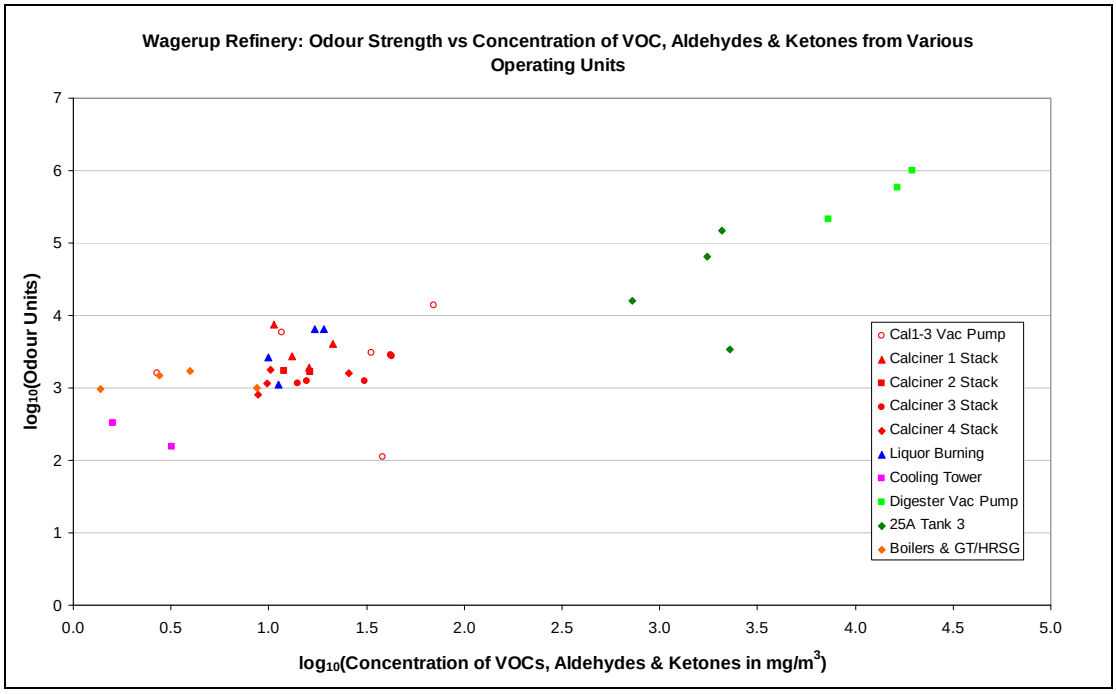
Notes on the Relationship Between Measured Odour Units and Concentration of VOCs, Aldehydes and Ketones of Gases Emitted from Various Units at Wagerup Refinery
- Updated as of 04 February 2005

During 2001, 2002, 2003 and 2004, samples of emitted gas were taken from operating units at the Wagerup Refinery. Some samples were subjected to analysis for content of Volatile Organic Compounds (VOCs), aldehydes and ketones and others were measured by olfactometry to produce Odour Unit (OU) measurements. In some cases, samples were taken on the same day from the same units. This enabled us to obtain, for what we believe to be similar gases from the same operating unit, both a measurement of OU and a measurement of concentration of VOCs, aldehydes and ketones.

The measurements of OU were then plotted against concentrations of gases taken on the same day. Most of the data were from 2002 but some are more recent. The OU measurements ranged from 110 to 984,000 while total VOC, aldehyde and ketone concentration ranged from 1.38 to 19652 mg/m^3. The fact that both variables ranged over several orders of magnitude led to plotting of $\log_{10}$ values rather than raw data values. The following chart was produced.

