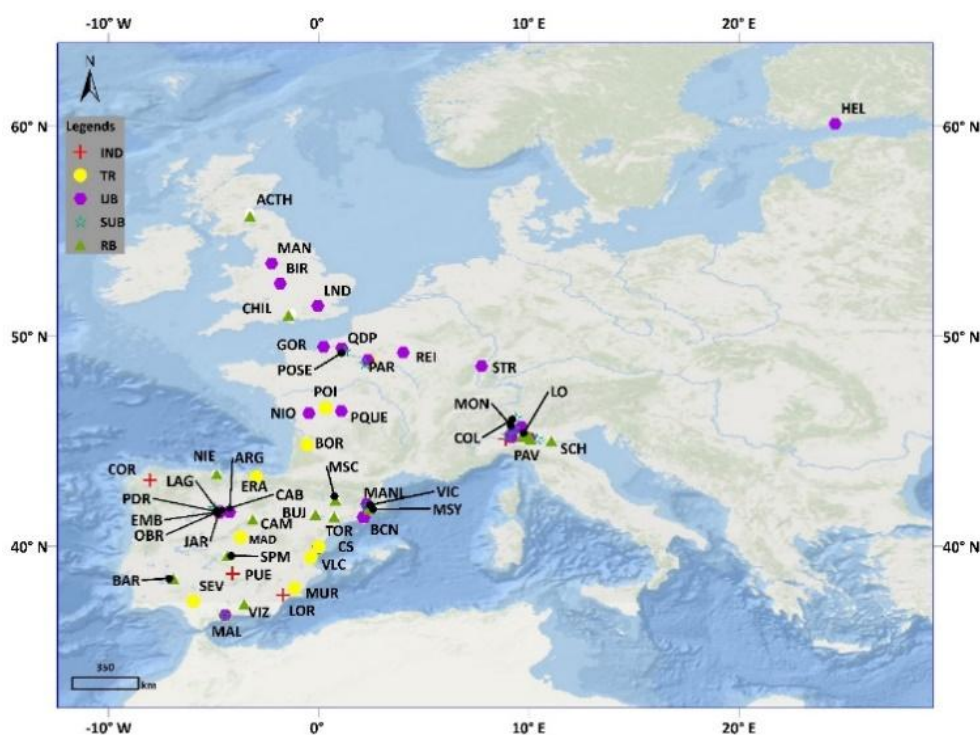


Figure 3. Location of the sites supplying data on NH₃ concentrations for the present study and the type of station. IND, industry (red point); TR, Traffic (yellow point); UB, Urban background (violet point); SUB, Suburban background (turquoise point); RB, Regional background (green point). Figure adapted from Liu et al. (2024).

As shown in Table 1 there was a wide range of instrumentation used to measure NH₃ concentrations. These included the following techniques with number of sites included:

- Active denuder sampling and passive samplers (resolution 1 week to 1 month) coupled with offline treatment and analysis using different analytical approaches (Twigg et al., 2022) (21/69 sites).

- Online measurements with a high time resolution, such as chemiluminescence equipped with an NH₃ converter (Sharma et al., 2010) (30/69 sites), Optical CRDS (Cavity Ring-Down Spectroscopy) and Optical OA-ICOS (Off-axis integrated cavity output spectrometer) (the two latter, 11/69 sites).
- Near-real-time high time resolution measurements, such as the ones equipped with an annular denuder sampling with on-line analyses (4/69 sites), and those with an online ion chromatography-based system that measures water-soluble gases and aerosols on an hourly basis (3/69 sites).

Table 1: Instruments used to measure NH₃ in the different stations. Abbreviations used: IND, Industrial; UB, Urban Background; TR, Traffic; SUB, Suburban Background; RB, Regional Background; RBCH, Regional Background Closed Hotspot; D-PS, active denuder sampling or passive samplers with offline analyses; Chem, Chemiluminescence; Res., Time resolution.; CRDS, Optical Cavity Ring-Down Spectroscopy; OA-ICOS, Off-axis integrated cavity output spectrometer; Min, minute; H, hour; D, day; W, week; MTH, month. Modified from Liu et al. (2024).

