



Knowledge brief

## Comparison of bulk and wet-only deposition measurements of $\text{NH}_4^+$ and $\text{NO}_3^-$ in the Netherlands

### *Nederlandse samenvatting: Een vergelijking van twee meetmethoden voor natte depositie van ammonium en nitraat*

De natte depositie van ammonium en nitraat<sup>1</sup> kan op twee manieren bepaald worden: met een wet-only- of een bulkregenvanger.

Een wet-only vangt alleen water op als het regent. Er zit een deksel op dat bij regen automatisch open gaat. De meeste wet-only's houden het opgevangen regenwater ook koel. Een bulkvanger bestaat alleen uit een trechter en een opvangfles. Bulkvangers worden veel gebruikt, omdat het instrument goedkoop is en geen stroom nodig heeft.

Depositiewaarden van een bulkvanger zijn onzekerder dan van een wet-only. Dit komt doordat er in een bulkvanger ook stoffen neerslaan wanneer het niet regent. Een bulkvanger vangt dus natte depositie én iets extra's op<sup>2</sup>. Daarnaast koelt een bulkvanger het regenwater niet, hierdoor kan er water verdampen en kunnen stoffen met elkaar reageren. Om die reden kan de hoeveelheid ammonium en nitraat in het water van de bulkvanger lager zijn.

In deze kennisnotitie onderzoekt het RIVM hoe goed de depositiewaarden van een bulkvanger lijken op die van de wet-only. In twee experimenten in Nederland hebben op negen locaties een bulkvanger naast wet-only gestaan. De experimenten laten zien dat een bulkmeetwaarde een onzekerheid heeft van minstens 45 procent. Jaargemiddelde bulkwaarden hebben een kleinere onzekerheid van ongeveer 20%. In werkelijkheid is de onzekerheid van de bulkmeting nog iets groter, dit komt omdat de wet-only meting zelf ook een onzekerheid heeft die hier niet is meegenomen. Voor ammonium meten de twee instrumenten gemiddeld ongeveer hetzelfde. Voor nitraat meet de bulkvanger gemiddeld ongeveer 20% meer natte depositie dan de wet-only.

Het verschil tussen de bulkvanger en wet-only verschilt per locatie en per maand. Het RIVM heeft het effect van sommige omgevingsfactoren onderzocht. In het experiment met verschillende meetlocaties blijkt dat de hoeveelheid ammoniak of nitraat in de lucht en de meetlocatie invloed hebben op de resultaten. In het experiment met vergelijkbare meetlocaties, zien we dit niet. Misschien kunnen omgevingsfactoren gebruikt worden om een lokale correctie van de bulkmeetwaarde te bepalen. Om dit te onderzoeken is een grotere dataset nodig.

Het RIVM adviseert om wet-only regenvangers te gebruiken als een nauwkeurige bepaling van de natte depositie belangrijk is. Bulkvangers hebben hiervoor te hoge onzekerheden. Daarom is het ook niet mogelijk om bulkmeetwaarden te corrigeren. Bulkjaarwaarden zouden wel gecorrigeerd kunnen worden. Het RIVM adviseert om dan een lokale correctie te gebruiken, door op één plek beide instrumenten naast elkaar te zetten.

<sup>1</sup> Bij natte depositie komen stoffen via regen uit de lucht op de grond. Ammoniak uit de lucht komt als ammonium terecht in het regenwater, en stikstofoxides als nitraat

<sup>2</sup> Let op: Deze extra depositie is niet hetzelfde als de droge depositie op de aarde. Planten en bodem nemen ammoniak en stikstofoxides actief op en plastic doet dat niet. Met een bulkvanger kan dus **niet** de totale depositie (nat en droog) worden gemeten.

RIVM

A. van Leeuwenhoeklaan 9  
3721 MA Bilthoven  
P.O. Box1, 3720 BA Bilthoven  
The Netherlands  
www.rivm.nl/en

T 088 689 89 89

**Authors:**

Miranda Braam,  
Pim Meijer,  
Albert Bleeker,  
Marianne Heida,  
Roy Wichink Kruit,  
Arjan Hensen – TNO

**Center:**

Environmental quality

**Contact:**

miranda.braam@rivm.nl

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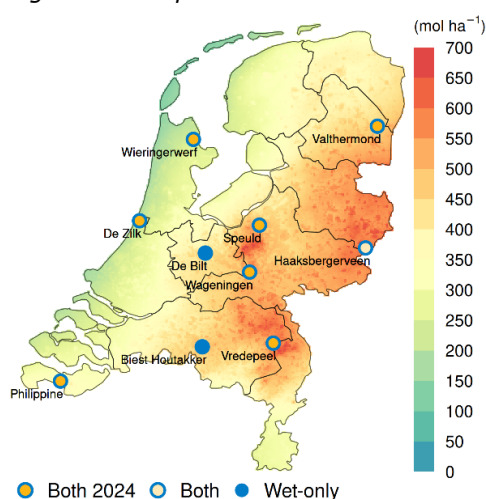
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## Introduction

Ammonia and nitrogen oxides from the air ends up in nature in two ways. Plants, and also the soil, can absorb the substances directly from the air, which is called dry deposition. Rain can also bring these substances to the ground, which is called wet deposition. The RIVM measures the wet deposition at 10 locations (the National Rainwater Monitoring Network/ Landelijk Meetnet Regenwater, abbreviated as LMRe) with a wet-only rain collector (see also Figure 1). In several regional measurement campaigns bulk collectors are used instead of wet-only collectors.

Figure 1 A map of the LMRe locations.



The LMRe locations with only a wet-only instrument are blue, and with both wet-only and bulk instruments are blue and yellow. In the background the model values of the wet deposition of ammonia are given.

The wet-only is a rain collector that collects the water when it rains ([Eigenbrodt NSA181-KHT](#), see the appendix for more information about the wet-only instruments of the LMRe). Under dry conditions, the collector is covered with a lid. The wet-only collects the rainwater in bottles, which are kept cool and in the dark. The wet-only collectors automatically changes these bottles every two weeks. The water is analysed in a laboratory to determine how much ammonium (dissolved ammonia) and nitrate (dissolved nitrogen oxides) are present in the water. A disadvantage is that the wet-only rain collector needs power to open and close the lid and to keep the bottles cool. The wet-only rain collector is a relatively expensive instrument due to the active cooling and the automatic bottle changer.

The bulk collector is a simpler instrument than the wet-only rain collector. In essence it is just a funnel with a collection bottle and is therefore always open.