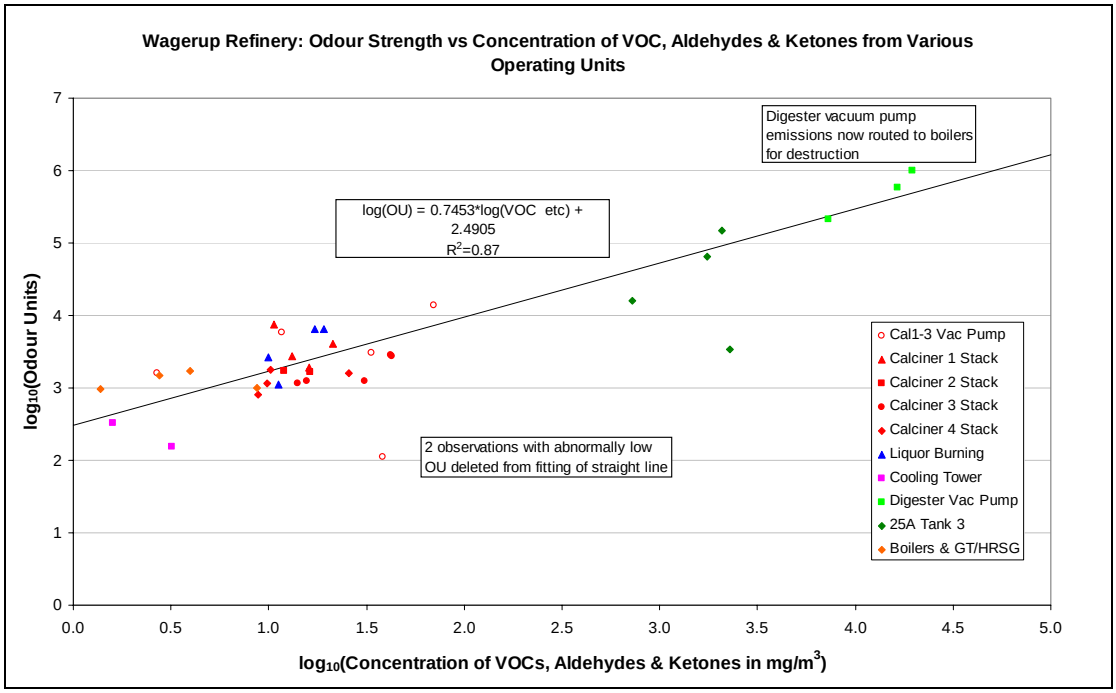


A line of best fit to these data (excluding the one anomalous observation for each of the Calciner Vacuum Stack and 25A-3 tank) was produced by linear regression. Its equation is:

$$\log_{10}(\text{OU}) = 0.7453 \times \log_{10}(\text{Total VOC etc}) + 2.4905$$

with $R^2 = 0.87$ and standard deviation of the residual equal to 0.32.

The fitted line is shown in the following chart.



We note that this equation is equivalent to:

$$OU = 309.4 \times (\text{Total VOC etc})^{0.7453}$$

and an error term that is multiplicative to Total VOC etc. concentration.

This equation is of a form that we expect if what we are detecting in the odour is the concentration of the VOCs, aldehydes and ketones. That is, the number of dilutions required till we can no longer detect an odour is (roughly) proportional to the concentration of the VOCs and other gases.

The equation says that given a certain concentration of the gases, we can predict, (subject to some uncertainty, as is inherent in any measurement of OU), what the OU of the gas will be as measured by olfactometry.

