

# ALUMINA REFINING AND AIR QUALITY: VOCS AND ODOUR

Galbally I<sup>1\*</sup>, Lawson S<sup>1</sup>, Brodie G<sup>2</sup>, Loh J<sup>2</sup>, Cheng M<sup>1</sup>, Hibberd M<sup>1</sup>, Power G<sup>2,3</sup>

<sup>1</sup>CSIRO Marine and Atmospheric Research, Aspendale, VIC 3195, Australia,

<sup>2</sup>CSIRO Process Science and Engineering / Parker Centre CRC for Hydrometallurgy, PO Box 7229, Karawara WA 6152, Australia

<sup>3</sup>Arriba Consulting Pty Ltd, PO Box 975, Canning Bridge, Applecross, WA 6153, Australia

## Abstract

The importance of understanding the nature and origins of volatile organic compounds and the associated odour emitted from alumina refineries has become increasingly evident in recent years, driven by the need to respond to community and workforce concerns, and regulatory requirements. This paper outlines the current state of knowledge of volatile emissions based on measurements at a refinery in Western Australia, describes laboratory experiments which model key refinery sub-processes, and provides explanations of the presence of the main VOCs based on chemical reaction mechanisms. Real time measurements of VOCs in air approximately 2 km away from an alumina refinery showed that acetone, acetaldehyde, methanol and NO<sub>x</sub> have sources in the direction of the refinery. Measurements of VOCs and odour from the digester vents, calciner, and liquor burner in the refinery revealed many compounds of which methanol, acetaldehyde and acetone occurred at the highest concentrations. Odours were observed but the compound/s responsible could not be determined, nor was odour directly related to total VOC concentrations in the samples. A laboratory study which measured VOC emissions from slurry mixtures simulating bauxite milling and pre-desilication sub-processes generated VOCs consistent with those found in emissions from those parts of the refinery. This knowledge will be a key to the design of equipment and strategies for improving refinery ambient air quality into the future.

## 1. Introduction

The association of odour with alumina refining has probably been known since bauxite was first digested in caustic soda in the 1880s, and as recently as 1996 it was described as not constituting a "serious environmental problem" (Forster and Grocott, 1996). This situation has now changed as illustrated by the community response that followed the commissioning of a liquor burner at the Wagerup refinery; odour is now a key issue to be taken into account in the design and operation of industrial facilities such as alumina refineries, particularly those processing bauxites that are high in organic carbon content (Coffey and Donoghue, 2006). Odour is undoubtedly associated with volatile organic compounds (VOCs) produced in bauxite digestion and by combustion (e.g. hydrate calcination and liquor burning) processes associated with alumina refineries. Health risk assessments (HRAs) have concluded that the health risk of refinery emissions to surrounding communities is negligible (Donoghue and Cullen, 2007), however community concerns remain.

Research at Wagerup (Coffey and Ioppolo-Armanios, 2004) has found that it is possible to account for the total refinery odour emissions (determined by dynamic olfactometry) in terms of chemical emissions, based on the odour thresholds presented by Ruth (1991). The agreement between the odour strength calculated by adding the chemical odour unit (COU) contributions from individual compounds to the total odour measured by olfactometry suggested that it was valid to simply add the contributions of individual odorants to estimate the total odour strength, and that interactions between odorants were not important in determining the overall odour strength. However there is considerable uncertainty inherent in the threshold data used, which are calculated as simple averages compiled from all of the available literature data (Ruth 1991). More comprehensive work on odour thresholds has since been reported by Nagata (2003) covering 20 years of testing in up to 137 laboratories and up to 223 compounds. When the odour thresholds from Nagata (2003) are used, it is more difficult to fully account for the odour emissions at Wagerup on the basis of the individual chemicals detected.

A study of emissions from the Worsley refinery found that acetaldehyde and other carbonyl compounds were key odorants in both digestion and calcination emissions (Forster et al., 2005). Other odorants present in the digestion vapours included trimethyl amine, dimethyl sulphide and some cyclic unsaturated hydrocarbons. It was also noted however that the qualitative nature, or character, of the odour could not be explained by summation of the odours of the components; it was concluded odour character was probably a product of the effects of trace levels of other (probably unknown) compounds and/or interactions between compounds.