Because the bulk collector does not require electricity, it can be placed anywhere. This allows for more measurement locations, which gives a better picture of how the wet deposition varies spatially. Model values show that wet deposition of ammonia varies on a local scale (Figure 1). That is why researchers also use the bulk collectors in regional initiatives, such as Regiodeal Foodvalley, Liefstinghsbroek, and Nieuwkoopse plassen. However, a bulk collector also has disadvantages. Firstly, substances enter the funnel even when there is no rain. This means that it measures wet deposition plus something extra. This extra deposition is not the same as the dry deposition in nature, as plants and soil absorb ammonia and nitrogen oxides through different active biophysical mechanisms. The bulk collector does not do that.

Secondly, water can evaporate from the collection bottles. This is possible because the funnel is always open and the bottles in the bulk collector are not kept cool. Finally, chemical interactions and biological conversion take place in the bottle, which can influence the results.

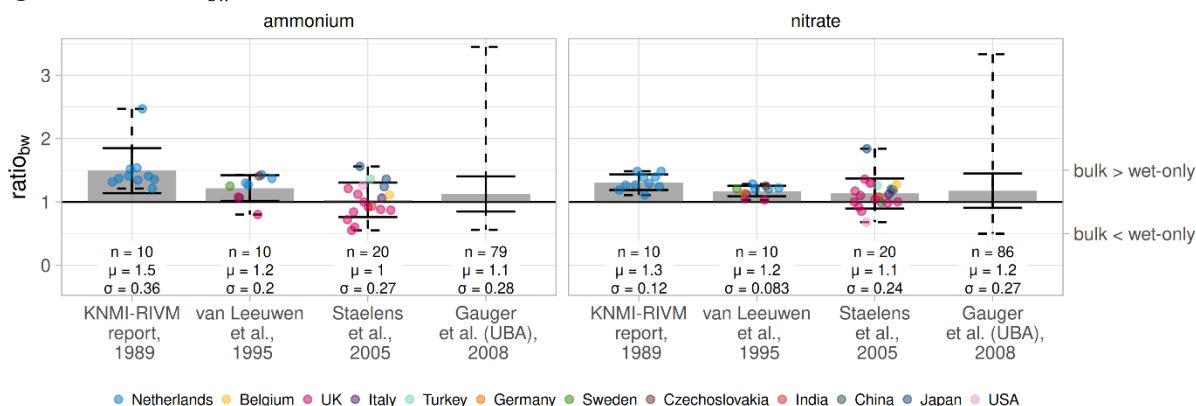
To determine the wet deposition with a bulk collector, it is necessary to correct its measured values (Frantzen *et al.*, 1989; van Leeuwen *et al.*, 1995; Staelens *et al.*, 2005; Gauger *et al.*, 2008 and the references mentioned therein). The correction ( $ratio_{bw}$ ) can be determined by simultaneous measurements with a bulk collector next to a wet-only:

$$ratio_{bw} = \frac{D_{wet\ bulk}}{D_{wet\ wet-only}} \quad Eq. 1$$

$$D_{wet\ bulk\ corrected} = \frac{1}{ratio_{bw}} \cdot D_{wet\ bulk\ measured} \quad Eq. 2$$

The  $ratio_{bw}$  is different for each substance. The difference between bulk and wet-only measurements depends on local emission sources, gas and aerosol concentrations in the air, turbulence and the type of bulk collector (Staelens *et al.* 2005). In the literature the average  $ratio_{bw}$  ranges for ammonia between 1 and 1.5 and for nitrate between 1.1 and 1.3 (see also Figure 2). The standard deviation for ammonia ranges from 0.2 to 0.36. For nitrate it is lower and ranges from 0.083 to 0.27.

Figure 2 The  $ratio_{bw}$  for ammonium and nitrate from the literature.



The grey bar is the average, the solid errorbar is the average  $\pm$  standard deviation, the dashed errorbar is the minimum - maximum. The colors represent the different countries. Gauger *et al.* only reported statistical values of  $ratio_{wb}$ , which are reversed using a Taylor-series approximation to the second order.

The most recent experiment with wet-only and bulk instruments side by side throughout the Netherlands happened several years ago (Frantzen *et al.*, 1989). As stated before, the  $ratio_{bw}$  depends on aerosol concentrations in the air, which change over time. Therefore, the RIVM conducted a new experiment and placed bulk collectors next to the wet-only instruments at 8 LMRe locations. More information about the instruments is available in the appendix.

With these measurements we want to answer the following questions:

- What is the uncertainty of uncorrected bulk measurements for ammonium and nitrate?
- What is the value for  $ratio_{bw}$  ammonium and nitrate?
  - o Is there a fixed  $ratio_{bw}$  for the whole country and / or per month?
  - o If not, are there identifiable causes for its variation?

## ***The two datasets***

In this note we analyse two datasets. Firstly, the LMRe dataset: this dataset is the result of placing bulk collectors next to 8 LMRe wet-only collectors from February 2024 until February 2025. Data from 7 of these sites are used in this analysis (see appendix for details). These 7 LMRe locations cover the entire country. This section provides a global explanation of this dataset, and the appendix provide a more comprehensive and detailed description of all the steps taken in the analysis.

In addition, we analyse data from the Maasvlakte experiment (MV). Hensen et al. (2017) described this dataset in detail. During this experiment, in Goeree and Solleveld a bulk and wet-only instrument stood side by side from 2011-2016.

Both experiments using the same bulk collectors, which are more 'advanced' than other designs (Erisman *et al.*, 2003). For both datasets, we sum the approved wet deposition per period to calculate annual wet deposition values.

### *LMRe experiment*

The wet-only instruments in the LMRe network automatically switch between bottles every two weeks at Sunday midnight. Two consecutive samples are then combined to obtain a composite sample that covers a four-week period. An RIVM staff member manually changes the bottles of the bulk instruments during working hours, approximately every four weeks.

Because the measurement periods of the bulk and wet-only instruments differ somewhat, they may capture different rain events. To solve this problem, we convert the wet-only period to the bulk period. We use a precipitation dataset from KNMI for this purpose. In this note, we refer to 'per period' to indicate that the dataset covers the bulk periods.

The laboratory determines the mass of water within the bottle and the concentration of ammonium and nitrate. It also reports the concentration of other substances in the rainwater, but in this note we only focus on ammonium and nitrate. However, the concentrations of the other substances are used as criteria in the quality control step ('validation', see the appendix).

After this validation, we determine the total amount of precipitation and deposition of both instruments (see the appendix).

In addition to validation based on the reported concentrations, we compare the collected amount of water with the precipitation reported by the KNMI. If the value of the rain collectors differs by more than  $\pm 50\%$  from the KNMI, we reject the measurement.