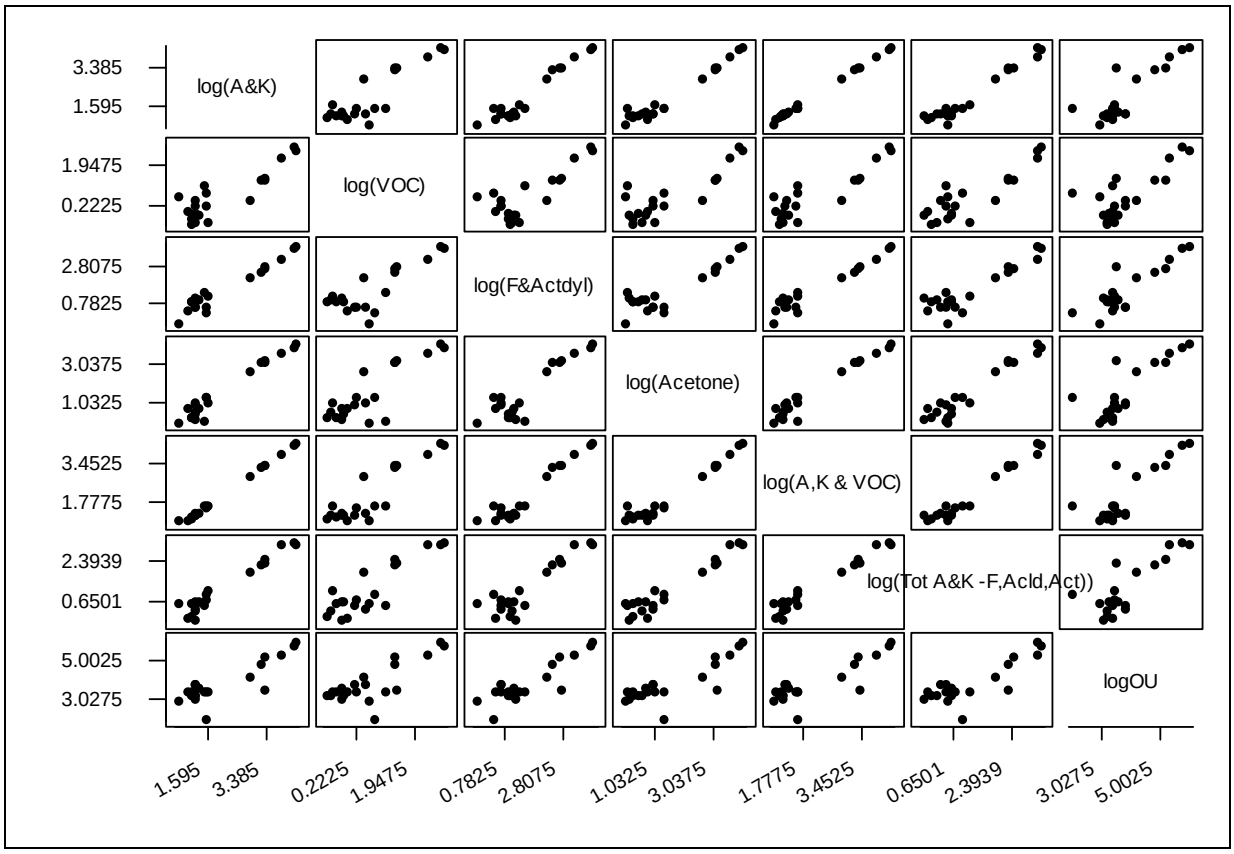
Generation of the Regression Equation

Some alternatives were examined for generating the regression equation.

Logarithm values were used rather than raw values in producing the charts above because of the range of several orders of magnitude and because by using logarithms we obtain an easy-to-visualise straight line relationship. The taking of the logarithmic transformation also means that we get stability of variance across the range of the x-variable, as required to produce the linear regression model.

Attempts were made to break the concentration of VOCs etc into component parts of VOCs, aldehydes, ketones and also to consider acetone as a separate component. These did not yield any benefit in terms of a significantly better linear fit or

explanation of the relationship by components. The reason for this can be seen in how closely the various concentrations are generally aligned with each other. This is shown in the following plot.