All of the work described so far has focused on understanding the compositions of emission sources and relating them to the odours of those sources. In this paper we describe the extension of the measurement of VOCs and odour to the ambient air surrounding an alumina refinery. This is a much more difficult task for three main reasons: first, the concentrations of substances and odour are orders of magnitude less due to dispersion; second, ambient concentrations are strongly influenced by local meteorological transport and mixing, and vary greatly in space and time; and third, ambient air already contains significant quantities of many of the compounds that are emitted by refineries, including key VOCs such as acetone, formaldehyde and acetaldehyde, oxides of nitrogen and sulphur compounds. Addressing the problems of sampling, analysis and interpretation demands highly sensitive, time-resolved analytical equipment, good background data, and sophisticated atmospheric dispersion modelling. The first part of the paper provides a brief overview of a study carried out by CSIRO at the Wagerup refinery using a suite of analytical equipment centred on a Proton Transfer Reaction - Mass Spectrometer (PTR-MS) in combination with The Air Pollution Model (TAPM) to examine the dispersion of VOCs and odour in the surrounding atmosphere. This work is supported by information from sampling and analysis of key emission sources at the refinery, in which we demonstrate very large differences in the odour to VOC ratio between sources, highlighting the need to understand the characteristics of individual sources in order to attribute odour outcomes to VOC emission rates. We then describe preliminary

laboratory studies aimed at simulating the emissions from specific refinery processes, and interpret the results in terms of chemical reaction mechanisms.

## 2. Methodology

### 2.1 Field studies

Alcoa World Alumina Australia's Wagerup alumina refinery is situated about 130 km south of Perth, Western Australia, and 25 km inland from the coast, in the western foothills of the north-south Darling escarpment. A study, which was commissioned by Alcoa and carried out independently by CSIRO, was conducted over 8 weeks in winter 2006 to identify volatile organic compounds present in ambient air and to identify their most likely sources, both natural and man-made, based on measurements in the Wagerup area, at a location just south of the refinery. A detailed technical report describing the atmospheric composition measurements, the meteorological and other ancillary measurements and their interpretation is publically available (Galbally et al. 2008).

Volatile organic compounds were measured by three techniques. PTR-MS measures all volatile organic compounds with a proton affinity greater than water (de Gouw and Warneke 2007). This covers most volatile organic compounds with the exception of a small number of short chain alkanes and alkenes and some halogenated hydrocarbons. The PTR-MS method features fast response (seconds) and high sensitivity (sub parts per billion), but cannot distinguish between VOC compounds with the same molecular mass. Compounds are normally detected at their molecular mass plus 1 amu due to the addition of a proton, which is an inherent step in the method. Two other methods, both utilizing 8 hour integrated samples, were used to complement the PTR-MS and provide specific VOC identification. VOCs ( $C_4$  to  $C_{10}$ ) were collected using adsorbent tubes which were thermally desorbed and analysed by gas chromatography with flame ionization (FID) and Mass Selective (MSD) detectors (ISO 2000). VOCs ( $C_1$  to  $C_6$  carbonyls) were collected using dinitrophenylhydrazine (DNPH) coated air monitoring cartridges and analysed by High Performance Liquid Chromatography (HPLC) with a Photodiode Array (UV) detector (USEPA 1999).

Point source sampling with concurrent odour and VOC analyses was conducted. Duplicate samples were collected in bags directly from refinery point sources (diluted with  $N_2$  by a factor 19) and were analysed by PTR-MS within an hour of sampling. One duplicate from each source was sent for odour analysis at a commercial laboratory by the standard dynamic olfactometry method; the other duplicate was re-analysed by PTR-MS.

Meteorological and air pollution modelling was undertaken using TAPM, a 3 dimensional prognostic chemical transport model (Hibberd et al. 2008, 2011).

### 2.2 Laboratory studies

Laboratory studies were carried out to briefly investigate VOCs emitted during simulated a) pre-desilication and b) liquor burning. For the pre-desilication study, a sample of Darling Range bauxite was mixed with synthetic Bayer liquor or with plant liquor from an Australian refinery. The bauxite was representatively split and ground to <100  $\mu m$  prior to use. It had a total organic carbon content of 0.22 %. The liquor was prepared by passing it through a +45  $\mu m$  Supor membrane to remove aluminium hydroxide and other solids. 1 L of 500 g/L bauxite slurry was placed in a 4 L water jacketed stainless steel vessel, connected to a thermostatted re-circulating water bath which enabled the temperature to be controlled to within 1 °C. The lid of the vessel was fitted with a stirring shaft with two impellers (set to 250 rpm) and a thermocouple probe. After charging with liquor and bauxite, the vessel was equilibrated at 25 °C and the headspace was flushed with high purity nitrogen at the start. The slurry was heated from

25 °C to 91 °C over 40 minutes, with a small flow of ultra high purity (UHP) nitrogen gas passing through the vessel headspace throughout the experiment. The headspace gas from the stainless steel vessel was diluted by additional nitrogen before entering the PTR-MS inlet.

