Analysis of aerosol nitrate in the Yakima valley in the winter of 2015/ 2016

Author: Ranil Dhammapala

Washington State Department of Ecology

ranil.dhammapala@ecy.wa.gov; 360-407-6807

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Background

The Yakima Air Wintertime Nitrate Study (YAWNS) was conducted in January 2013, with measurements made mostly in the upper Yakima valley. The objective of the study was to investigate the scientific reasons behind high aerosol nitrate content in $PM_{2.5}$ in the area. The YAWNS study found that ammonia emissions from agricultural operations combined with NOx from vehicles under the right meteorological conditions to produce aerosol nitrate. However one of the limitations of the study was that no representative measurements of nitrate were conducted in the lower Yakima valley, in spite of most ammonia sources being located in the lower Yakima valley.

To address this limitation, Ecology collected several gravimetric samples using Federal Reference Method (FRM) $PM_{2.5}$ samplers in Sunnyside and Toppenish, between November 2015 and January 2016. The Teflon filters were analyzed for nitrate at Ecology's Manchester Environmental Laboratory.

Figure 1: Map of study area with monitoring sites identified by red circles

Main findings

While detailed analyses are presented in the Appendix, data show that on days with elevated $PM_{2.5}$ concentrations:

- Average aerosol nitrate levels were lowest in Yakima and highest in Toppenish, with Sunnyside in between.
- On average, nitrate accounted for about a quarter of the $PM_{2.5}$ mass at Yakima and Toppenish, and a third at Sunnyside
- Elevated nitrate levels occurred in both valleys simultaneously, on days with high relative humidity, low temperatures and low winds. This suggests common sources of aerosol nitrate precursors in both valleys.
- Nitrate levels in the upper valley were slightly higher than the average of the previous 5 winters.
- While Yakima experienced slightly lower $PM_{2.5}$ than recent years, Toppenish had more $PM_{2.5}$.

Recommendations

The main YAWNS study concluded that the pathway to reducing aerosol nitrate was not obvious, and recommended an air quality modeling study to help ascertain the most effective controls. The only added recommendation that can be made based on these 2015/ 2016 nitrate measurements, is that such a modeling study needs to take these data into consideration and accurately simulate upper and lower valley aerosol nitrate relationships.

Appendix

Choice of an analytical method

Manchester Environmental Laboratory (MEL) does not use the same analytical method for aerosol nitrate as the nationwide Chemical Speciation Network (CSN). However, the Washington State Department of Ecology (Ecology) requested that 16 archived FRM filters from Yakima, collected between January 2013 and March 2015 be analyzed for nitrate using MEL's Lachat analyzer, for comparison against the CSN Ion Chromatographic (IC) method. The FRMs were co-located with CSN samplers at the 4th Avenue monitoring site in Yakima, although FRM and CSN sampling and handling protocols are not identical. Filter storage could lead to some loss of nitrate aerosol, potentially biasing MEL results lower.

Nevertheless, 11 of the 16 MEL Lachat nitrate samples were within ±0.9 µg/m³ of the CSN IC method and have a linear correlation coefficient of 0.71, lending some credibility to the Lachat method in spite of a rather indirect comparison with the CSN IC method. These differences showed no dependence on sample age, $PM_{2.5}$ or nitrate concentration as shown in Figure A1.