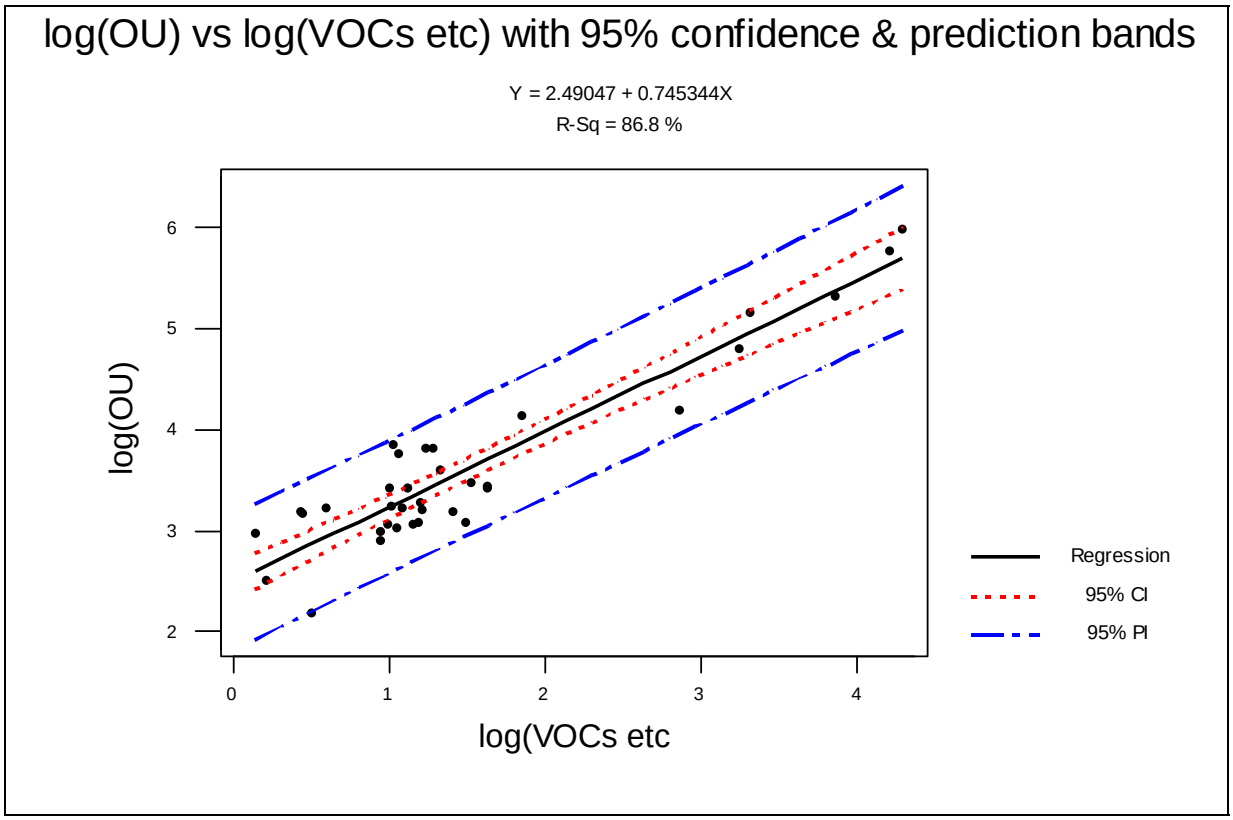
log(A&K)=log_{10}(concentration of Aldehydes & ketones)
log(VOC)=log_{10}(concentration of VOCs)
log(F&Actdyl)=log_{10}(concentration of Formaldehyde and Acetaldehyde)
log(Acetone)=log_{10}(concentration of Acetone)
log(A,K&VOC)=log_{10}(concentration of Aldehydes, Ketones and VOCs)
log(A&K-F,Acld,Act)=log_{10}(concentration of Aldehydes & Ketones minus concentration of Formaldehyde, Acetaldehyde and Acetone)
logOU=log_{10}(OU)

Thus, because of the co-linearity between the various components, it was decided to build the model for log(OU) using just log(concentration of Total VOCs, aldehydes and ketones).

The following chart shows the line of best fit with 95% confidence interval for the mean log(OU) based on the exhibited linear equation using log(VOCs etc) and also the 95% prediction interval around the line of best fit. We expect that for units operating under the same conditions and using the same measuring methods as used to generate the data for this plot, that 95% of future observations will fall within the blue dashed lines on the chart. The width of that band for log(OU) is approximately 1.4.

This prediction interval says that, for example, with a Total VOC, aldehydes and ketones concentration of 100 mg/m^3 (i.e. log(Total VOC etc)=2) we would expect to

observe 95% of OU measurements between 1,900 and 48,000 and with VOC, aldehydes and ketones concentration of 10 mg/m^3 we expect 95% of OU measurements between 340 and 8600.