### *Maasvlakte experiment*

In the MV experiment the wet only instruments were insulated, but not actively cooled. Moreover, the bottles of the wet only instruments were manually changed, so both instruments cover the same period ( $\approx 30$  days).

The MV dataset spans multiple years (2011-2016). The two sites Goeree and Solleveld are relatively close to each other ( $\approx 30$  km), and are similar in terms of environment. Both are located close to the sea in the dune area. In the LMRe dataset, Veenkampen and Speuld are also about 30 km apart, but these are two very different locations. Veenkampen has low vegetation and peat soil, while Speuld is located on a heath field surrounded by forest.

The MV dataset had already been validated prior to this research. Additionally, we apply the validation criterion in which the water quantity in the bottles may not differ by more than  $\pm 50\%$  from the precipitation quantity of the KNMI.

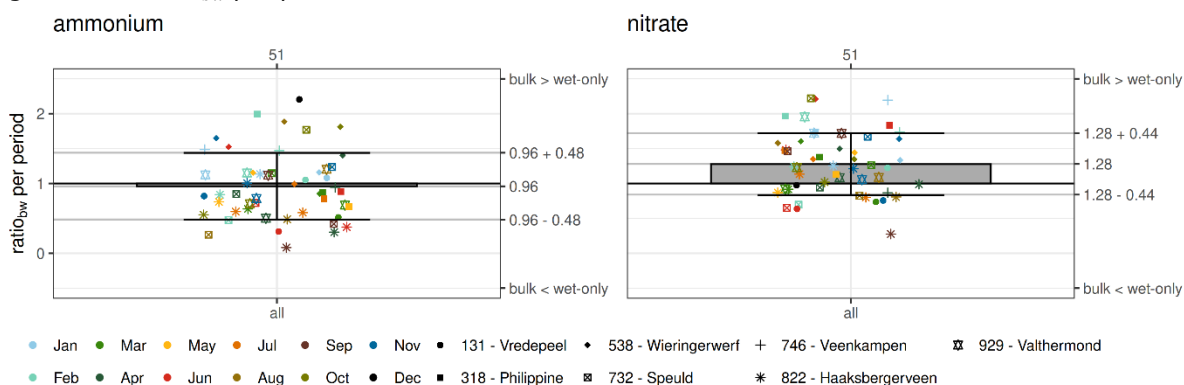
### Monthly and annual ratios

#### LMRe dataset

For each bulk period at each location, we calculate the ratio between bulk deposition and wet-only deposition ( $ratio_{bw}$  see Eq. 1). The results are shown in Figure 3. We see that  $ratio_{bw}$  varies between periods and locations. For ammonium,  $ratio_{bw}$  ranges from 0.08 to 2.20, with an average of 0.96 and a standard deviation ( $\sigma$ ) of 0.48. For nitrate,  $ratio_{bw}$  ranges from 0.027 to 2.22, with an average of 1.28 and  $\sigma$  of 0.44.

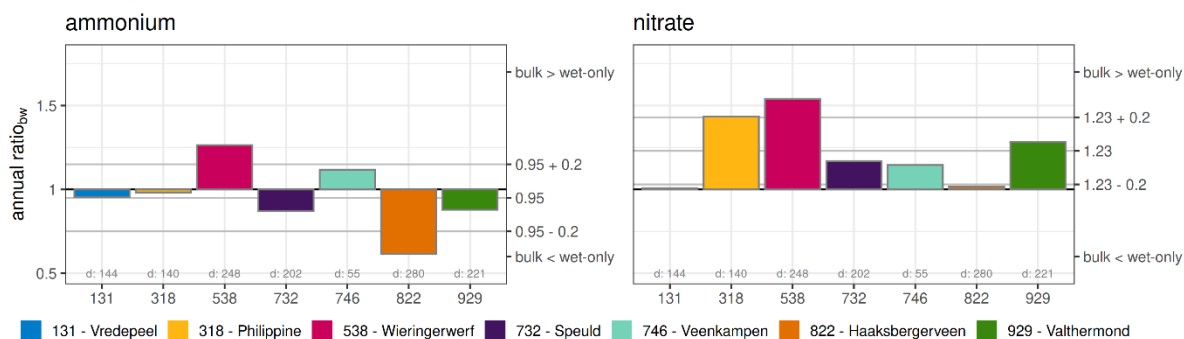
This means that for ammonium the uncorrected values from the bulk instrument are similar to the wet-only values on average, but the uncertainty per period is large ( $\sigma = 48\%$ ). For nitrate, in addition to the random uncertainty there is also a systematic difference: the bulk instrument values are on average 28% higher than the wet-only values.

Figure 3 The  $ratio_{bw}$  per period for ammonium and nitrate in the LMRe dataset.



The individual symbols represent the values for each bulk period (with different colors for months and different symbols for locations). The bar shows the average  $ratio_{bw}$  compared to 1. The error bars indicate the mean  $\pm$  the standard deviation. The corresponding values are next to the right axis.

Figure 4 The annual  $ratio_{bw}$  for ammonium and nitrate in the LMRe dataset.



The bar shows the annual  $ratio_{bw}$  compared to 1. The grey horizontal lines indicate the mean across the LMRe locations and the mean  $\pm$  the standard deviation, the corresponding values are next to the right axis. The number of days included in the analysis is displayed above the x-axis. The average annual ratios differ slightly from the average ratios per period. This is because averaging the ratios per period is not the same as averaging deposition values first, followed by calculating the ratio.

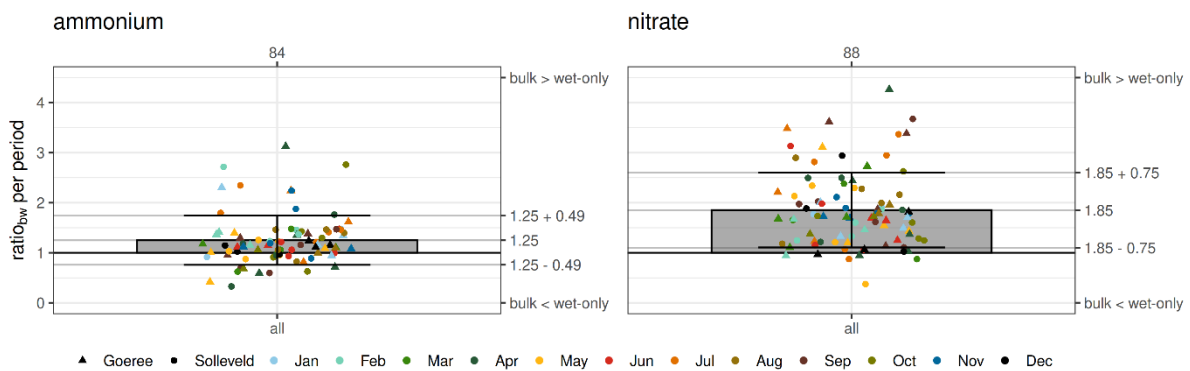
In addition, we calculate the annual deposition values from the bulk and wet-only instruments. We do this by summing the approved data for all available periods over February 2024 to February 2025. For these annual values we also calculate the  $ratio_{bw}$ . The results for the different locations are shown in Figure 4, along with the mean and standard deviation. For ammonium, the ratio ranges from 0.61 to 1.26 with a mean of