To simulate VOC production during liquor burning, a sample of Bayer plant spent liquor was concentrated by evaporation, mixed with alumina, and slowly oven-dried at 60 °C with occasional stirring to produce dry pellets. The pellets were then placed in a sealed stainless-steel tube which was heated in stages to a maximum temperature of 600 °C. The tube was continuously purged with high purity nitrogen which was diluted with additional nitrogen before entering the PTR-MS for analysis.

## 3. Results

### 3.1 Field Studies

The study site was located just north of Boundary Road and approximately 2 km due south of the main Wagerup refinery 100 m stack. This site was chosen because it is roughly mid-way between the refinery and the nearby town of Yarloop in a direct line. It was far enough from the refinery to be influenced by plume "grounding" from the tall stack, and close enough to be influenced by the lower level sources. Measurements were made for 60 days between 10 August and 7 October 2006. Winter had previously been a period of odour and health complaints by the community and so was chosen as the time for the study in consultation with Alcoa and other stakeholders. During the study period the refinery was in normal, stable operation with a bauxite throughput typical of the whole year. The refinery Liquor Burner was off line for most of the study period. During this time a new Regenerative Thermal Oxidiser was being installed and commissioned to reduce the VOC emissions from the Liquor Burner. Consequently, any particular chemical characteristics of Liquor Burner emissions are not significantly represented in this data set.

#### 3.1.1 Refinery VOC and Odour Plumes

##### *Identification of Molecular Masses and Compounds*

A total of 24 molecular masses were detected at measurable concentrations in the PTRMS data from Boundary Rd. In addition to the 24 molecular masses identified in measurable concentrations, there was also the detection of mass 31 by the PTR-MS, which is indicative of formaldehyde. The PTR-MS response to formaldehyde is widely recognized to be poor, so the formaldehyde concentrations used in this study are those measured by the independent DNPH method. All VOCs identified by the two other techniques were also detected by the PTR-MS. The median concentration of the Total VOCs (TVOC, calculated as the sum of the VOC concentrations) in ambient air was 4.6 ppb. For the sum of the concentrations of the 24 masses detected by the PTR-MS, 99 % of the observations were less than 21 ppb. Considering the whole data set, methanol (mass 33) makes up 55 % of the concentration of TVOC. Formaldehyde contributes 9%, acetone 6.5%, and acetaldehyde 2.8 % of the TVOC concentration. Masses 41 and 43, make up 13% of the TVOC concentration, but could not be uniquely assigned to specific compounds. The statistics of 13 compounds that were both identified and present in the largest concentrations (after allowing for masses 41 and 43) are presented in Table 1. Significantly, the analysis shows that the compounds and masses detected in this study occur in the air for all wind directions. However, the data from Boundary Rd, analysed by wind direction, indicates that a number of masses, mainly 59 (acetone), 45 (acetaldehyde), 33 (methanol) and  $NO_x$  have sources in the direction of the refinery (Fig 1). Apart from methanol, this is consistent with the previously existing knowledge of refinery emissions (Coffey et al. 2005).

## Sources

All of the VOCs identified, including the 13 present in the highest concentrations (Table 1), have more than one possible source in the Wagerup region. The possible sources of these VOCs include industrial, domestic, biological, combustion and transport processes, and they are also produced in the atmosphere from other organic compounds. The analysis of concentrations by wind direction also provides evidence that NO<sub>x</sub>, CO<sub>2</sub> and mass 81 (monoterpenes) have sources in directions other than that

of the refinery, which are consistent with domestic, transport, biological/vegetation and other industrial sources of these gases. From observations of vehicle numbers on the nearby South Western Highway, atmospheric stability and the observed ratio of benzene to toluene concentrations (which has a distinct ratio for vehicle emissions compared to woodheater and agricultural burning), it was assessed that motor vehicle emissions made a minor but observable contribution to the TVOC concentrations at Boundary Rd during this study (Galbally et al. 2008).

