VARIABILITY AND UNCERTAINTIES IN THE AIR EMISSIONS INVENTORY FROM THE WORSLEY ALUMINA REFINERY

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Abstract

An inventory of air emissions has been constructed for the Worsley Alumina Refinery from measurements made from major refinery sources since 2003. Over 700 chemical substances were assessed in the construction of the inventory, with 306 substances identified at concentrations above the analytical detection limit. Major emissions in terms of emission rates include CO_2, SO_2, NO, particulates, CO and NO_2. Other substances with significant emission rates include acetone, acetaldehyde, hydrocarbons, ammonia, fluoride, chloride, methanol and some aliphatic amines. Total refinery VOC emissions are in the order of 148 tpa, with approximately 80% of those emissions due to the contributions for the above mentioned organics.

Of importance for use of the emissions inventory for purposes such as dispersion modelling and ground level impact assessments, is an understanding of the variability in the emission rates from the respective sources. This paper describes the variations observed for some key emissions over a range of time averaging from hourly to yearly. An assessment has been conducted of the uncertainty in the measurements for these substances that allows the contributions from process variability and measurement uncertainty to be considered when assessing the variability in the emissions data. Relatively low uncertainties have been determined for parameters such as combustion gases and total particulates from the more "stable" sources such as calciners and boilers, which suggests the majority of the observed variability is due to process changes. Higher variability in emissions is observed for digestion related sources, which is predominately due to process variability but also has a large component from the uncertainty in individual measurements.

This paper will present some findings from the evaluation of measurement of uncertainty for key parameters and an assessment of the variability in the emissions. The implications for use of the Emissions Inventory will also be discussed. Some discussion on the assessment of variability in odour emissions will also be included.

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1. Introduction

The Worsley Alumina Pty Ltd (WAPL) Air Emission Impact Assessment (AEIA) project commenced in mid 2003 with a comprehensive emissions monitoring program implemented to construct the first refinery wide emissions inventory in 2005. The emissions at inventory provided the basis for a health risk assessment of the refinery emissions, which identified the emissions of SO_2, NOx and particulates accounted for >90% of acute health risk and >80% of chronic health risk in neighbouring communities and residences (Toxikos, 2005). Other substances that were deemed to be of interest (but not necessarily significant contributors to potential health risk) were volatile organic compounds (VOCs), metals, PCBs, PAHs, dioxins and furans, halogens and halides, amines, alcohols, aldehydes and ketones (A&Ks), hydrocarbons, sulfides and thiols. Many of these substances contribute to the unique odour associated with the emissions, which was also a significant factor in the impacts of refinery emissions.

A key consideration for a health risk and other assessments conducted of the emissions data is the variability in the emissions and how that is accommodated in those assessments. A typical health risk assessment would utilise average emission rate data with an assumption made that the use of an average emission rate is appropriate for assessment of longer term (chronic) health impacts. However, substances that present potential for acute health impacts require an understanding of the magnitude and frequency of the highest emission rates to facilitate a realistic assessment of those risks.

The measured variability in emissions data reflects the actual variability and the uncertainty in the measurements. Therefore, an understanding of the measurement uncertainty (MU) is essential for estimation of the uncertainty in a health risk assessment. However, uncertainty in stack emissions measurements is rarely evaluated as part of the reporting of emissions data. In addition, uncertainty in dispersion modelling that is used to predict ground level concentrations of emissions for assessment of health and other impacts, is also not well characterised. As a consequence, extra conservatism is often built into health risk assessments of emissions from industrial sources to accommodate the unknown measurement MU. In some cases, the conservatism is excessive and creates an unrealistic impression of the impact of refinery emissions that is not supported by field observations and measurements.

To address this issue, WAPL has included an evaluation of stack emissions measurement uncertainty with the construction of the emissions inventory. This paper presents some of the findings from the development of the emissions inventory, the assessment of variability of key emissions substances and an evaluation of measurement uncertainty for determination of the emission rates of those substances from the WAPL refinery.