0.95. For nitrate, the ratio ranges from 1.01 to 1.54 with a mean of 1.23. The standard deviation is approximately 0.2 for both ammonium and nitrate. For ammonium, the average  $ratio_{bw}$  is lower than most values reported in the literature (see Figure 2 for comparison). For nitrate, the average  $ratio_{bw}$  is more consistent with previous results. The standard deviations for the annual ratios are similar to those found in literature.

*Maasvlakte dataset*

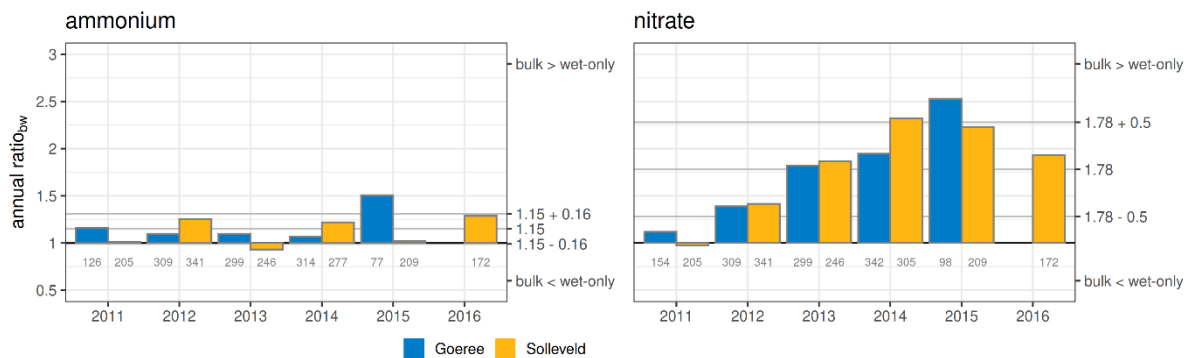
There is also a large variation in the  $ratio_{bw}$  per period for the MV dataset (Figure 5). For ammonium, the  $ratio_{bw}$  varies between 0.32 and 3.13 with an average of 1.25 and  $\sigma$  of 0.49. For nitrate, the  $ratio_{bw}$  is higher, ranging from 0.37 to 4.26 with the average  $ratio_{bw}$  of 1.85 and  $\sigma$  of 0.75. For the annual values, the average  $ratio_{bw}$  for ammonium is smaller (1.15), with  $\sigma$  is 0.16 (Figure 6). For nitrate, the annual average is 1.78 and  $\sigma$  is 0.5. Here, a clear year-to-year pattern can also be observed, with low ratios in 2011 and the highest ratios in 2015.

Figure 5 The  $ratio_{bw}$  per period for ammonium and nitrate in the MV dataset.



The individual symbols represent the values for each bulk period (with different colors for months and different symbols for locations). The bar shows the average  $ratio_{bw}$  compared to 1. The error bars indicate the mean  $\pm$  the standard deviation. The corresponding values are next to the right axis.

Figure 6 The annual  $ratio_{bw}$  for ammonium and nitrate in the MV dataset.



The bar shows the annual  $ratio_{bw}$  compared to 1. The grey horizontal lines indicates the mean across the years and the locations and the mean  $\pm$  the standard deviation, the corresponding values are next to the right axis. The number of days included in the analysis is displayed above the x-axis. The average annual ratios differ slightly from the average ratios per period. This is because averaging the ratios per period is not the same as averaging deposition values first, followed by calculating the ratio.

### Cause of the variation in the ratio<sub>bw</sub>

To investigate the causes of the variation in the difference between the bulk and wet-only collectors, we fit different statistical linear models.

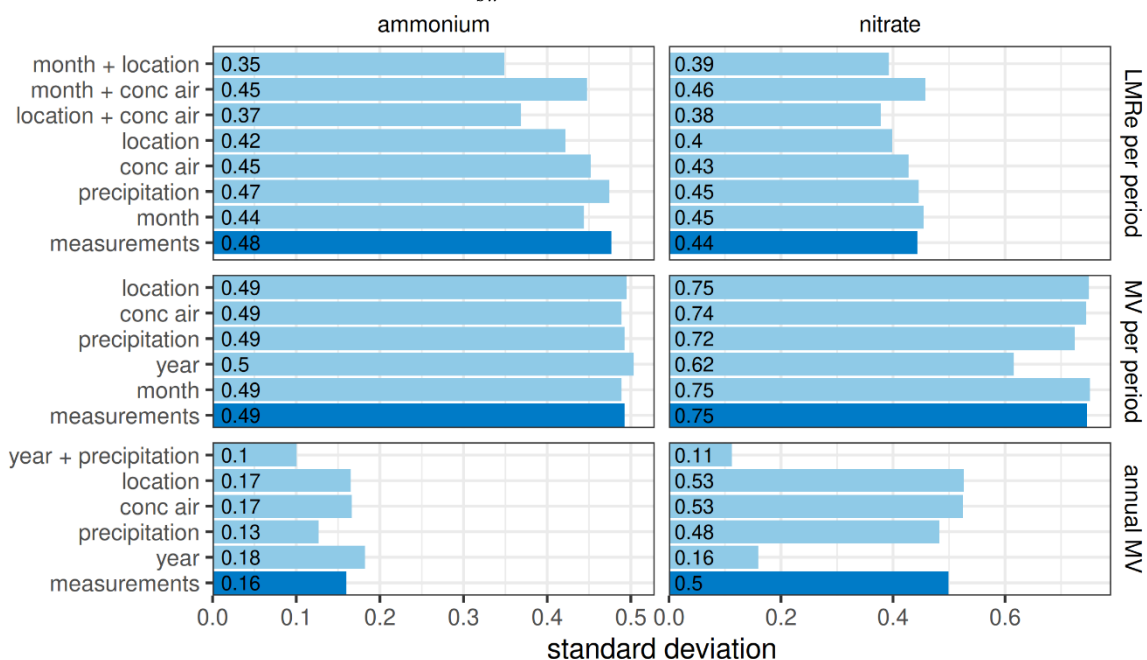
We start with the simplest model:  $ratio_{bw} = a$ . The standard deviation of the residuals from this model is the same as the standard deviation of the measurements. We then expand the model by adding different variables one by one. If the model standard deviation decreases after adding a variable, this indicates that the variable has predictive value for ratio<sub>bw</sub>.