**Table 1. The observed concentration statistics of the 13 masses/compounds that were present and identified in measurements from all wind directions at Boundary Road, Wagerup.**

Compound	Concentration (ppbV)			Sources	
	Median	90th %ile	Max	Other Known Sources <sup>a</sup>	Refinery <sup>b</sup>
Formaldehyde	0.39	0.90	1.72	A	Yes
Methanol	2.5	6.4	33.1	A, V, B	No
Acetonitrile	0.03	0.12	2.8	B	Yes
Acetaldehyde	0.1	0.5	2.2	A, O, V	Yes
Formic acid	0.09	0.4	3.3	A, V	No
Acetone	0.3	0.9	6.8	A, O, V	Yes
Acetic Acid	0.05	0.2	1.3	A, B	Yes
Isoprene	0.09	0.7	4.9	V	No
MVK/MACRC	0.03	0.2	1.1	A	Yes
MEK	0.03	0.2	1.1	A, V, B	Yes
Benzene	bdl	0.2	1.6	M, B	Yes
Monoterpenes	0.09	0.4	4.2	V	No
Toluene	0.02	0.4	6.9	M	Yes

<sup>a</sup> A = atmospheric photochemical production; V = vegetation; B = biomass burning; O = oceanic; M = motor vehicles. bdl = below detection limit; <sup>b</sup>Wagerup emissions inventory (Coffey et al. 2005); <sup>c</sup> CAS numbers 78-94-4, 78-85-3

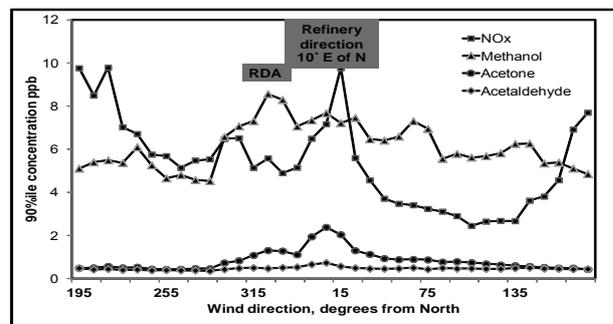
The overall concentrations of VOCs observed in the Wagerup region in this study are low compared with most rural environments in Australia and overseas (Galbally et al. 2008). This indicates both low natural and anthropogenic VOC production rates in the region, including from the refinery, and the influence of oceanic air, which has extremely low concentrations of VOCs and is carried inland to Wagerup by westerly winds during winter.

## Odour

Two odour events were observed at Boundary Rd during this study by CSIRO staff. The only mass of the 24 masses detected from the PTR-MS measurements that appeared to vary in parallel with the odour variations on these two occasions was mass 59 (acetone). The atmospheric chemical transport modelled by TAPM indicated that the low level vents in the refinery contributed to these acetone concentrations. The measured acetone concentrations were below the odour detection threshold for acetone and so were too low to be directly responsible for the odour. An investigation of these events (Galbally et al. 2008) concluded that it was not possible to identify the specific chemical(s) causing the odour. The possible reasons for this are:

- the PTR-MS does not respond to the odorous compound, e.g. because it has a proton affinity less than water;
- the odorous compound(s) can be smelled at concentrations lower than can be detected by the PTR-MS;
- the odorous compound(s) has a molecular mass that corresponds with one of the identified PTR-MS masses but the contribution of the odorous compound to that mass has not yet been identified.

The first possibility is unlikely due to the chemical properties of known odorous compounds. There is insufficient information to say which of the other two possibilities is the more likely. This highlights the difficulty of identifying the source of an odour at a distance from the refinery or other potential sources.



**Figure 1.** The 90th %ile of observed concentrations for 10 degree segments of wind direction at the PTR-MS site, Boundary Rd Wagerup during August to October 2006. RDA = Residue Disposal Area.

### 3.1.2 Point Source Sampling in the Refinery for VOCs and Odour

The alumina refinery sources sampled were the: Pre-desilicator Tank Vent; Clarification Tank (Green Liquor) Vent; Calciner Stack; Calciner Vacuum Pump Vent; Liquor Burner Stack and Cooling Tower Discharge (it is noted that the Liquor Burner had only been started up overnight the night before the morning sampling and may not have stabilized). The TVOC and odour concentrations observed in the samples are listed in Table 2.