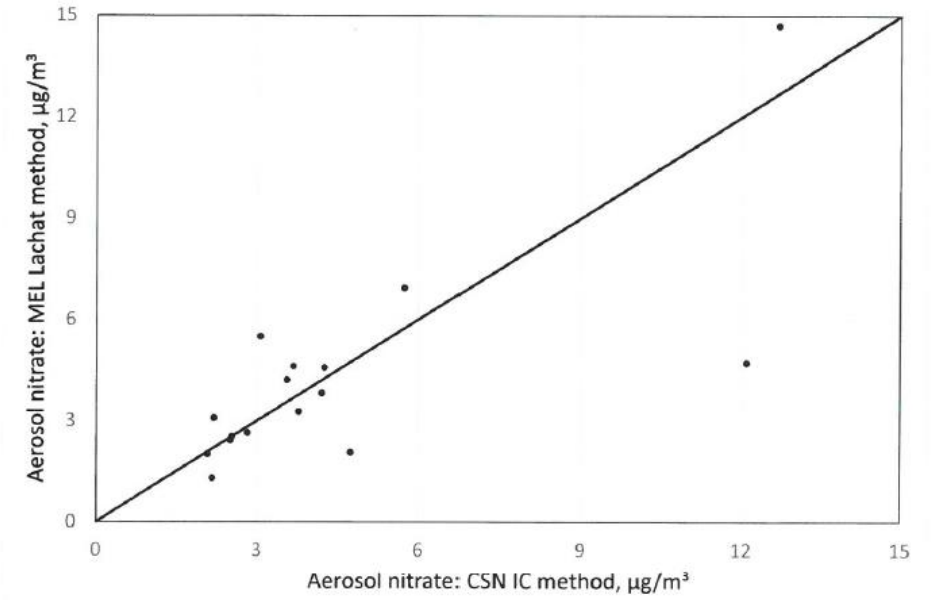

Figure A1: Testing the MEL Lachat method on archived FRM filters from Yakima, Jan 2013- Mar 2015

$PM_{2.5}$ and nitrate in Yakima, Toppenish and Sunnyside

Figure A2 shows the $PM_{2.5}$ and aerosol nitrate levels measured at Yakima (by the CSN sampler), Toppenish and Sunnyside (by Ecology) in the winter of 2015. The CSN site at Yakima has a sampling frequency of 1-in-6 days, but Ecology sampled in the lower valley on a 1-in-3 day schedule. However a few sampling days were missed and a few samples from both Toppenish and Sunnyside had to be invalidated due to shipping problems and storage concerns. $PM_{2.5}$ measurements from FRMs or continuous monitors are available daily.

To fill in missing nitrate concentrations in the timeseries, a Generalized Additive Model (GAM) was setup using available measurements and basic meteorological parameters (temperature, relative humidity and windspeed). Wind direction was not considered, as 24-hr average directions are not very meaningful. GAMs are powerful statistical models that help visualize how a variable (in this case, aerosol nitrate levels) responds to different parameters, even if the input data distributions are unknown. All but 10 randomly chosen measurements were used to develop the model and its output was verified against the unused data points- which it reproduced to within 3%, with an R^2 of 0.93. The GAM-modeled nitrate is also overlaid on Figure A2 (teal). For the most part, nitrate at all 3 sites follow the same temporal trend, in that they all rise and fall together. Higher nitrate levels are seen when the daily average relative humidity is over 85%, daily average windspeeds are under 4 mph and daily mean temperatures are under 35F.

As nitrate in the upper and lower valleys respond similarly to comparable meteorological conditions, they are very likely to have common precursor sources.

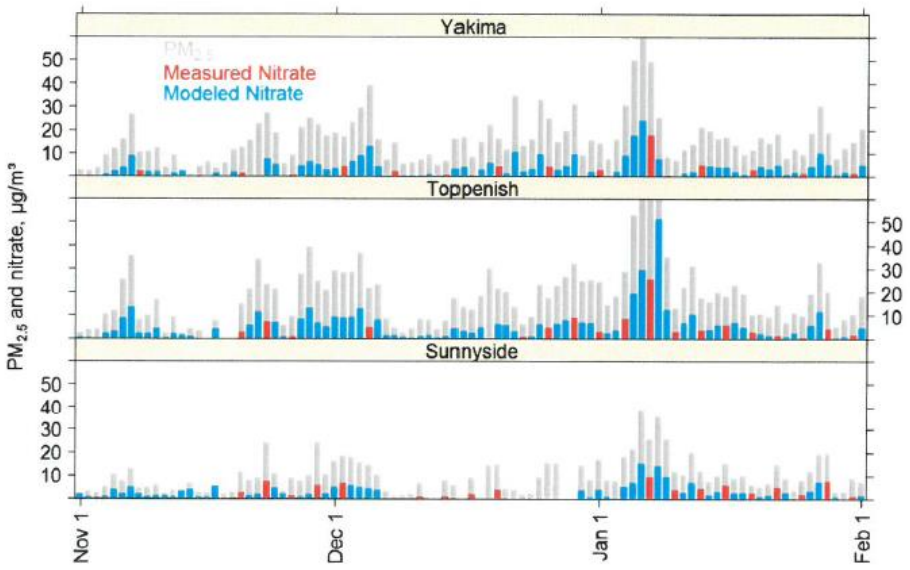

Figure A2: $PM_{2.5}$ and nitrate timeseries in the upper and lower Yakima valley, winter 2015/ 2016.