We do this for the different datasets: the ratio<sub>bw</sub> per period for LMRe and MV datasets, and the annual ratios for the MV dataset. We focus only on the reduction of the model standard deviation, because all these datasets are too small to use the values of the model coefficients and associated statistics. In other words, we do not interpret the direction or size of the relationships, but only whether a relationship exists.

The variables we analyze are: month, location, precipitation amount (KNMI) and air concentration of NH<sub>3</sub> (for ammonium) and NO<sub>2</sub> (for nitrate). See the appendix for a description of air concentration data. Because the MV dataset covers multiple years, we also add year as a variable. Note that month, year and location do not cause the variation in ratio<sub>bw</sub>, but are proxies for the actual, underlying causes of variation such as distance to emission sources and meteorological variables.

For the LMRe dataset per period, Figure 7 shows that a model including only *locations*, *month* or *air concentration of ammonia* reduces the standard deviation for ammonium from 0.49 to 0.42-0.45. This means that for ammonia different *locations*, *month* or *air concentrations* have a different ratio<sub>bw</sub>. It also indicates that there is no fixed ratio<sub>bw</sub> for the whole country or per month.

Figure 7 The standard deviation of the ratio<sub>bw</sub> of the different model runs.



The standard deviation of the ratio<sub>bw</sub> for the measurements (dark blue) and of the different model runs (light blue) for ammonium (left) and nitrate (right) for the different datasets (different rows).

Furthermore, Figure 7 shows that the model standard deviation does not decrease for the model with only the *precipitation*. This means that the amount of precipitation has little influence on the difference between bulk and wet-only collectors.

The standard deviation is smallest when combining *month* and *location*, or combining *air concentration ammonia* and *location*. With these combinations, the standard deviation decreases from 0.46 to  $\approx 0.35$ . Combining *month* and *air concentration of ammonia* does not further reduce the standard deviation. This indicates that these two variables have the same effect, and that the month-to-month differences are likely explained by the air concentration of ammonia. Ammonia concentrations follow an annual cycle, with low concentrations in winter, a peak in spring, sometimes a peak in autumn and an average concentration in summer.

For nitrate, we observe that the model standard deviation mostly decreases when we include *location* as variable in the model. In that case, the standard deviation decreases from 0.44 to  $\approx 0.40$ . For nitrate, the variable *month* has almost no effect.

For the MV dataset per period, we observe that for ammonium almost none of the models have a lower standard deviation than the measurements. This is different from the LMRe dataset, where *air concentration of ammonia*, *location* and *month* did have an effect. A possible reason is that the locations in the MV dataset are relatively close to each other and are also similar in terms of environment. In contrast, the LMRe locations are either further apart or located in very different types of environments. This suggests that there is no fixed  $\text{ratio}_{\text{bw}}$  for the entire country, but there might be a fixed  $\text{ratio}_{\text{bw}}$  for a specific region with similar conditions. To further investigate the variation between these two locations, we calculated the difference in  $\text{ratio}_{\text{bw}}$  for all available measurement periods between the two locations. For ammonium, the differences have an average of 0.46 and range from 0.05 to 2.8. For nitrate, the average is 0.49 and the range is 0.03 to 1.8. This means that, when the data are analyzed per period, there are still large differences between locations.

One reason for little influence of month and air concentration could be that the air concentrations of ammonia in these two areas are relatively low (around  $2 \mu\text{g}/\text{m}^3$ ) and show less variation ( $\sigma \approx 1.4 \mu\text{g}/\text{m}^3$ ) than the locations in the LMRe dataset (where  $\sigma$  is higher). This suggests that if the air concentration of ammonia is not too high and does not fluctuate too much, the ratio remains more constant over the year.

For nitrate, the MV dataset shows a different pattern. The standard deviation decreases significantly when we add year as a variable to the model. This means that there are large differences in the  $\text{ratio}_{\text{bw}}$  from year to year. For ammonium, adding the year as a variable does not decrease the standard deviation.

The main difference between the MV dataset per period and the annual dataset is the influence of adding precipitation amount to the model. For the per period dataset, we saw no effect, but for the annual dataset, adding precipitation amount decreases the standard deviation. This may indicate that precipitation amount has a stronger influence on the annual  $\text{ratio}_{\text{bw}}$  than on the  $\text{ratio}_{\text{bw}}$  for shorter periods.

## **Discussion and outlook**

In this study, the RIVM compared bulk wet deposition measurements with wet-only wet deposition measurements at stations of the National Precipitation Monitoring Network (LMRe). We determined the  $\text{ratio}_{\text{bw}}$  between the two instruments for each period (about four weeks). The LMRe experiment shows that the bulk collector, without correction, has an uncertainty of at least  $\pm 45\%$  ( $1\sigma$ ) for such a period. This is the uncertainty on the ratio between the wet-only and bulk measurements; the total uncertainty on the bulk measurements is larger, as it also includes the inherent uncertainty of the wet-only measurements.

On an annual basis, the uncertainty decreases to about 20%. This annual uncertainty corresponds well with values in the literature.

Note that we apply a strict quality control to the data in this study. This was possible because the laboratory also determined the concentrations of other substances in the rainwater. If these substances are not measured, only a less stringent validation can be performed. This would increase the uncertainties mentioned above.

We also check the volume of water against the precipitation measured by the KNMI. This extra validation step reduces the uncertainty further. Moreover, our bulk collectors are 'advanced' compared to other designs. Using more simple collectors would also increase the uncertainties.

For ammonium, the average  $\text{ratio}_{\text{bw}}$  is around 1. This means that, on average, the bulk and wet-only provide similar results. For nitrate, the average  $\text{ratio}_{\text{bw}}$  is around 1.2, meaning that the bulk collector systematically overestimates wet deposition by about 20%. The Maasvlakte experiment (MV) gives different values for the average  $\text{ratio}_{\text{bw}}$ : for ammonium the bulk collector overestimates with 25% ( $\pm 49\%$ ), and for nitrate with 85% ( $\pm 75\%$ ).