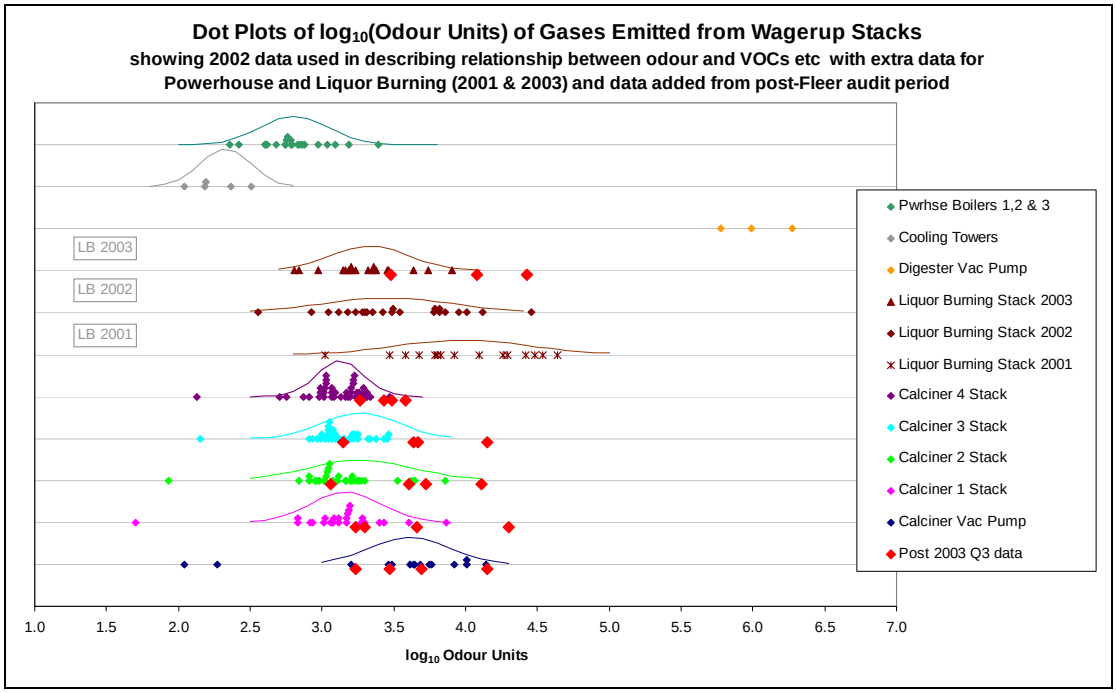
The prediction intervals for measured OU when a certain concentration of Total VOC, aldehydes and ketones is observed as quoted above may seem very wide. However, the historical record of measured OU from the various operating units is that there is considerable variability from occasion to occasion when OU is measured for the emissions from the same unit. This is discussed in the next section.

Variability of VOC, aldehyde and ketone concentrations and OU measurements

In the full set (i.e., not limited to days of co-incident measurements) of OU and Total VOCs, etc. measurements, we have observed a greater range of variability of these measures on each of the refinery operating units. The variability for $\log_{10}$(OU) is represented in the following dot plots where we have also shown fitted normal distribution curves. Note in the plot how similar the distributions are for the four calciners.

In the plot we have distinguished odour measurements made after the audit of Alcoa measurement processes conducted in 2002. It is known (communication from operations personnel) that some changes were made to the sampling methods for odour unit measurement (but not Total VOC etc concentrations) after that audit. Also, some changes were made to emissions routing in regard to the Calciner 1-3 vacuum pump. It was expected that they would lead to less odourous emissions. The data as

presented below (and as a probability, confirmed by calculations) appear to show a slight increase in measured OU in the period after, as compared to before, the audit. We are not aware of any changes that would have led to more odourous emissions (personal communication from operations and TDG personnel).



Note that the relationship between OU and concentration of Total VOCs etc discussed in the first part of this note was generated on data collected mostly before the audit. As a result some small change may be necessary to the equation for estimating log(OU).

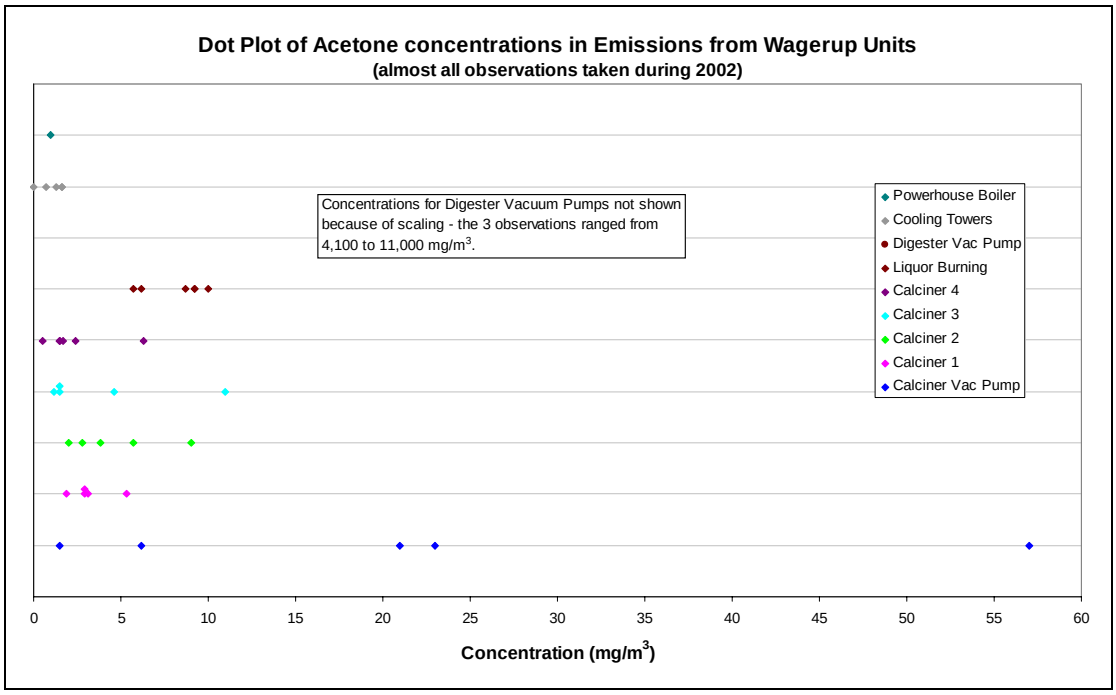
Note also, that the ranges of OU measurements from a single unit are typically over 1.5 to 2 logarithm units, i.e., 1.5 to 2 orders of magnitude.