2. Construction of the Emissions Inventory

The Emissions Inventory was constructed from measurements conducted of the emissions of over 700 chemical substances from 23 emission sources, with 306 substances identified at concentrations above the respective analytical detection limits. Multiple measurements were made of the emission rates for many of the substances, which provided data to assess the

variability over the short term (minutes to hours) and longer term (weeks, months and years). The following process was involved in the construction of the WAPL Emissions Inventory.

- Acquisition of the emissions data from stack testing
- Included in the stack testing program were specific tests to assess variability of key emissions such as SO_2, NOx, particulates and metals from major sources (boilers, calciners, digestion)
- Addition of data for particulate emissions from the Bauxite Residue Disposal Areas (BRDAs) and odour emissions from the Refinery Cooling Lake (RCL)
- Comprehensive checking of all emissions data provided by the stack testing company to ensure only validated data were entered into the database
- Development and implementation of a protocol for handling of non-detect results in reporting of average emissions rates for multiple measurements of a substance from a source.
- Reporting of emission rates for all substances from all sources, including average, minimum and maximum rates for assessment of variability of the emissions
- Calculation of total emission rates from sources with multiple emission points, where some sources were not tested for all substances
- Audit of the reported emission rates to ensure calculations were correct
- Final reporting.

The Inventory was then presented for assessments of the variability and measurement uncertainty, as well as dispersion modelling and a health risk assessment.

3. Approach to evaluation of Measurement Uncertainty

A screening health risk assessment was conducted of the data obtained from the initial emission testing conducted in 2003 and 2004, which identified SO_2, NOx and PM_{10} as the substances most likely to present a potential health risk and therefore should be considered for assessment of variability and measurement uncertainty. The uncertainties in measurement of those substances and others of interest were evaluated using the methodology and guidelines outlined by the National Association of Testing Authorities (NATA) and International Organisation for Standardisation Guide to the Expression of Uncertainty in Measurement (ISOGUM) guidelines. These guidelines outline a six step approach to evaluating MU.

- Construct a model of the measurement system
- List the sources of uncertainty
- Calculate standard uncertainties
- Calculate sensitivity coefficients
- Calculate combined uncertainty
- Calculate expanded uncertainty.

The estimation of standard uncertainties can be completed using two approaches, namely "top-down" or "bottom-up". A top-down approach involves the use of performance data from measurement of standard reference materials or equivalent traceable standards, whereas a bottom-up approach involves the estimation of uncertainties for all components of the measurement process which are combined to provide the standard uncertainty for the measurement. For this study, a bottom-up approach was considered appropriate, given that standard reference materials do not existed for alumina refinery stack emissions. However, the evaluation was greatly simplified by the provision of uncertainty estimates from the laboratories for the analysis of stack emission samples and the use of the isokinetic variation relationship to derive the uncertainty for sampling. Hence a detailed evaluation of each step of the sampling and analysis procedures was not required to estimate the overall expanded uncertainties for the respective parameters.

Stack emissions monitoring involves the use of a variety of equipment and methods which may include different sampling media for iso-kinetic or non-isokinetic sampling. Uncertainties can be mainly attributed to the metering of stack gas volume through the sampling media, the efficiency in capturing the sample by the sample media and recovery of the analytes of interest from the media for analysis. Additional uncertainty is introduced from the measurement of velocity, gas composition (density and molecular weight) and stack gas moisture. Finally, the instrumental analysis of the substances recovered from the sampling media presents another layer of uncertainty.

The measurement system for stack emissions monitoring consists of two components, the emissions concentration (expressed as g/Nm^3) and emissions rate (g/s). These components are defined below by equations 1 and 2.

$$C = M/V \dots\dots\dots \text{(Equation 1)}$$

Where,
   C = Concentration (g/Nm^3)
   M = Mass of analyte (g)
   V = Volume of gas sampled (Nm^3) (N is defined as $0°C$, 101.3 kPa)

$$ER = C \times Q \dots\dots\dots \text{(Equation 2)}$$

Where,
   ER = Emission rate
   C = concentration as defined above
   Q = volumetric flow rate (Nm^3/s)

Hence, if standard uncertainties are available for the analysis (M) and sampling (V), then the combined uncertainty for the concentration is readily determined. Similarly, if the standard uncertainty is available for the flow rate (Q) then the combined uncertainty is readily determined for the emission rate.