Site	City	Start	End	Re	Method	Site	City	Start	End	Res.	Method
LOR_IND_UB	Lorca (ES)	2018/0	2023/0	H	Chem	PAR_UB	Paris (FR)	2020/0	2021/1	H	CRDS
PAV_IND_UB	Sannazzaro (IT)	2013/1	2022/0	H	Chem	PAV_UB	Pavia (IT)	2012/0	2022/0	H	Chem
PUE_IND_UB	Puertollano (ES)	2007/0	2023/0	H	Chem	PDR_UB	Valladolid (ES)	2021/0	2022/1	H	Chem
COR_IND_SUB	Coruña (A) (ES)	2020/0	2022/1	D	D-PS	PQUE_UB	Rouen P.Q. (FR)	2016/0	2019/0	H	CRDS
CS_IND_SUB	Castellón (ES)	2022/0	2023/0	D	Chem	QDP_UB	Rouen Q.P. (FR)	2020/0	2020/0	H	CRDS
BCN_TR	Barcelona (ES)	2013/1	2018/0	D	D-PS	REL_UB	Reims (FR)	2016/0	2023/0	H	CRDS
BOR_TR	Bordeaux (FR)	2022/0	2022/1	2	D-PS	STR_UB	Strasbourg (FR)	2019/0	2022/1	H	CRDS
EMB_TR	Valladolid (ES)	2023/0	2023/0	H	Chem	COL_SUB	Colico (IT)	2013/1	2022/0	H	Chem
ERA_TR	Erandio (ES)	2014/0	2022/0	H	Chem	CRE_SUB	Cremona (IT)	2013/0	2018/0	H	Chem
MAD_TR	Madrid (ES)	2012/0	2012/0	2	D-PS	JAR_SUB	Valladolid (ES)	2020/0	2021/0	H	Chem
MAL_TR	Málaga (ES)	2014/0	2021/1	3	D-PS	MAL_SUB	Málaga (ES)	2011/0	2013/1	2W	D-PS
MUR_TR_SUB	Murcia (ES)	2023/0	2023/0	D	Chem	MIL_SUB	Milano (IT)	2021/0	2021/1	H	Chem
PAR_TR	Paris (FR)	2020/1	2021/1	H	CRDS	MON_SU	Monza (IT)	2013/0	2019/0	H	Chem
POI_TR	Poitiers (FR)	2022/0	2022/1	2	D-PS	PAR_SUB	Paris (FR)	2017/0	2021/0	5Min	AMANDA
SEV_TR	Sevilla (ES)	2011/0	2022/1	2	D-PS	PAR_SUB	Paris (FR)	2012/0	2013/0	H	AMANDA
VLC_TR1	Valencia (ES)	2015/0	2023/0	H	Chem	PAR_SUB	Paris (FR)	2018/0	2018/0	1W	D-PS
VLC_TR2	Valencia (ES)	2021/0	2021/1	H	Chem	POSE_SU	Poses (FR)	2023/0	2023/0	H	CRDS
AGR_UB	Valladolid (ES)	2019/1	2020/0	H	Chem	VIC_SUB1	Vic (ES)	2018/0	2018/0	10Min	Chem
BCN_UB1	Barcelona (ES)	2011/0	2022/0	1	D-PS	VIC_SUB2	Vic (ES)	2015/0	2015/0	1Min	Chem
BCN_UB2	Barcelona (ES)	2011/0	2011/0	1	AMANDA	ACTH_RB	Auchencorth M.	2018/0	2021/0	H	MARGA
BCN_UB3	Barcelona (ES)	2011/0	2011/0	1	AMANDA	BAR_RB	Barcarrota (ES)	2012/0	2013/1	1W	D-PS
BER_UB	Bergamo (IT)	2021/0	2022/0	H	Chem	BUJ_RBC	Bujaraloz (ES)	2020/0	2023/0	2W	D-PS
BIR_UB	Birmingham (UK)	2019/0	2021/0	H	OA-ICOS	CAM_RB	Campisábalos	2004/0	2022/1	1W	D-PS
CAB_UB	Valladolid (ES)	2018/1	2019/0	H	Chem	CHIL_RBC	Chilbolton (UK)	2018/0	2021/0	H	MARGA
CRE_UB	Cemona (IT)	2011/0	2022/0	H	Chem	CRE_RBC	Cremona (IT)	2011/1	2021/1	D	Chem
GOR_UB	Gonfreville (FR)	2020/0	2023/0	H	CRDS	CRE_RBC	Cremona (IT)	2007/0	2021/1	H	Chem
HEL_UB	Helsinki (FI)	2009/1	2010/0	H	MARGA	LO_RBCH	Bertonico (IT)	2009/0	2021/1	D	Chem
LAG_UB	Valladolid (ES)	2019/0	2019/1	H	Chem	MSC_RBC	Montsec (ES)	2011/0	2021/0	MTH	D-PS
LND_UB	London (UK)	2019/0	2020/1	H	OA-ICOS	MSY_RB	Montseny (ES)	2011/0	2022/0	MTH	D-PS
MAL_UB	Málaga (ES)	2011/0	2011/1	2	D-PS	NIE_RB	Niembro (ES)	2004/0	2022/1	1W	D-PS
MAN_UB	Manchester (UK)	2018/0	2020/1	H	OA-ICOS	SCH_RBC	Schivenoglia (IT)	2013/0	2022/0	H	Chem
MAN_UB	Manlleu (ES)	2021/0	2023/0	2	Chem	SPM_RBC	S. P. Montes (ES)	2012/0	2022/1	1W	D-PS
MIL_UB	Milano (IT)	2007/0	2021/1	H	Chem	TOR_RBC	Els Tormes (ES)	2012/0	2022/1	1W	D-PS
NIO_UB	Niort Venise (FR)	2022/0	2022/1	2	D-PS	VIZ_RB	Viznar (ES)	2012/0	2022/1	1W	D-PS
OBR_UB	Valladolid (ES)	2019/0	2019/0	H	Chem						

The wide range of methods used and the lack of calibration and meta information on measurement accuracy limited the direct comparison of the data compiled. Currently, a European CEN standard

method is available only for passive sampling (EN 17346:2020), but it cannot be confirmed that measurements using passive samplers in the compiled data followed this CEN standard. EMEP sites followed the EMEP (denuders) method described in prior chapters. This compilation of data highlights the need for online reference methods of NH₃. Furthermore, some of these methods might have also had sampling artefacts depending on the sampling approach that was used (even with same instruments). This means that sampling specifications should also be considered in developing reference protocols (for methods that use active sampling). For detailed information on available instrumentation and evaluation of the different methods, the reader is addressed to Twigg et al. (2022).

4.2.2. Interannual trends of urban and regional NH₃ in Europe

For the evaluation of the inter-annual and seasonal variations of NH₃ concentrations, only datasets with >5 years' coverage were selected. This included three industrial, five traffic, five urban background, two suburban background and eleven regional background sites. Details of the analyses are reported in Liu et al. (2024).

4.3. Levels of NH₃

4.3.1. Spatial variability of concentrations

Figure 4 shows the (mostly yearly) average NH₃ concentrations obtained at each of the 69 sites and evidences very large differences across the five European countries for which data was evaluated. The average of all sites reached $8.0 \pm 8.9 \mu\text{g}/\text{m}^3$, with minimum and maximum of 0.2 and $54.4 \mu\text{g}/\text{m}^3$. The vast majority of the sites exceeded the UNECE CLe threshold of $1 \mu\text{g}/\text{m}^3$ set for NH₃ to protect ecosystems and the $3 \mu\text{g}/\text{m}^3$ threshold for other vegetation.