It has been proposed to use the developed relationship for estimating the odour flux from the refinery from measured and estimated total concentration of VOCs, aldehydes and ketones emitted from the various units where this relationship has been shown to hold. The rationale for doing this, rather than direct measurement for current units and some other unspecified method in the case of projected units, is the perceived greater reliability (i.e., less variability) in the measurement methods (including sampling) for concentrations of VOCs etc compared to those for Odour Units. It has been claimed (TDG personnel) that the sampling methods for concentrations of VOCs etc involving adsorption onto trapping media are inherently more reliable than those for Odour Unit measurement involving collection and containment of emitted gas along with diluting gases in bags.

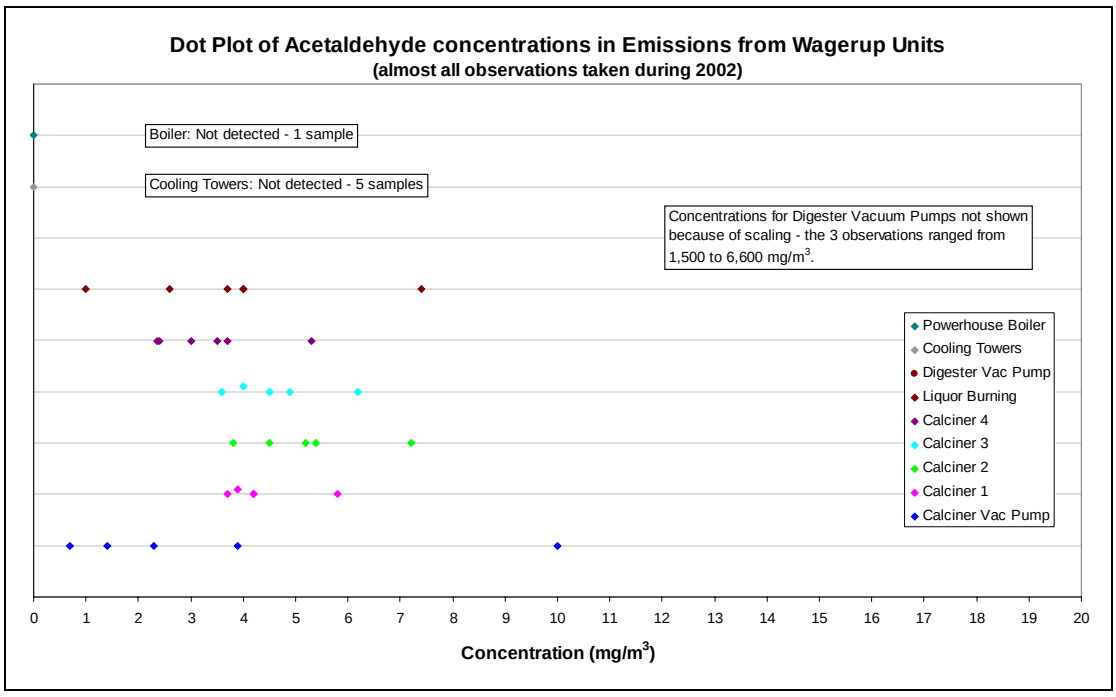
The charts below are produced to test the assertion that there is less variability (for a single operating unit) in the measurements of concentration of components and Total VOCs, aldehydes and ketones than in the measurements of Odour Units. In examining the plots and comparing with the OU plot above, one should keep in mind that there

are generally fewer observations and for this reason alone, we will tend to see somewhat less variability.