Comparison of $PM_{2.5}$ and nitrate averages on more polluted winter days

Figure A3 shows the average $PM_{2.5}$ and nitrate content on days with $PM_{2.5}$ levels over 12 µg/m³ for the time period of November 1, 2015 through January 31, 2016. Values for Toppenish and Yakima between 2010 and 2014 are provided for comparison. Toppenish recorded slightly more nitrate than Sunnyside, and Yakima saw about 1 µg/m³ less than Sunnyside.

Main inferences:

- While Yakima's nitrate content has increased slightly over the previous 5 years, its $PM_{2.5}$ concentrations dropped a bit, pushing the nitrate fraction from about one sixth to one quarter.
- In Toppenish, the $PM_{2.5}$ comparison is in the opposite direction, with the 2015/ 2016 winter recording higher $PM_{2.5}$ than the previous 5 years. It is unknown if nitrate content has changed over time, as no previous measurements exist.
- In Sunnyside, nitrate makes up about one third of $PM_{2.5}$. In spite of having the lowest $PM_{2.5}$ levels of the 3 communities, nitrate at Sunnyside was comparable to Toppenish. This is consistent with the nature of secondary pollutant formation: as ammonia and NO_x sources are spread over much of the lower valley, nitrate is unlikely to be confined to localized hotspots.
- It is unknown how nitrate and $PM_{2.5}$ levels have changed over time in Sunnyside.
- Caution must be exercised when comparing the 2015/ 2016 winter data with previous years, as year-to-year meteorological and source fluctuations can account for much of the differences. It does not necessarily imply a sustained improvement or worsening of emissions.

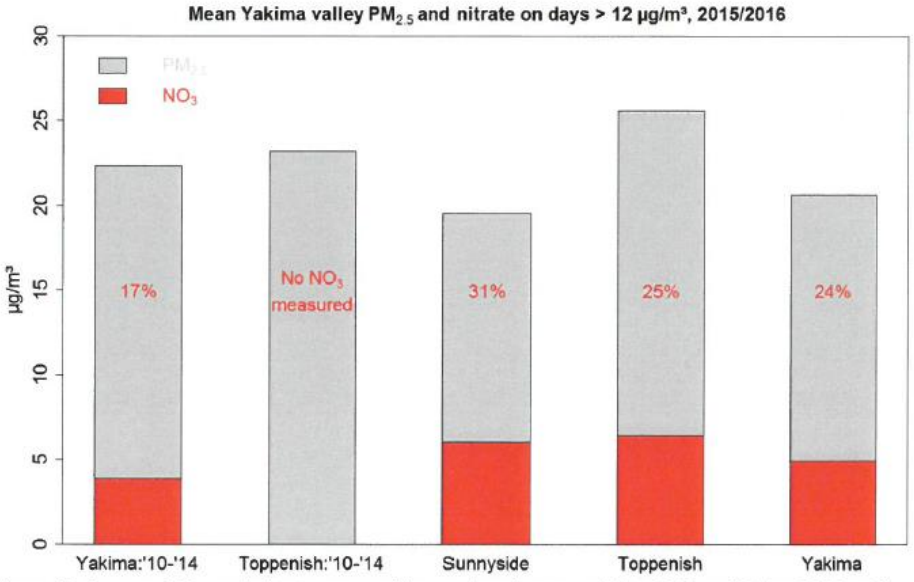

Figure A3: Average $PM_{2.5}$ and nitrate composition on days between 1 Nov 2015 and 31 Jan 2016, with $PM_{2.5}$ > 12µg/m³. Percentages in red are the average nitrate content in $PM_{2.5}$.