4.3.1.1. *Concentrations of NH₃ out of the farming/agricultural hotspots (non-FAHs)*

For the group of sites excluding FAHs (non-FAHs, Figure 4a and Figure 5), the mean concentration reached $3.2 \pm 1.8 \mu\text{g}/\text{m}^3$. For these non-FAH sites, the highest annual average concentrations, 4.7 ± 3.2 and $4.5 \pm 1.0 \mu\text{g}/\text{m}^3$, were recorded at IND and TR sites, 3.3 ± 1.5 and $2.7 \pm 1.3 \mu\text{g}/\text{m}^3$ at UB and SUB sites, and $1.0 \pm 0.3 \mu\text{g}/\text{m}^3$ at an RB site (Figure 5). Thus, NH₃ levels were higher at TR sites compared to UB sites, owing probably to NH₃ slip from vehicles. Ambient concentrations of NH₃ from the traffic source may quickly decrease due to aerosol uptake and dry deposition. Furthermore, UB sites might receive NH₃ contributions from other sources, such as waste management and sewage systems that could also significantly impact urban NH₃ levels (Pandolfi et al., 2012; Reche et al., 2012). Therefore, in non-FAHs, IND, TR and UB sites urban sources are the

main contributors to NH₃ ambient concentrations, and probably not always these are adequately accounted in the emission inventories.

For non-FAHs UB sites, UB in Paris reached the highest NH₃ concentration, $5.8 \pm 1.9 \mu\text{g}/\text{m}^3$, followed by UB in Strasbourg, $4.9 \pm 1.6 \mu\text{g}/\text{m}^3$, and UB in Reims, $4.7 \pm 3.2 \mu\text{g}/\text{m}^3$ (Figure 4a), all of them from northern France. On the other hand, the lowest UB concentrations were recorded at UB in Niort, France, with $2.3 \pm 1.1 \mu\text{g}/\text{m}^3$, and UB in Helsinki, $0.2 \pm 0.3 \mu\text{g}/\text{m}^3$ (Figure 4a). Considering only non-FAHs, very similar concentrations were observed across the UB sites if excluding the very low concentrations from Helsinki and the high from Paris.

4.3.1.2. Concentrations of NH₃ in the farming/agricultural hotspots (FAHs)

According to Van Damme et al. (2018), northern Italy is one of the critical FAHs in Europe. In the study of Liu et al. (2024), the average for the 12 sites from this region reached $16.9 \pm 14.1 \mu\text{g}/\text{m}^3$, with the maximum average concentrations measured in northern Italian and Spanish regions. The highest concentration ($54.4 \mu\text{g}/\text{m}^3$) was observed in Cremona (Figure 4b).

When considering only FAHs (Figure 5), NH₃ concentrations were similar at SUB, RBCH, UB, TR sites ($14\text{--}15 \mu\text{g}/\text{m}^3$), and $10.0 \pm 2.3 \mu\text{g}/\text{m}^3$ at the IND sites. Thus, in this case, SUB and RBCH reached slightly higher NH₃ concentrations, probably because in these FAH sites, very large volumes of NH₃ are emitted by nearby agriculture and livestock (Sutton et al., 2022). Thus, UB-FAH NH₃ average concentration ($14.0 \pm 5.3 \mu\text{g}/\text{m}^3$) was 4-fold higher than the one for UB-non-FAH sites ($3.3 \pm 1.5 \mu\text{g}/\text{m}^3$).

It is very important to state that Sutton (2022) in the framework of studies done for UNECE reported very detailed recommendations to reduce emissions of NH₃, but also N₂O and NO_x from Agriculture and farming, at the time that N is recycled in the whole production system by evidencing nitrogen opportunities for agriculture, food and environment. The suggested implementing the following type of category of measures:

- Dietary measure to reduce N in animals' food.
- Housing measures: Design and operational measures to reduce the emissions in the farm.
- Manure measurements: Handling and management of manure to reduce emissions.
- Nutrient recovery to recycle nitrogen with major emissions.
- Field measures to reduce emissions for the application of fertilizers.
- Land use management to reduce emissions.