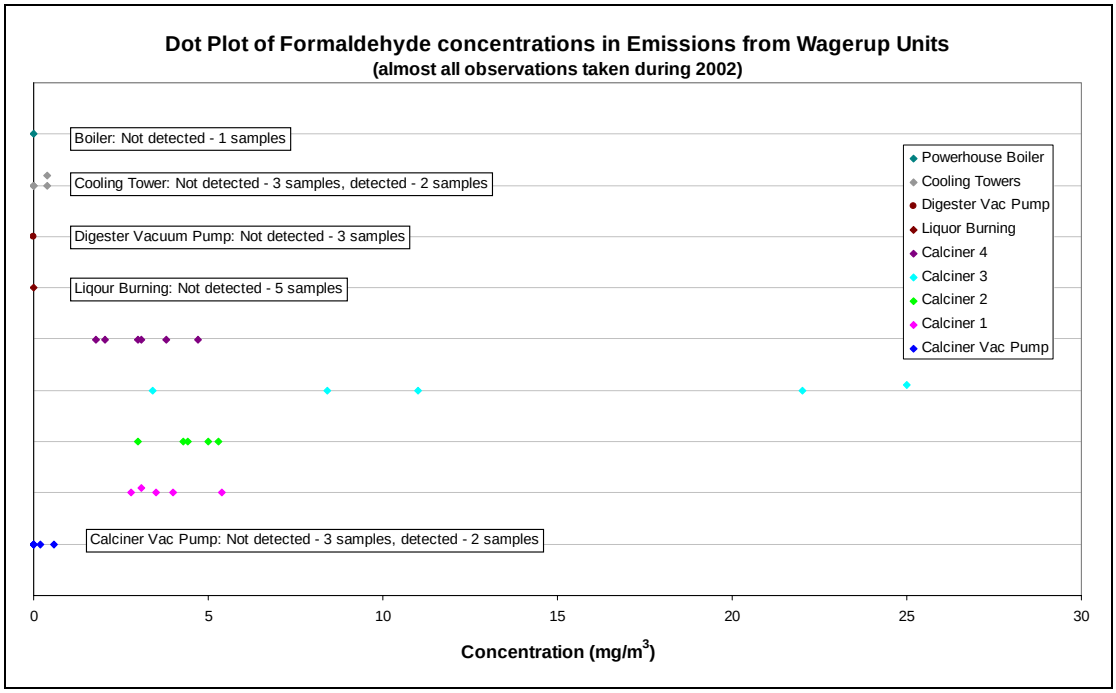
The first of the plots shows concentration of acetone. The ranges of concentrations are mostly within one order of magnitude, although for the Calciner Vacuum Pump the range is from 1.5 to 57 (1.5 orders of magnitude).



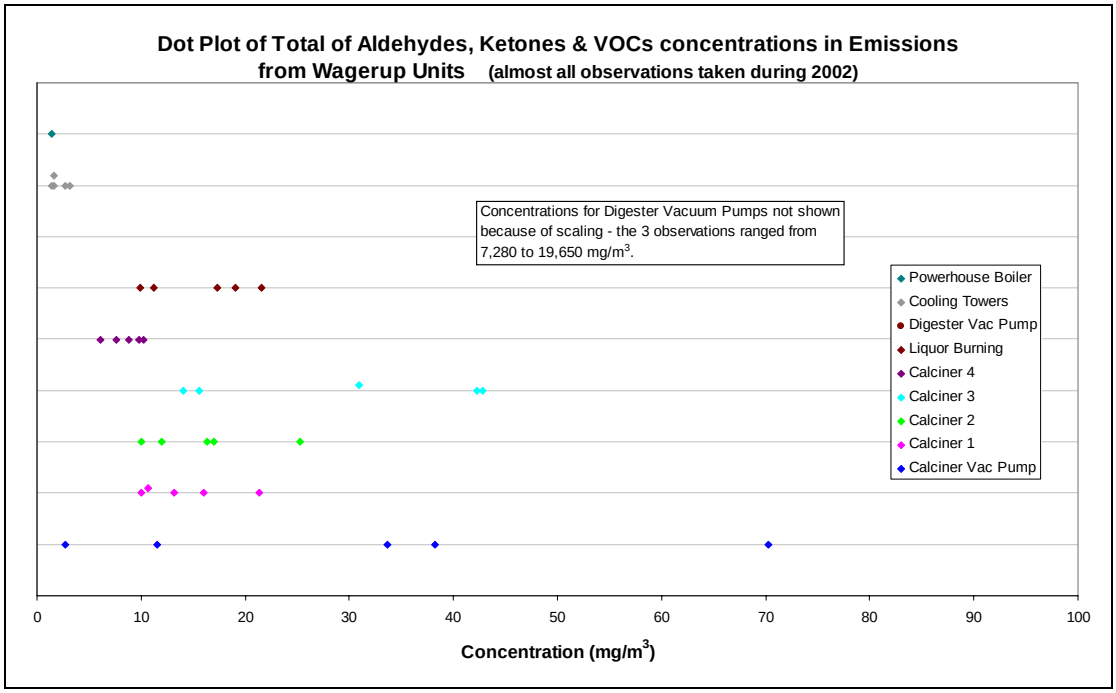
The following plot for acetaldehyde concentration shows that, where acetaldehyde is detected, the variation is considerably less than one order of magnitude, with the exception of the Calciner Vacuum Pump where the range is from 0.7 to 10 mg/m^3.