Uncertainties for the analysis component of monitoring of emissions are usually provided by the laboratories who are accredited to ISO/IEC 17025. These are generally based on determinations of precision (reported standard deviations for replicate analyses) and accuracy (reported as recoveries of surrogate and/or matrix spikes). Uncertainties for the sampling are not so readily available other than for some of the sampling methods which provide information on precision and accuracy of the method as tested by the issuing agency. Stack testing companies generally do not assess uncertainties in the sampling of emissions from alumina refineries primarily due to the additional costs involved but also because they are not requested to conduct uncertainty evaluations.

Two general methods are used for emissions sampling, isokinetic and non-isokinetic sampling. For isokinetic sampling the gas velocity entering the nozzle of the sampling train is matched to that in the stack, while in non-isokinetic the sampling rate is fixed regardless of the stack gas velocity. Isokinetic sampling has greater complexity than non-isokinetic sampling and hence greater potential for error. WAPL has adopted a conservative approach in that it is assumed the uncertainty associated with the metering of a known volume of gas derived from isokinetic sampling would also apply to non-isokinetic sampling.

The accuracy of isokinetic sampling is defined by the "isokinetic variation" parameter which is a measure of the ratio of velocity in the stack to velocity in the sampling probe. It is defined by the following expression

$$I = 100 T_S \left[K_3 V_{IC} + \left(\frac{V_M}{T_M} \right) \left(P_{bar} + \frac{\Delta H}{13.6} \right) \right] / 60 \theta V_S P_S A_n$$

Where,

    I = isokinetic variation (%)
    A_n = Nozzle cross-section area (mm^2)
    K_3 = 0.003454 mm Hg.m^3/mL
    P_{bar} = barometric pressure (mm Hg)
    P_S = stack gas pressure (mm Hg)
    T_M = meter temperature (K)
    T_S = stack temperature (K)
    V_{IC} = volume of water captured in impingers and silica gel (mL)
    V_M = volume of gas at meter (dry m^3)
    V_S = stack gas velocity (m/s)
    ΔH = average pressure differential across meter orifice (mm Hg)
    θ = total sampling time (min)

The isokinetic variation equation contains all the key elements of the sampling procedure, including pressure, temperature and the volume of gas metered in the sampling. As a consequence, the actual isokinetic variations observed for a large number of sampling runs will provide an estimate of the uncertainty in the sampling process. True isokinetic sampling has a variation of 100% which means the velocities are perfectly matched. This provides a reference value to compare the distribution of variations obtained from a monitoring program. USEPA isokinetic sampling methods have a specification that isokinetic variation for a sampling run must be between 90 and 110% (inclusive) for the sampling to be considered representative. This constrains the operation of the method to ensure relatively low variability is obtained.

Walter Smith and co-workers (Shigehara, *et al.*, 1970) have determined the MU for isokinetic variation,[1] which presents a simple solution to the evaluation of MU for sampling of emissions. However, their studies were carried out on "stable" sources where flows were very consistent and moisture low (e.g. incinerator, boiler). Many important alumina refinery emissions sources have high moisture (e.g. calciners with >50% moisture) and inconsistent flows (e.g. digestion sources), therefore the evaluation conducted by Smith and co-workers probably underestimates to the true uncertainty in isokinetic sampling from alumina refinery sources.