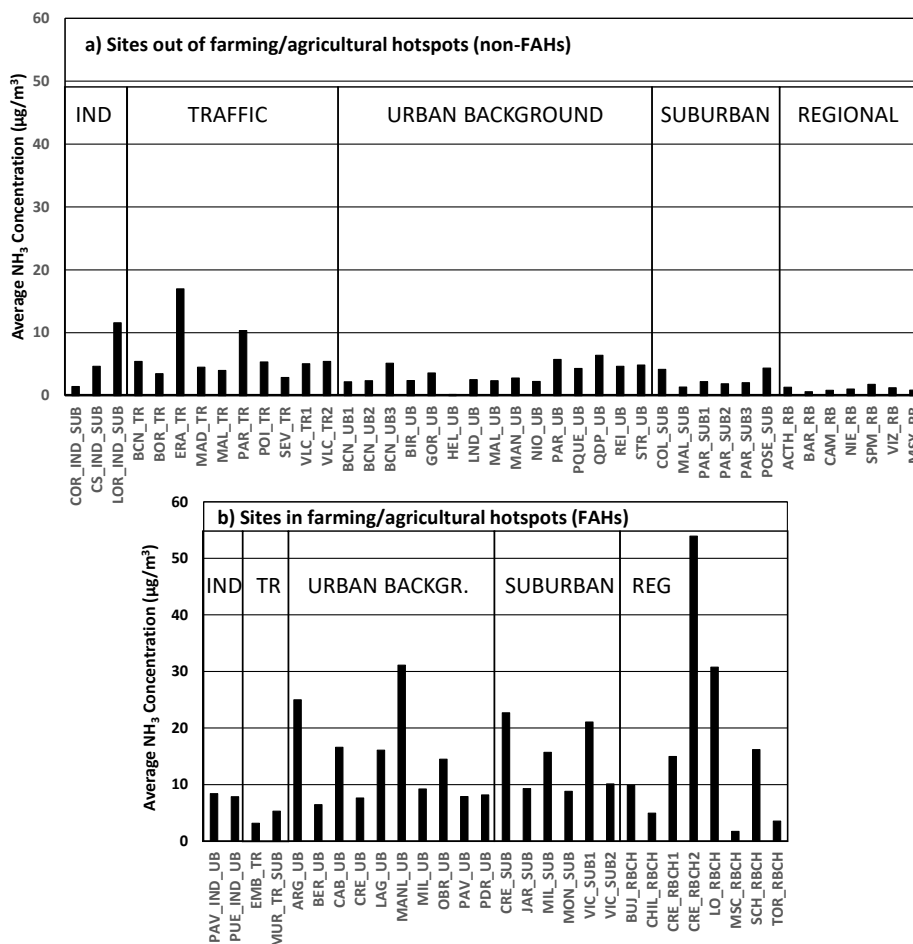


Figure 4. Average NH₃ concentrations of the 69 European datasets compiled in the Liu et al. (2024) study: a) Sites outside farming/agricultural hotspots. b) Sites in farming/agricultural hotspots. Industry, IND; traffic, TR; urban background, UB; suburban background, SUB; regional background, RB; regional background close to farming/agricultural sources in FAHs, RBCH. Figure is modified from Liu et al. (2024).

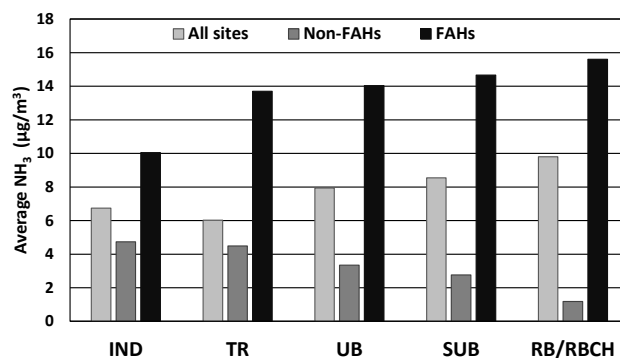


Figure 5. Average NH₃ concentrations for all (69) sites, outside (non-FAHs) and inside (FAHs) farming/agricultural hotspots, according to the type of environment: Industry, IND; traffic, TR; urban background, UB; suburban background, SUB; regional background, RB; regional background close to farming/agricultural sources in FAHs, RBCH. Figure is modified from Liu et al. (2024).

4.3.2. Diel and seasonal patterns

Using datasets with only hourly resolution NH_3 data for non-FAH sites NH_3 diel cycle exhibited varying peaks in intensity, amplitude, and period of the day. In London, NH_3 slightly peaked during the morning traffic rush hour at the UB site. In Paris (TR and UB), Strasbourg (UB) and Puertollano in Spain (IND_UB), NH_3 peaked at 10 a.m. In the Spanish site the peak was sharp while at the French sites the peak had a lower intensity. The main reason for the peak at 10 a.m. might be the Hewson-type fumigation, where industrial, urban and agricultural sources of NH_3 emitted during the evening and night are accumulated into the air close to the surface, below a frequently formed thermal inversion layer in a closed basin. In the morning hours the inversion layer is broken by sunlight heating the surface leading to enhanced convection and to the break-up of the inversion layer. Consequently, surface layer accumulated NH_3 fumigates surface levels. On other hand, it has been also found that during the night and early morning condensation of water in the sampling inlets might cause trapping of NH_3 and NH_4NO_3 aerosols. In the next morning, heating of the inlet by insolation might cause the dissociation of the accumulated NH_4NO_3 into HNO_3 and NH_3 , and then typically causing a morning artefact peak that frequently takes place around 9–10 a.m. (Twigg et al., 2022). Most of the remaining sites had a variation characterized by a progressive smooth hump with maxima between 12 and 16 h. One potential explanation for this pattern may be the thermodynamic balance of NH_4NO_3 , which tends to dissociate into NH_3 and HNO_3 as temperatures increase (Behera et al., 2013). As with seasonal patterns, the diel pattern of NH_3 may be regulated by the interplay between daytime temperatures (causing evaporative emissions from soils, wastes, and ammonium salt dissociation), traffic and industrial activities, and variations of meteorology (such as wind speed and boundary layer height). However, influences of sampling artefacts cannot be excluded as mentioned earlier. This highlights the complexity and comprehension of this pollutant and the need for standardisation of sampling and measurement methods, and the limitations of interpreting diel NH_3 concentrations.

At traffic sites, autumn and winter NH_3 concentrations were higher, probably due to lower dispersion conditions and higher NH_3 emissions from vehicular cold starts near traffic sites (Farren et al., 2021). The relatively new EURO 6/VI diesel vehicles might increase NH_3 emissions due to the implementation of SCR controls to abate NO_x (Song et al., 2015; Jeon et al., 2016; Hopke and Querol, 2022), and these may have accumulated around traffic sites in the stagnant conditions of winter. This possibility highlights the importance of considering the implementation of NH_3 emission limits

for all types of vehicles (including passenger cars and vans) to improve AQ in urban areas. Currently, NH₃ limit values apply only for heavy-duty vehicles (EURO VI and VII) in the EU.

At the UB sites, there is also a high seasonal heterogeneity, with Cremona (a FAH site) recording lower winter concentrations, while the remaining three UB sites (Barcelona, Milano and Paris) did not display significant fluctuations in NH₃ concentrations across seasons. NH₃ concentrations peaked in spring at UB non-FAHs sites compared to the low seasonal variation observed at UB-FAH sites, with similar concentrations in all seasons except the lower winter ones.