To investigate the reasons for the variation in the difference between the bulk and wet-only collectors, we fitted statistical linear models to the different datasets. These analyses show that the difference between the bulk and wet-only collectors is not the same across the entire country or from month to month. From the LMRe dataset, we find that *air concentration of ammonia and nitrogen oxides* and *location* are the most predictive variables for the  $\text{ratio}_{\text{bw}}$  for both ammonium and nitrate. From the MV dataset, we observe that for nitrate *year* is the most predictive value and *air concentration* and *location* are not important.

In all those cases the standard deviation decreases. This means that the uncertainty could potentially be reduced by not using a constant ratio for the whole country and all months, but instead by using a statistical model that includes other variables. Developing such a model is not possible with our current datasets, as they are too small. To develop such a statistical model, a much larger dataset is needed—covering several years and multiple locations.

Moreover, additional meteorological predictive variables such as *temperature* and *evaporation* could be added to the model, or chemical variables such as concentrations of ammonium and nitrate in aerosols.

In a future experiment, it would also be advisable to change the bottles of the bulk and wet-only instruments at the same time. In this way, no conversion from the wet-only period to the bulk period would be needed.

Furthermore, because air concentration appears to be important, it would be useful to measure the air concentration of ammonia and nitrogen oxides locally. For instance by placing passive samplers next to the rain collectors, and changing them at the same moment.

### **Conclusions and recommendations**

The measurement values of bulk instruments have high uncertainties, even after strict quality control. Therefore, if precise measurements are needed, we strongly advise using wet-only collectors when possible. We do not recommend correcting bulk monthly values. However, if only bulk collectors are available, applying a correction can improve the annual values. This research shows that the correction varies with location and year. We recommend using a local ratio instead of a fixed value. To do this, it is necessary to measure with both instruments at one location, preferably in the same area as the other bulk collectors. This approach can reduce the uncertainty from  $\pm 20\%$  to 10-15%. Determining the definition of the 'same area' is outside the scope of this research.

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## Appendix: Comprehensive method

### Description of the bulk and wet-only collectors in the LMRe

The wet-only instruments are manufactured by Eigenbrodt, model [NSA181-KHT](#) (white instrument in Figure 8).

The bulk collectors are provided by TNO (Erisman *et al.*, 2003; black instrument in Figure 8). The bulk collector consists of a funnel on a plastic pipe, which is the same height as the wet-only instrument. On top of the funnel are bird spikes to prevent birds from sitting on the bulk collector. This is to minimize bird droppings ending up in the collected water. The bottle that collects the water is dug in and covered with aluminum foil to minimize evaporation.

Figure 8 Photos of the wet-only and bulk collector.



Left photo: The wet-only (white) and bulk collector (black) at Vredepeel. Center photo: The wet-only collector with the lid is open. Right photo: and the bulk collector's bottle in the ground.

The wet-only instruments automatically switch the bottles every two weeks, except for the instrument at the EMEP-site the Zilk (444), which switches bottles every day. These daily analyses have the disadvantage that there may be too little water in the bottles to perform all the lab analyses, even though there was some precipitation that day. If this happens for several days in a row, the wet-only instrument underestimates the deposition compared to the bulk collector. Because the analysis of the wet-only bottles at De Zilk deviates too much from the other stations, we exclude this location from further analysis.

An RIVM staff member manually changes the bottles of the bulk instruments approximately every four weeks, on a work day close to the changing day of the wet-only.

### Chemical analysis

The laboratory Eurofins analyses the rainwater and determines the concentration of the following substances: ammonium ( $\text{NH}_4^+$ ), calcium ( $\text{Ca}^{2+}$ ), chloride ( $\text{Cl}^-$ ), fluoride ( $\text{F}^-$ ), phosphate ( $\text{PO}_4^{3-}$ ), hydrogen ( $\text{H}^+$ ), potassium ( $\text{K}^+$ ), magnesium ( $\text{Mg}^{2+}$ ), sodium ( $\text{Na}^+$ ), nitrate ( $\text{NO}_3^-$ ), sulphate ( $\text{SO}_4^{2-}$ ). Eurofins also measures the mass, alkalinity, acidity (pH) and electrical conductivity (EC) of the water.

For the bulk collector, the total nitrogen content is also determined. From this, we determine the concentration of organic nitrogen by subtracting the concentration of ammonium and nitrate.

$$[\text{org}_N] = [\text{total}_N] - [\text{NO}_3^-] - [\text{NH}_4^+] \quad \text{Eq. 3}$$

The amount of organic nitrogen is an indicator for chemical conversions in the bottle. Or an indicator of organic material, such as leaves, that are blown in since the bulk collectors are always open.

#### Validation criteria – LMRe

The wet-only dataset is validated as part of the LMRe (Somhorst *et al.*, 1994). The validation consists of five parts. The first four indicate that a component may have been determined incorrectly. For bulk collectors, we use the same criteria. We reject bottles if:

1. The ion balance deviates:  
 $|\sum \text{Eq}_{\text{cations}} - \sum \text{Eq}_{\text{anions}}| > 40 \frac{\mu\text{Eq}}{\text{L}}$ , where Eq stands for equivalent (the concentration of the ion times the charge number of the ion)
2. The acid balance deviates:  
 $|([\text{H}^+] + 2[\text{NH}_4^+]) - ([\text{NH}_4^+] + [\text{NO}_3^-] + 2[\text{SO}_4^{2-}] - 2[\text{Ca}^{2+}])| > 50 \frac{\mu\text{mol}}{\text{L}}$
3. The calculated electrical conductivity differs from the measured value:  
 $|\text{EC}_{\text{measured}} - \text{EC}_{\text{calculated}}| > 7 \frac{\mu\text{S}}{\text{cm}}$ , where  $\text{EC}_{\text{calculated}}$  is the sum of the concentration of the ions times the electrical conductivity of each ion
4. The ratios of different components are too large or small:  
 $0.99 > \frac{[\text{Cl}^-]}{[\text{Na}^+]} > 1.23$ ,  $0.10 > \frac{[\text{Mg}^{2+}]}{[\text{Na}^+]} > 0.14$  &  $0.09 > \frac{[\text{Mg}^{2+}]}{[\text{Cl}^+]} > 0.13$
5. There is a high phosphate concentration, which indicates bird droppings:  
 $[\text{PO}_4^{3-}] < 10 \mu\text{mol/L}$  (= 0.95 mg/L)

#### Combining bulk and wet-only dataset - LMRe

The measurement periods of the instruments are not the same. As a result, they may capture different rain events. Therefore, we convert the concentrations of the components and the water mass from the wet-only to match the bulk periods. For this, we use a KNMI dataset<sup>3</sup> with daily precipitation (Soenario and Sluiter, 2010). This dataset is a combination of precipitation measurements from 300 rain stations where volunteers manually record the precipitation daily at 08 UTC. These data have been interpolated to a 1x1km<sup>2</sup> grid. For each LMRe station, we use the daily precipitation from the grid cell in which the LMRe station is located.