As a consequence, actual isokinetic variation data derived from the sampling conducted to construct the emissions inventory was used to estimate MU for isokinetic sampling. In total, 54 measurements taken from various sources (calciner, mill vents, hydrate pan filters, boilers, etc) were evaluated. The distribution of these data is shown in Figure 1.
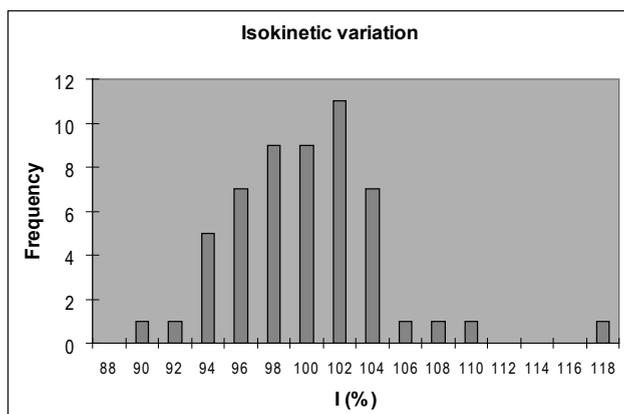

Figure 1. Histogram of Isokinetic Variation

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1 Walter Smith and his team developed the isokinetic methodology that was the basis for USEPA method 5 and all other isokinetic sampling methods promulgated by the USEPA.

The histogram shows that the majority of isokinetic variations were within the method specification. The accuracy in the variations was derived from the average of these data (I = 102%, bias = 2), with the spread a measure of the precision of the sampling (2 standard deviations = 11%).

Sensitivity Coefficients describe how the value for concentration varies with changes in mass of analyte recovered and volume of gas sampled, or for how the value for emission rate varies with changes in the concentration and the flow rate. These are simply linear relationships; hence coefficients of value 1 have been applied.

The combined uncertainties for the sampling and analyses were calculated for concentration and emission rates for the substances of interest using the following equations:

Concentration (C)

$$\left(\frac{U_c}{C}\right)^2 = \left(\frac{U_m}{M}\right)^2 + \left(\frac{U_v}{V}\right)^2 \dots\dots\dots\dots\dots\dots\dots\dots \text{(Equation 3)}$$

Where,
    U_c is the combined uncertainty for the concentration (C)
    U_m is the standard uncertainty for the amount (M) of substance in the sample
    U_v is standard uncertainty for the gas volume (V) of sample

Emission rate (ER)

$$\left(\frac{U_{ER}}{ER}\right)^2 = \left(\frac{U_m}{M}\right)^2 + \left(\frac{U_v}{V}\right)^2 + \left(\frac{U_Q}{Q}\right)^2 \dots\dots\dots\dots \text{(Equation 4)}$$

Where,
    U_{ER} is the combined uncertainty for the emission rate (ER)
    U_m is the standard uncertainty for the amount (M) of substance in the sample
    U_v is standard uncertainty for the gas volume (V) of sample
    U_Q is standard uncertainty for the volumetric flow rate (Q) of the emission source.

The relative uncertainties were calculated from the combined uncertainties by taking the square root of the sum of the squares of the standard uncertainties.

To simplify the evaluation, the average uncertainty for each compound class (e.g. VOCs) has been calculated and reported along with the range of uncertainties for the concentrations and emission rates.

The Expanded Uncertainties were calculated from application of a coverage factor (k) of 2, which represents the 95% confidence interval, by simple multiplication of the combined uncertainties by the coverage factor.

4. Results

4.1 Emissions Inventory

Major emissions in terms of emission rates include CO_2, SO_2, NO, particulates, CO and NO_2. Other substances with significant emission rates include acetone, acetaldehyde, hydrocarbons, ammonia, fluoride, chloride, methanol and some aliphatic amines. These emissions are predominately from the combustion sources, including boilers (which account for >99% of the refinery emissions of SO_2, 82% of the NOx and 29% of the CO), co-generation plant (13% of NOx and 0.1% of CO emissions) and calciners (4% of NOx and 70% of CO).[2] These percentages are based on the average emission rates for these gases from the various sources. The particulate emissions (as PM_{10}) are predominantly from the calciners (40%), boilers (37%) and BRDAs (23%). The average total refinery VOC emissions are in the order

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2 CO_2 emissions are not discussed for commercial reasons related to energy usage.

of 148 tpa, with approximately 80% of those emissions due to the contributions for the above mentioned organics.