At RB/RBCH sites, most monitoring sites recorded higher autumn and summer NH₃ concentrations, due to the increased fertilizer use and/or manure spreading activities and higher temperatures (Zhou et al., 2019).

The seasonal trends detected for industrial sites were very varying, with higher summer and autumn NH₃ concentrations in Italian and Spanish sites affected by relatively close emissions from agriculture and farming, but also by nearby leather manufacturing factories (Gabarrón et al., 2017) and oil refineries (Pasini, 2022). In Puertollano, higher winter NH₃ concentrations were detected due to the intense stagnation and thermal winter inversions occurring in this basin.

The interpretation of seasonal trends is complex for NH₃. The emissions from agriculture are likely to increase in hotter months, when NH₄NO₃ dissociation is also favoured. However, this is likely to be counteracted by an increased mixing depth, and the net outcome is uncertain. Another key factor is likely to be the seasonality of agricultural practices, such as application of fertilizers and disposal of animal waste slurry on the land. This will vary across Europe, with the different climates and crops existing across the continent, so no common behaviour is expected.

4.3.3. Inter-annual trends

Only 26/69 datasets contained data for over five years, and from these 13 were obtained at FAH sites. The trend analysis showed that a statistically significant trend at the 95% confidence level were obtained for 14/26 of the NH₃ datasets (Figure 6). Some sites, particularly SUB sites from northern Italy and France, recorded stable concentrations.

For industrial sites, Puertollano in Spain showed a significant annual increase (11 %/yr in 2007–2022), which was probably associated with the potential increase of emissions from the petrochemical estate close to the city. Trends obtained for the other IND sites pointed to constant concentrations along the study periods.

The non-FAH sites Erandio (TR), Valencia (TR1), Reims (UB), and the FAH sites Milano (UB) and Pavia (UB) experienced statistically significant decreases, probably due to policy actions to abate traffic emissions and other urban emissions (e.g., waste management), but in some cases also due to decrease of emissions from agriculture/farming. However, Malaga (TR) and Sevilla (TR) followed statistically significant increasing trends. In Barcelona, concentrations were constant at the TR site and increased at the UB site, suggesting that traffic was not the only source of NH₃ in Barcelona, although NH₃ was higher at the TR site than at the UB.

Three RB sites in Spain (Campisábalos, Montseny, Víznar) recorded constant concentrations along the study periods, while most of the RB FAH sites (Cremona, Lobertonico, Montsec, Schivenoglia, San Pablo de los Montes, and Els Torms) recorded a significant increase, indicating a potential increase in farming/agricultural emissions in the study areas during the corresponding period, or to the consumption of NH₃ to form SIA due to the drastic abatement of NO_x and SO₂ emissions (Aas et al., 2024). On the contrary, two RB sites (Cremona RBCH2 and Niembro RB) showed significant decreases throughout the years.

Considering all 26 datasets the trend analysis yielded a non-statistically significant increasing trend of NH₃ concentrations at a rate of 1.28 [-0.64, 3.19] %/yr. When considering independently non-FAH and FAH sites, 1.05 [-1.94, 4.03] %/yr; and 1.56 [-0.90, 4.03] %/yr changes, respectively, were obtained. Thus, the trend was increasing in all cases but without statistical significance and close to the detection limit (Figure 6).

For the **non-FAHs sites, the trend analysis** showed the following results (Figure 6):

- Trends were very variable for the different sites in all type of environments (UB, TR, RB, IND) and this yielded to non-statistically significant trends in the analysis of each type, and for all types.
- Regarding UB and TR sites (N=7), three sites followed a statistically significant decreasing trend, while other three sites followed a statistically significant increasing trend, and one site did not experience any change.
- For the RB sites, a slight non-significant decreasing trend was observed.

For the **FAHs sites, the trend analysis** showed the following trends (Figure 6):

- A statistically significant decreasing trend was obtained at two of the UB sites (N=3, Figure 6), yielding to an overall non-statistically significant trend for all UB sites.

- For the RBCH sites, an increasing trend was obtained for six (three with statistical significance) sites (Figure 6). As stated above, Behera and Sharma (2011), Banzhaf et al. (2013), Aas et al. (2024), and Jonson et al. (2022) attributed the NH₃ increasing trends of RB to their progressive decrease in the NH₃ consumption to generate (NH₄)₂SO₄ and NH₄NO₃ associated with the marked decreases in the emissions of SO₂ and NO_x. However, the articles referred to background NH₃ concentrations while these RBCH sites were located in NH₃ FAHs, where an increase in emissions of this pollutant cannot be discarded in addition to the cause above.