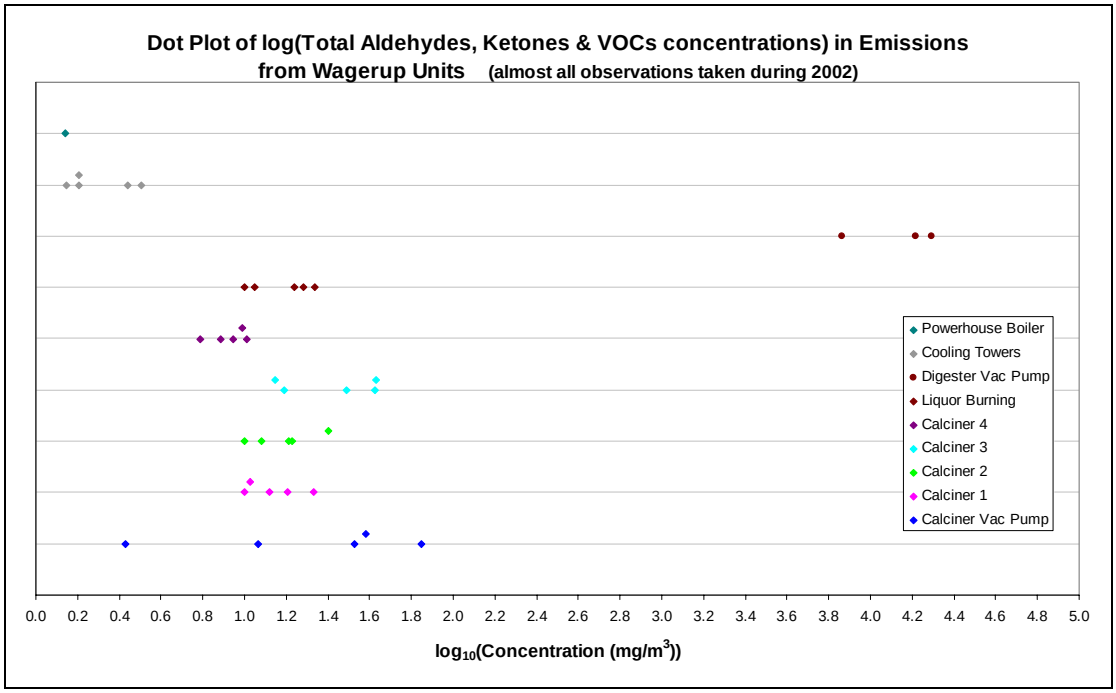


The following plot for formaldehyde concentration shows that where formaldehyde is detected the variation, in all cases, is considerably less than one order of magnitude.



The following plot for Total VOC etc concentration shows that the variation, with the exception of the Calciner Vacuum Pump, is considerably less than one order of magnitude. That is also shown in the plot of the same data using a logarithmic scale.





In summary, the variation observed from each unit for concentrations of VOCs, aldehydes and ketones is less than seen for variation of OU measurements from those same units. While we cannot say whether the greater variation in OU is due to variation in component species in the gases or to greater variability (less reliability) in the sampling and measurement method, the results are consistent with that latter cause as has been maintained by some practitioners.

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