Odour is also a key emission from some refinery sources that in the past has presented an unacceptable impact on the workforce and neighbouring communities. Significant reductions in the total odour emissions (> 50%) from the WAPL refinery have been realised with the installation of emission control systems on Digestion and Liquor Burning facilities. These measures have essentially eliminated odour impacts in the neighbouring communities and significantly reduced the on-site impacts to generally acceptable levels. The main contributors to odour are now the calciners (26% of total odour), uncontrolled digestion sources (16%), boilers (11%) and fugitive emissions from the refinery cooling lake and associated feed drains (16%). The two sources with emission controls, the Liquor Burning Facility and combined Digestion sources (flash condensate and heat exchange non-condensable emissions) now contribute < 0.5% each of the total refinery odour emissions.

4.2 Measurement Uncertainty

The uncertainties in the measurements of emission rates of SO_2, NOx, PM and odour are presented to aid in the assessment of the variability of these emissions. These are summarised in Table 1.

Table 1. Measurement uncertainties (k=2) for emission rates of key parameters

| Parameter	Boilers	Calciners	Uncontrolled Digestion sources	Controlled Digestion sources
Gases (SO_2 NOx, CO)	14.5%	13.2%	15.4%	14.5%
PM (as TSP)	15.7%	14.5%	73%	17.9%
PM_{10}	54.5%	54.2%	Not applicable	Not applicable
Odour	39%	39%	42%	39%

The majority of the uncertainty for measurement of gases was from the flow rate determinations, with standard uncertainties of 12-15% derived from the variability in the differential pressure readings at the various traverse points. The expanded uncertainty for isokinetic sampling of particulates (and other particulate containing samples including dioxins, PAHs, metals, halogens and halides, etc) was found to be ~9% (k=2) for relatively stable emission sources such as boilers, calciners and the Liquor Burning Facility, ~12% for controlled Digestion sources and ~72% for uncontrolled Digestion sources that have high moisture and high temperature.

4.2 Variability of emissions

Examples of the variability of SO_2 and particulates (TSP) for two major emissions sources are presented below to illustrate the outcomes from the assessments of variability for key emissions parameters. The application of the measurement uncertainties determined in this work is also included to highlight the importance in the assessment.

The boilers provide the majority of SO_2 emissions due to the sulfur in the coal feedstock. A summary showing the variability of daily average emission rates for the period June 2003-January 2006 is presented in Figure 2.

The variations in daily emission rates can described in terms of the relative standard deviations (rsds), which were 12, 20 and 15% for Boilers 1, 2 and 3, respectively. However, less variability was observed for short term emission rates, with one test conducted where 16-18 measurements were made over a 6 hour period showing rsds of 4.2, 2.3 and 4.7% for the 3 boilers.
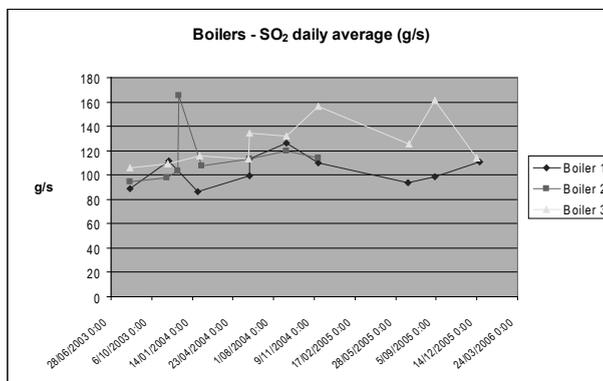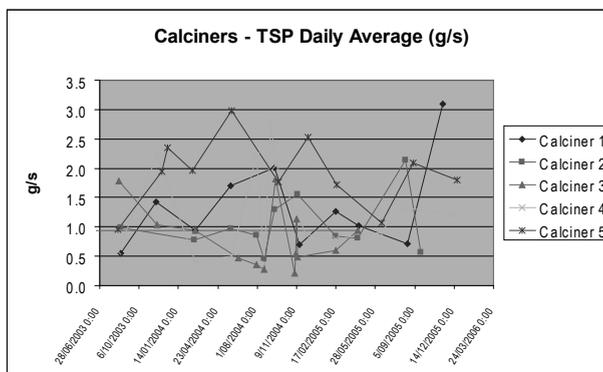