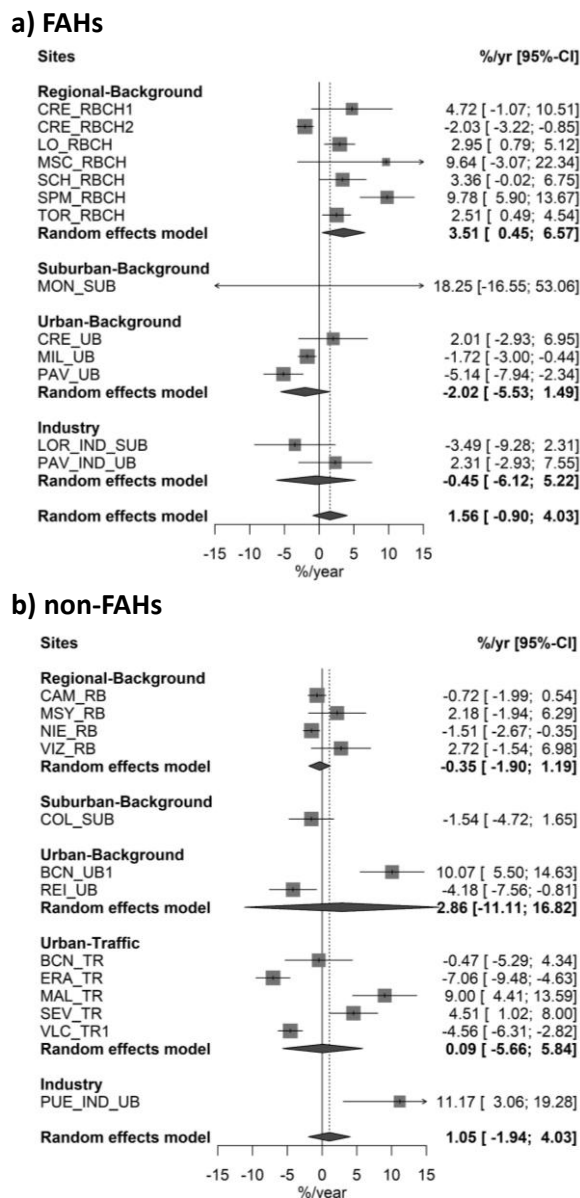


Figure 6. Annual NH₃ trends at (a) FAHs and (b) non-FAHs. Values represent change per year (%/yr) with 95% confidence level range in square brackets. Modified from Liu et al. (2024).

5. RECOMMENDATIONS AND MAIN FINDINGS

5.1. Recommendations on measurements, quality control and data management

The instrument intercomparison by Twigg et al. (2022) demonstrated that the same model of online RT and NRT instrument had variable precision and accuracy. Harmonisation of measurement protocols and data handling procedures are therefore essential, for datasets to be comparable for long-term trends to be studied to understand the success of mitigation strategies and to undertake process studies. In the study by Liu et al. (2024) for example, comparisons are limited by the certainty in the quality of the datasets due to the lack of harmonisation between monitoring methods. The following provides the current recommendations based on current literature on measurements, quality control and data management for measurements.

5.1.1. Sampling system

The design of the sampling system for NRT and RT closed path systems has been demonstrated by several studies to be essential (von Bobruzki et al., 2010; Norman et al., 2009; Twigg et al., 2022). As a 'sticky' molecule, NH₃ is observed to have a strong adsorption and desorption interactions with surfaces of the sampling system and detecting instrument.

- In the sampling system design, where possible, the inlet length should be minimised to limit the adsorption of NH₃ (Kim et al., 2021), as well as the residence time and surface to air volume ratio of the inlet (Twigg et al., 2022).
- Materials used for the sampling system also are a controlling factor in adsorption/desorption interactions of NH₃ (Whitehead et al., 2008; Ellis et al., 2010; Vaittinen et al., 2014; Vaittinen et al., 2018; Kim et al., 2021). Materials evidenced in the literature to be optimal are polyethylene (PE) and polytetrafluoroethylene (PTFE), or those coated with a silicone coating.

As NH₃ is highly reactive and water soluble, if water is present on surfaces of the sampling system and in the detection instrument, there are potential losses due to adsorption to water, desorption of water from the surface, dissolution of ammonia into the adsorbed water and dissociation of ammonia in water and on the surfaces (Vaittinen et al., 2018).

- Every effort should be made to limit condensation on the sampling system by heating to a few degrees above the ambient temperature (Norman et al., 2009). This has been demonstrated to result in an improved time response of systems (Ellis et al., 2010; Kim et al., 2021).

- In heating the sampling system, caution is however required. If inlet temperatures are too high, they have been associated to the dissociation of NH_4^+ in NH_4NO_3 back to the gas phase, resulting in an artefact in the reported NH_3 concentrations (von Bobruzki et al., 2010; Twigg et al., 2022).

To prevent degradation of the instrumentation some RT systems require the removal of PM either within the sampling system or detecting instrument, using either filters or an inertial inlet.

- The use of filters and inertial inlet is not ideal, as it introduces another surface for which NH_3 can adsorb too. Therefore, every effort should be made to minimise the number of filters used in a system without degradation to the detecting instrument.
- Filters can act as a source of NH_3 either through the desorption of adsorbed NH_3 or volatilisation of NH_4^+ in PM back to gas phase (von Bobruzki et al., 2010; Stieger et al., 2018). Frequent changing of the filter is therefore recommended. It is recommended that filters in RT systems be replaced every two weeks to monthly, depending on PM concentrations and climate conditions (warm/cold) (He et al., 2020).

As well as filters, the inlet can be a source of PM as the sampling system ages.

- There is evidence that inlet degrades with age due to contamination of the walls (Moravek et al., 2019). It is therefore recommended either cleaning or replacing the inlet on a frequent basis. In NRT systems with online IC, replacement or cleaning of the PM head and inlet has routinely been carried out on frequent basis to remove this potential bias in performance for routine monitoring of NH_3 (Makkonen et al., 2014; Twigg et al., 2015).

For open path system the set-up is crucial to ensure accuracy of the measurements. Consideration needs to be given to ensure the reflector is within line of sight of the instrument and in a fixed position. Details of the requirements are outlined in Volten et al. (2012).

For offline techniques discussed above, a sampling line is generally not used, eliminating the potential artifacts caused by ammonia adhering to the surfaces of the sampling line. In the case of the EMEP 3-stage filter pack method, it is however not fully possible to distinguish NH_3 (g) from NH_4^+ in the PM, meaning that alternative quantitative methods may be more beneficial for monitoring long trends and processes of NH_3 . Evaporation of NH_3 is a considerable risk especially during warmer periods, and thus, the samples should be kept refrigerated when storing samples prior to analysis.