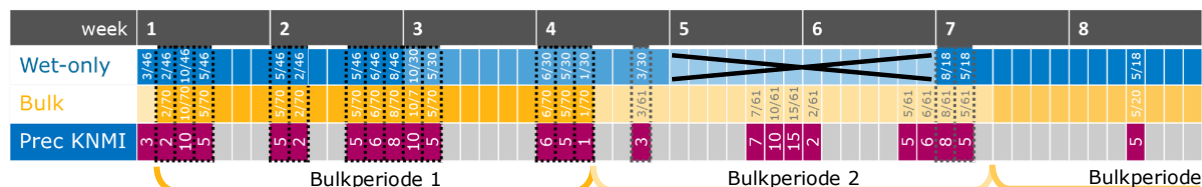
We then create a daily dataset from the wet-only dataset. This consists of the following steps, see also Figure 9 for an illustrative example.

1. We determine the precipitation fraction ( $f_N$ ) per day:  $f_N = N_{\text{day}}/N_{\text{period}}$  (where  $N_{\text{day}}$  is the amount of precipitation on a single day, and  $N_{\text{period}}$  the total amount of precipitation in that period. In Figure 9 the precipitation fraction of the first day is 3/46).
2. We multiply  $f_N$  by the concentrations of the components and the water mass. This gives the weighted concentration or weighted volume of the wet-only per day.
3. Finally, we sum the weighted concentration and volume for all days on which the bulk sampler was collecting precipitation (black bordered columns in Figure 9). This results in the concentration and volume of the wet-only for the days when the bulk collector was operating.

In some cases, the wet-only has no results (see week 5 & 6 in Figure 9). To be able to calculate  $\text{ratio}_{\text{bw}}$  in these cases, we also create a daily dataset from the bulk data. We determine the concentration and volume of the bulk and wet-only over the days for which both instruments have a value (grey bordered columns in Figure 9).

<sup>3</sup> <https://dataplatfom.knmi.nl/dataset/rd1-5>

Figure 9 Illustrative example of combining the wet-only and bulk dataset, because the instruments do not measure at the same time.



Each box represents a day. The numbers in the precipitation row indicate the amount of precipitation in mm. The numbers in the wet-only and bulk row are the precipitation fraction. The black and grey bordered columns indicate the days used in the combined dataset. See the text for further explanation.

**Determination of precipitation and wet deposition**

Finally, we determine the total amount of precipitation and deposition of both instruments. The precipitation is [mm] determined by:

1. Dividing the mass [g] of water by the density (1 g/mL) → volume ( $V_{\text{water}}$ )
2. Dividing the volume [mL] by the surface area of the instrument's opening [cm<sup>2</sup>] ( $A_{\text{wet-only}} = 500 \text{ cm}^2$  and  $A_{\text{bulk}} = 391 \text{ cm}^2$ ) → precipitation [mL/cm<sup>2</sup>]
3. Multiply by 10 → precipitation  $\left[\frac{\text{mL}}{\text{cm}^2}\right] \rightarrow \left[\frac{\text{L}}{\text{m}^2}\right] = [\text{mm}]$ .

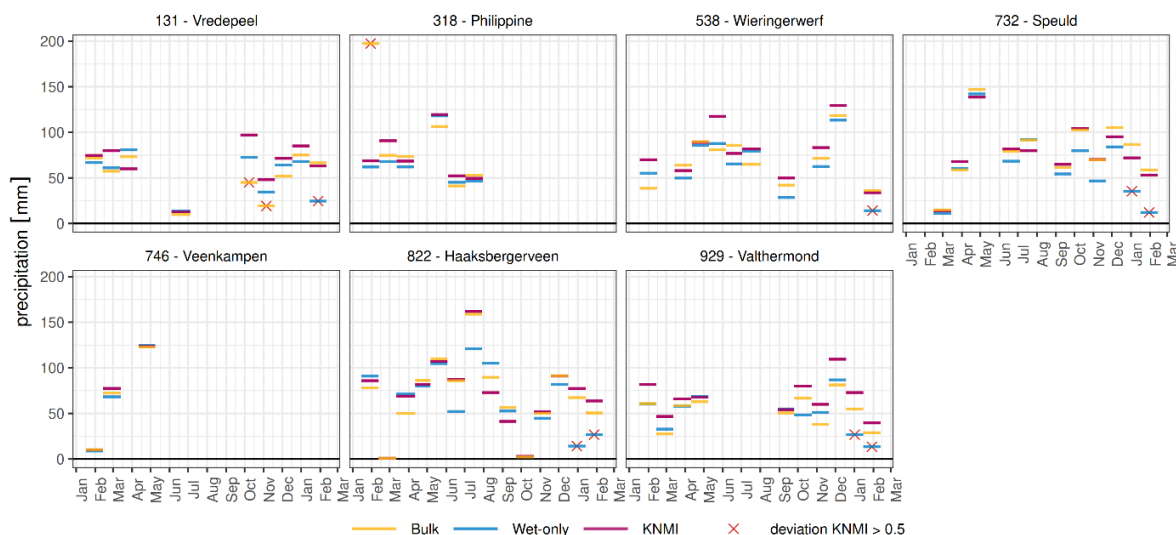
The wet deposition is calculated by multiplying the concentration ( $c$ ) in the water by the water volume ( $V_{\text{water}}$ ) in the bottle and dividing by the area of the instrument ( $A$ ):

$$D_{\text{wet}} = \frac{c \cdot V_{\text{water}}}{A} \tag{Eq. 4}$$

**Extra validation – precipitation quantity**

Figure 10 shows the amount of precipitation measured by both instruments and the interpolated data from the KNMI. The precipitation is recalculated for the bulk periods.

Figure 10 Time series of the total precipitation in mm.



The total precipitation of the bulk collector is in yellow, of the wet-only collector in blue and the KNMI grid data is in violet. The length of the bars represents the duration of the bulk periods. Red crosses are excluded samplers.