Figure 2. Daily average SO_2 emissions from the boilers

The variability in the SO_2 emissions can be considered in light of the uncertainty in the measurement of SO_2 emission rate. An expanded uncertainty of 14.5% was determined for this substance. This implies that the true value for each measurement has a 95% probability of being within ±14.5% of the measured value. Clearly, all of the results from the 6 hour experiment are within that range which suggests the natural variability in the short term emission rates (expressed as 2 standard deviations of 8.4, 4.6 and 9.4%) cannot be distinguished from the variability associated with the measurements. However, the daily average emission rates show greater variability (2 standard deviations) of 24, 40 and 30%, respectively, which are well in excess of the measurement uncertainty and clearly reflect the variability in the process.

In this case, the use of an overall average for the emission rate for SO_2 for assessment of the health impacts would potentially underestimate the true impacts and the assessment would require consideration of the higher emission rates which are clearly a function of the variability in the emissions and not due to uncertainty in the measurement.

A similar analysis of daily average TSP emission rates from the calciners is summarised in Figure 3.

Figure 3. Daily average TSP emissions from the calciners

The variations in daily emission rates (rsds) were 57, 47, 65, 65 and 31% for Calciners 1, 2, 3, 4 and 5, respectively. These can be compared with the expanded uncertainty in the measurements of 14.5% for TSP from calciners. The 2 standard deviations for the daily averages are well in excess of the measurement uncertainty, indicating the trends in the emission rates reflect changes in the process that gives rise to the emissions. An example of the significance of the measurement uncertainty is presented in Figure 4 for Calciner 5 TSP emissions.
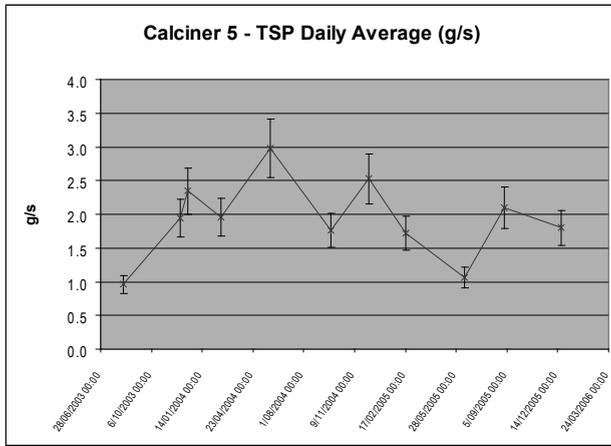
Figure 4. Daily average TSP emissions and expanded uncertainties for Calciner 5

Again, the use of an overall average for the daily emission rates in a health risk assessment would underestimate the potential health impacts and consideration should be given to the significance of the variability in the emissions rates which are again a function of the upstream process and not due to uncertainty in the measurements. Importantly, additional conservatism is not required in a health risk assessment since the variability in the reported emission rates already encompasses uncertainties in the measurements.

5. Conclusions

The emissions inventory constructed for the WAPL refinery has identified CO_2, SO_2, NOx, CO and particulates as the most significant emissions from the 306 substances identified at concentrations above the analytical detection limit. The uncertainties in the measurements of key substances have been evaluated from actual emissions data, including isokinetic variations to establish the uncertainties in the sampling. The variability of these emissions has been examined with consideration given to the uncertainties determined for the measurements. In most cases, the variability in the daily average emission rates for these parameters far exceeds the uncertainties in the measurements which suggest consideration must be given to the variability in the risk assessments but that additional conservatism is not required to account for the uncertainties in the measurements.

References

Shigehara, R.T.; Todd W.F. and Smith W.S. (1970). "Significance of errors in stack sampling measurements". Air Pollution Control Association, 14 June 1970