For passive samplers, it is strongly recommended to follow the CEN standard (EN 17346:2020), and the best performing samplers in the intercomparison conducted by Braban et al. (2018) and Martin et al. (2019). The expanded uncertainty of the tested passive samplers ranged from 11 to 23 % at the reference concentration of 1 $\mu\text{g}/\text{m}^3$, i.e., a concentration representative of the lower critical level. Therefore, the use of passive samplers is recommended because of their low cost and because the uncertainty is adequately known. If NRT and RT equipment is used, it is advisable to intercompare their results in situ with passive samplers on a regular basis.

5.1.2. NH₃ measurements

The available online (real-time and near-real-time) methods are described in section 3.5. Currently, there is no reference online method for NH₃ in the Air Quality Directive 2024/2881/EC.

- Online methods offer near real-time or real-time information and short time resolution of data enabling detecting the diel cycles of this pollutant, which is highly important to understand the NH₃ processes in the atmosphere.
- Drawbacks of these methods include generally higher instrumentation costs, lack of measurement protocols and harmonized QA/QC, and typically high maintenance needs in the field.
- There is a lack of quantification of the uncertainties in the reported concentrations and the comparability of methods across networks.
- Preparation of harmonized measurement protocols for real-time and near-real-time is needed following a similar framework to that of other monitoring networks which have standard operating protocols (SOPs) such as ACTRIS, WMO GAW and/or CEN.
- It is recommended that routine intercomparisons are undertaken to evaluate the performance in networks. For example, WMO GAW/ACTRIS aerosols instrumentation that report particle number counts undergo periodic intercomparison studies to ensure instruments report within an acceptable range (Wiedensohler et al., 2012).
- Caution is recommended for the chemiluminescence method as it is not a direct measurement and there are potential artefacts in the reported concentration.

Offline techniques include passive samplers, denuders and filter packs (refer to section 3.5). A CEN standard is available for passive samplers, while EMEP Manual describes the use of denuders and filter packs.

- Advantages of offline techniques include available measurement protocols, harmonized QA/QC, and typically low costs. Also, passive sampler and denuder techniques are quantitative methods with reasonable measurement uncertainty. In addition to NH₃, filter packs may collect NH₄⁺, which is the largest drawback of the method. Generally, the offline techniques (especially passive samplers) have long sampling periods, but if concentration are expected to be high short periods might be used, taking always in the account that considering period duration and concentration, the filter are not oversaturated.
- The selection of the method depends on the requirement of the measurement. For example, to evaluate long-term trends and spatial variations passive samplers are appropriate, but for process understanding for modelling and source attribution, NRT or RT methods are required to provide highly resolved temporal information.
- Martin et al. (2019) evaluated the performance of specific commercial passive NH₃ samplers, with large differences between some of them. It is recommended to follow the CEN standard (EN 17346:2020), and the best performing samplers in this study.

5.2. Instrument performance, maintenance and quality control

For NRT and RT there are no harmonized protocols (EN standards or international guidance documents) that provide detailed instrument performance requirements for monitoring NH₃; instead, the technical specifications are typically outlined in the individual instrument manuals. As discussed in section 3.5, cross interferences from other atmospheric species are known in the literature. Therefore, it is recommended that further studies are undertaken to evaluate the performance of methods and quantify the cross interferences of other atmospheric species, in order to provide confidence in measurements of NH₃ at ambient concentrations.

For maintenance and quality control, the following recommendations are given:

- For offline measurements, following the procedures in EN 17346 and EMEP Manual regarding maintenance and quality control are recommended.
- For NRT and RT, as discussed there are currently no harmonised protocols for these instruments but in peer review literature, there is evidence of maintenance and quality control procedures taking place within sites and networks. Below, a list of specific items that need to be considered in the future development of a harmonised protocol to ensure data are of highest standard:
 - Routine maintenance as recommended by the manufacturer.

- Recording of all raw parameters produced by instrumentation to ensure data is traceable prior to producing quality assured datasets (where possible).
- Frequent replacement of filters (where applicable).
- Periodic cleaning or replacement of sampling systems (where applicable).
- Traceable calibrations and span checks of instrumentation using a gas standard (where applicable).
- Participation in routine intercomparison studies to ensure datasets are comparable (where possible).

5.3. Calibration infrastructures

- For offline measurements, following the procedures in EN 17346 and EMEP Manual regarding calibration are recommended.
- For offline measurements it is highly recommended that laboratories participate in relevant intercomparison studies to ensure accuracy and precision of the analytical methods used. These are mainly organised for the ammonium content in liquid sample rather than ammonia. However, EMEP organises laboratory intercomparisons for ammonia that are especially suitable for those laboratories using the filter pack method.
- Regular international comparisons would be recommended both under controlled conditions and in the field for both offline and online methods (similar to studies described by von Bobrutzki et al., 2010; Martin et al., 2019; and Twigg et al., 2022).
- For open path methods, the availability of a zero-air facility to calibrate systems on NH₃ free air would be recommended (Twigg et al., 2022).
- Currently there is no standard method to calibrate closed path RT and NRT instruments with NH₃ gas standards. There have been a number of metrology and research institutes working on developing standard calibration systems both with dry and humidified air in national and international Projects such as MetNH₃ (ENV MetNH₃, 2017; Martin et al., 2019; Macé et al., 2022) and quantiAGREMI (EMRP, 2024).
- It is recommended zero and span checks should be routinely carried out to determine the accuracy and precision of instruments, as without this information on instrument performance cannot be determined (Twigg et al., 2022).

5.4. Data management

It is recommended to follow the EBAS protocols for data reporting and data management (<https://ebas-data.nilu.no/>). The existing NH₃ data submitted by RI-URBANS to EBAS can be used as a template for the submission of new NH₃ data. As with all data sets, the FAIR (Findable, Accessible, Interoperable, Reusable) principles (Wilkinson et al., 2016) should be applied. In EBAS, there are three data submission levels (Level 0 to 2) to ensure traceability of data.

