Appendix 22 - Analysis of the correlation between NMVOC emissions and ammonia emissions

Although Hobbs et al found a significant correlation between NMVOC (Non-methane Volatile Organic Compound) emissions and ammonia emissions for swine and poultry slurries, they did not find a significant correlation between NMVOC emissions and ammonia emissions for the dairy cattle slurry in their studies, as the former were too low. District staff evaluated this concern and found that the lack of a significant correlation at low VFA concentrations in particular tests could be expected, and that it clearly did not mean that the Hobbs et al data could not be used in emission factor development as Hobbs et al did in their publication. After reviewing the Hobbs et al paper, the staff found that:

1. The correlation between ammonia and NMVOC emissions from manure slurries is expected to be scientifically valid. Hobbs et al noted up front in the abstract of his publication that “there is a close association between ammonia and NMVOC emissions from manure”. He also noted within the publication that emissions of NMVOCs are a result of decay processes of organic matter, and that “ this proportionality has a physical basis. Henry’s law recognizes proportionality between the concentration in the liquid phase and that in the gaseous phase equilibrium can be approximated from the ratio of vapor pressure to solubility.”

2. The concentration of dimethyl sulfides from the laying hen tests was reported as 753 +/- 263 g m^{-3} day^{-1}. The concentration of volatile fatty acids from the dairy slurry tests was reported as 6.3 +/- 3.1 g m^{-3} day^{-1}.

3. The population coefficient of correlation, p, as used in the Hobbs study to determine correlation, is determined as the covariance of the variables, Cxy, divided by the product of the square roots of the variances of the two variables, σ_x and σ_y:

   $$p = C_{xy} / \sigma_x\sigma_y$$

   The covariance Cxy is determined as sum of the product of the deviation of each data point from the mean, divided by the number of samples.

   $$C_{xy} = 1/n \, \Sigma \, (x - x_{mean})(y - y_{mean})$$

   From these equations it is clear that with higher measured values of x and y (as in the poultry studies where NMVOC emissions were as much as an order of magnitude higher the emissions in the dairy slurry studies), the absolute differences between the measured values and means $(x - x_{mean})$and $(y - y_{mean})$ can be much larger, resulting in a higher covariance and a higher population coefficient of correlation. With lower measured values of x and y (as in the dairy slurry studies), the absolute differences between the measured values and means must of course be much lower, resulting in a lower covariance and population coefficient of correlation. That is, less correlation would be expected to be demonstrated in the dairy slurry studies because, as Hobbs at al state, the NMVOC values were lower.

Therefore, APCO concluded that the fact that less correlation between NMVOC and ammonia data was found in the dairy slurry study in no way indicates that this scientific relationship is invalid (Hobbs et al certainly did not find it to be invalid).

4. Although, the significant correlation between NMVOC and ammonia emissions was not actually demonstrated mathematically in this study for reasons described above, it is logical to conclude, as Hobbs et al did, that the relationship exists. That is, in the absence of other better valid data, if 14 grams of ammonia and six grams of VFAs were measured in a laboratory test of a wet dairy manure slurry, and it was known that 14 lb of ammonia was emitted from the wet manure in a dairy lagoon with similar characteristics to the laboratory slurry, that the VFA emissions from the lagoon could be estimated as six pounds, even in the absence of laboratory data confirming the mathematical correlation for these particular tests.