We see that in some periods, the precipitation from the bulk or wet-only instruments deviates from the KNMI precipitation. For example, the precipitation of the bulk instruments in January in Philippine, and the precipitation of the wet-only instruments in January and February at Speuld and Valthermond. In this study, we only include the periods where the deviation from the KNMI precipitation is less than 50% ( $|p_{KNMI} - p_{\text{sampler}}|/p_{KNMI}$ ). This results in a total of 51 bulk periods.

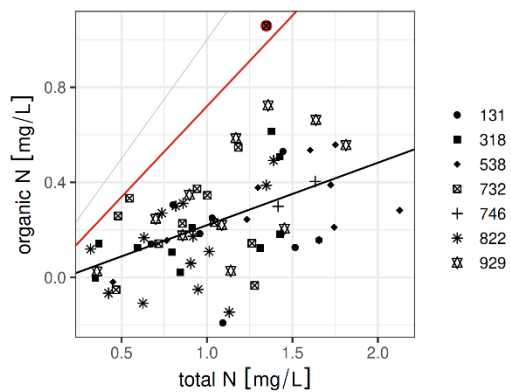
Furthermore, we see that in 40% of the periods, the precipitation measured by the wet-only collector is higher than that from the bulk collector, for example in March at Vredepeel. A possible explanation is that water may evaporate from the bulk collectors. However, in most periods, the bulk collector captures more water than the wet-only instrument. It is known that the wet-only may miss the beginning of rain events (because it takes some time for the lid to open), as well as very light rain events. We also observe that in most cases the KNMI precipitation is higher: for the bulk collectors this is the case in 68% of the periods, and for the wet-only instruments 78%.

#### *Additional validation – Organic nitrogen*

Because the bottles in the bulk collector are not kept cool, substances in the bottle can react with each other or be converted due to biologic processes. Leaves or other organic material may also be blown into the bulk collector. An indicator for this is the amount of organic nitrogen. For this purpose, the laboratory also determines the total amount of nitrogen in the bulk collectors. If the amount of organic nitrogen is too high compared to the total amount of nitrogen, we reject the bottle.

To determine what is too high, we compare the amount of organic nitrogen in all bottles to the total amount of nitrogen (Figure 11). Through these data points we have fitted a linear regression (black line in Figure 11). With this regression equation, we also calculate the fitted amount of organic nitrogen  $[\text{org}_N]_{\text{fit}}$  for each bottle. If the difference between the measured value and calculated value is more than 50% of the total nitrogen, we reject the bottle ( $[\text{org}_N]_{\text{gemeten}} - [\text{org}_N]_{\text{fit}} > 0.5 \cdot [\text{totaal}_N]$ ).

Figure 11 A comparison of the amount of organic nitrogen and the total amount of nitrogen.



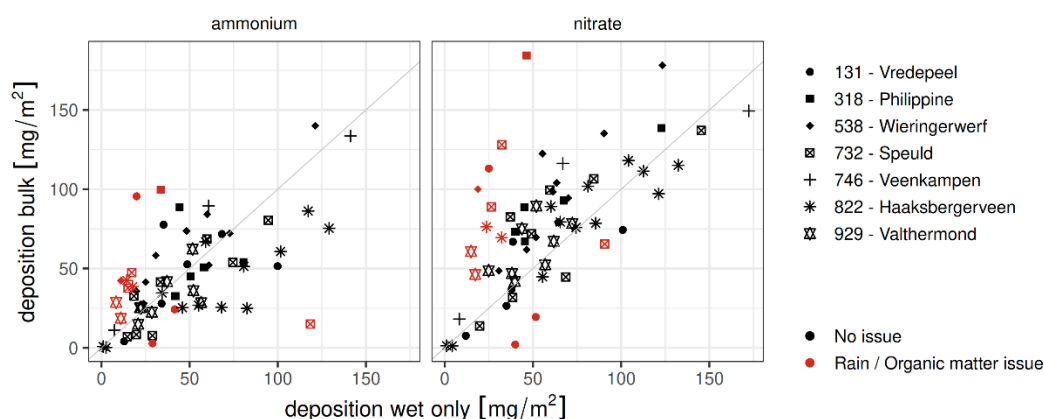
The different symbols indicate the different locations. The black line is the regression line:  $[\text{org}_N] = -0.0326 + 0.26 \cdot [\text{tot}_N]$ . The red line and red points indicate when the measured organic nitrogen minus the calculated organic nitrogen is more than 50% of the total nitrogen.

### Extra validation – Results LMRe

Figure 12 shows the wet deposition of ammonium and nitrate measured with the wet-only instrument compared to that of the bulk collector. The red points indicate cases when the precipitation from one of the instruments deviated too much from the KNMI precipitation or when the organic nitrogen was too high.

One measure of variation is  $R^2$ . The closer  $R^2$  is to one, the less variation there is within the data, and the more similar the datasets are. Excluding the red points increases the  $R^2$  for ammonium from 0.19 to 0.39. For nitrate, it increases from 0.23 to 0.70.

Figure 12 A comparison of the deposition measured with bulk and wet-only instruments for ammonium and nitrate.



The different symbols indicate the different locations. If the data point is red, the precipitation from one of the instruments deviated too much from the KNMI precipitation or the organic nitrogen was too high.

### Additional data – air concentration of ammonia and nitrogen oxides

To determine the air concentration of ammonia to use in the statistical model, we use data from the national air quality monitoring network (Landelijk Meetnet Luchtkwaliteit, LML<sup>4</sup>) and the ammonia monitoring network in the Netherlands (Meetnet Ammoniak Nederland, MAN<sup>5</sup>).

Some of the LMRe locations are also part of the LML, where a miniDOAS instrument measures hourly air concentrations of ammonia (stations 131, 538, 929). For these stations, we calculate an average value over the bulk collection period. For the other locations (318, 732, 746, 822, Goeree and Solleveld), we use the monthly value from the nearest MAN tube. Note that, because the exact location and period may differ, these values are less representative for the LMRe locations.

For the air concentration of nitrogen dioxide, we use the hourly data measured with the Teledyne instrument from the LML. Because the national coverage of  $\text{NO}_2$  measurements with high temporal resolution (about 70 stations) is much greater than for  $\text{NH}_3$  (about 8 stations), we use the Teledyne instrument at that location (131, 318, 538, 929) or the nearest Teledyne instrument (732, 746, 822, Goeree and Solleveld).

Note that at the time of preparation of this report, the concentration data for January 2025 were not yet available and we therefore did not include this month in the statistical model.

<sup>4</sup> <https://data.rivm.nl/data/luchtmeetnet>

<sup>5</sup> <https://man.rivm.nl/>