Below summarises the levels but further descriptions can be found in Laj et al. (2020):

- Level 0: Report raw concentration data and associated instrument parameters in the ‘native’ time resolution of the reporting instrument.
- Level 1: Data processed to final version including calibrations applied, alongside the removal of invalid and calibration periods in the ‘native’ time resolution.
- Level 2: Quality assured averages (typically hourly).

The approach used by the aerosol community in Laj et al. (2020) has standard operating protocols on data handling. It is recommended that a similar approach be adopted for NH₃ reporting with NRT and RT, as there is no standard reporting methodology available currently.

5.5. Main findings for NH₃ in urban Europe

5.5.1. Instrument and data management

- The compilation of 69 NH₃ datasets from (mostly) urban Europe evidenced that a wide variety of measurement protocols were implemented which likely impacted comparability of datasets.
- There is a need to advance unified monitoring technologies/protocols to enhance the precision and accuracy of measuring NH₃ concentrations, enabling a more effective tracking and understanding of its dynamic variations.
- Meanwhile, the use of denuders and passive samplers with offline NH₃ analyses, following EMEP and CEN recommendations, might be implemented alone or collocated with real-time measuring instruments.

5.5.2. Concentrations of NH₃

- Unlike the air quality criteria pollutants, NH₃ does not have Air Quality Standards in Europe. However, several studies recommended specific targets for the protection of vegetation (UNECE, 2007; Cape et al., 2009) that were implemented by specific Member States. Thus, UNECE long-

term Critical Levels (CLE) have been set at $1 \mu\text{g}/\text{m}^3$ for lichens and bryophytes and at $3 \mu\text{g}/\text{m}^3$ for higher plants. Furthermore, it has been suggested by Franzaring and Kössler (2022) that the protective effect of this long-term UNECE CLE cannot be assumed for long periods of more than 20 to 30 years, and a maximum monthly value of $12 \mu\text{g}/\text{m}^3$ should be also applied.

- The average NH_3 concentration of all sites ($N=69$) reached $8.0 \pm 8.9 \mu\text{g}/\text{m}^3$, which exceeded the critical thresholds for safeguarding ecosystems.
- After excluding sites in farming/agricultural hotspots (FAHs), the average NH_3 concentration decreased down to $3.2 \pm 1.8 \mu\text{g}/\text{m}^3$ compared to the $13.6 \pm 12.1 \mu\text{g}/\text{m}^3$ average at sites in FAHs.
- Excluding FAH sites, IND and TR sites recorded on average the highest concentrations, 4.7 ± 3.2 and $4.5 \pm 1.0 \mu\text{g}/\text{m}^3$, followed by UB, SUB, and RB sites, with 3.3 ± 1.5 , 2.7 ± 1.3 , and $1.0 \pm 0.3 \mu\text{g}/\text{m}^3$, respectively. This gradient indicates that industrial, traffic, and other urban sources were primary contributors to NH_3 outside FAH regions.
- When referring exclusively to the FAHs, concentrations ranged from 10.0 ± 2.3 to $15.6 \pm 17.2 \mu\text{g}/\text{m}^3$, with the highest concentrations being recorded at the RB sites close to the farming/agricultural sources, and that, on average, there is a decreasing NH_3 concentration gradient towards the city for these FAHs as the distance to these sources increased.
- A significant number of these NH_3 FAHs (12 sites in total) were in northern Italy and recorded the highest average concentration ($16.9 \pm 14.1 \mu\text{g}/\text{m}^3$) and included the highest one ($54.4 \mu\text{g}/\text{m}^3$).
- NH_3 concentrations exhibited a high seasonal variability among datasets, without consistent trends. This high variability is attributed to a wide range of combinations of seasonality of emission and meteorological patterns. At FAHs, NH_3 tended to be higher in summer and autumn. In urban areas, seasonal fluctuations were notably affected by emissions from their surrounding environments.
- Diel NH_3 concentrations were influenced by the interplay between daytime high temperatures (causing evaporative emissions from soils and waste, and due to ammonium nitrate instability), traffic and industrial activities, and diurnal variations of meteorology (such as wind speed and boundary layer height). The concentrations are influenced by both pollution sources, sinks and meteorological factors. However, it must be mentioned that sampling artefacts (for methods that use active sampling) can interfere or hide the real trends.
- A revision of emission inventories to ensure that the inventories account adequately for all sources, such as road traffic and fugitive emissions from city waste management and sewage systems, is recommended. To this end, RI-URBANS also recommends implementing NH_3

measurements in urban background and traffic sites, in addition to the ones of rural and industrial sites.

- It is recommended following the directions by Sutton et al. (2022) to abate the NH₃ emissions from farming/agriculture.

5.5.3. Inter-annual concentration trends

- The trend analysis for the regional background close to farming/agricultural hotspot (RBCH-FAH) sites showed a statistically significant increase, which is opposite to the reported decrease in emissions from agriculture and farming in a number of official inventories. This increase has been attributed to the lower consumption of NH₃ to generate (NH₄)₂SO₄ and NH₄NO₃ due to the clear decreases in the emissions of SO₂ and NO_x. However, the fact that this increase is only found at RBCH sites might also imply an increase in agricultural/farming emissions. It is recommended to abate these emissions following the directions by Sutton et al. (2022).
- A number of urban traffic and background monitoring sites showed a significant decrease in NH₃ concentrations in the last decade, which could be attributed to the reduction of emissions from non-agricultural sources as a result of the implementation of measures such as traffic control, upgrading of transportation systems and waste management. A few sites followed increasing trends, pointing to an opposite trend of these emission sources and/or to the effect of decreasing NH₃ consumption for PM formation due to the abatement of SO₂ and NO_x.
- It is important to consider these trends, with those on emissions and atmospheric processes to assess the current situations and to devise effective NH₃ abating policies.

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