**Table 2. Total VOC and odour concentrations in the emission source samples, and the associated chemical odour concentrations in the most concentrated sources.**

Emission Source	Total VOC (ppm) (measured)	Odour Concentration (OU) (measured)	Chemical Odour Concentration (OU) (from threshold values)
Pre-desilicator Tank Vent	215	41,700	177,283
Green Liquor Clarification Tank Vent	10	25,700	-
Calciner Stack	2	4,540	-
Calciner Vacuum Pump	5	41,700	2,283
Liquor Burner	9	253,000	4,660
Cooling Tower Discharge	1	1,330	-

#### VOCs

The masses detected by PTR-MS in the point source samples and the most likely VOC candidate compounds are shown in Table 3, in which the most prevalent compounds, methanol, acetone and acetaldehyde, are highlighted.

**Table 3. Masses detected by PTR-MS in the refinery source samples, and the compounds assigned. The most prevalent compounds are highlighted in bold.**

PTR-MS mass	Compound(s)	PTR-MS mass	Compound(s)
33	<b>Methanol</b>	59	<b>Acetone</b>
41	Not identified	60	Trimethyl amine
42	Acetonitrile		Acetone with one <sup>13</sup> C
43	Not identified	71	Methacrolein
<b>45</b>	<b>Acetaldehyde</b>		Methyl vinyl ketone
51	1,3-butadiyne	93	toluene
52	2-propenal		

This sampling confirmed the presence of methanol in refinery emissions that had been inferred from the field study, in which it was observed to increase in concentration when the wind direction was from the refinery, as shown in Figure 1. Methanol has now been confirmed as a major contributor to the TVOC in the aggregate refinery emissions comparable with, if not larger than, those of acetone and acetaldehyde. This result was initially surprising, as methanol had not to our knowledge been identified in refinery emissions previously. Its presence is consistent with laboratory measurements and has been shown to be highly likely on the grounds of chemical principles (see below). It is also consistent with the field observations, although the refinery effect is superimposed on a relatively large background, due to the large natural atmospheric cycle of methanol (Galbally and Kirstine 2002).

#### Odour

An inspection of Table 2 reveals no correlation between odour and TVOC in the data from the different sources surveyed, as expected (Forster et al., 2005). The approach used by Coffey and Ioppolo-Armanios (2004) was then applied to the three samples with the highest odour concentrations (Pre-desilicator Tank Vent, Calciner Vacuum Pump and Liquor Burner) to see if the observed odour intensities could be correlated with the published odour thresholds for the compounds found to be present. Where there was more than one possible VOC for a mass detected by the PTR-MS, the calculation was repeated for each compound. The odour detection thresholds used were from Nagata (2003) and the VOCBASE database (Jensen and Wolkoff 1996). The results, shown in the last column of Table 2, indicate that this method over-estimates the odour from the Desilicator Tank Vent but greatly under-estimates the odour from the other two sources. Given that there is considerable uncertainty in the applicable values of the odour thresholds and in odour measurements *per se*, it is reasonable to conclude that the odour from the Pre-desilicator Tank Vent is accounted for by the compounds

observed. In contrast, the odour levels from the Calciner Vacuum Pump and the Liquor Burner appear to be far greater than can be accounted for by the compounds observed. This means that for these two sources (as was the case for the field observations), either the odorous compound(s) can be detected by the human nose at concentrations lower than by the PTR-MS, or the odorous compound(s) has a molecular mass that corresponds with one of the masses detected by PTR-MS but its contribution to that mass has not yet been assigned.

### 3.2 Laboratory simulations of pre-desilication and liquor burning

#### Pre-desilication

The results of the pre-desilication simulation are shown in Figure 2. No detectable VOC emissions were observed at temperatures up to 60 °C. Significant VOC generation occurred at 80 °C and above. The main VOCs generated were methanol, acetone and acetaldehyde, with lesser amounts of butene and methyl-ethyl ketone (MEK). The results shown are from an experiment with bauxite mixed with plant spent liquor; similar results were obtained with bauxite mixed with synthetic liquor, but with plant spent liquor alone only very minor amounts of VOCs were observed. These results indicate that significant evolution of VOCs can be expected during bauxite pre-desilication, and that virtually all of the VOCs result from the reaction of the organic compounds from the bauxite itself, not from the residual organics in the process liquor. The results at 90 °C correlate well with the analysis of a sample of vapour taken from a pre-desilication tank in the refinery, as shown in Figure 3.

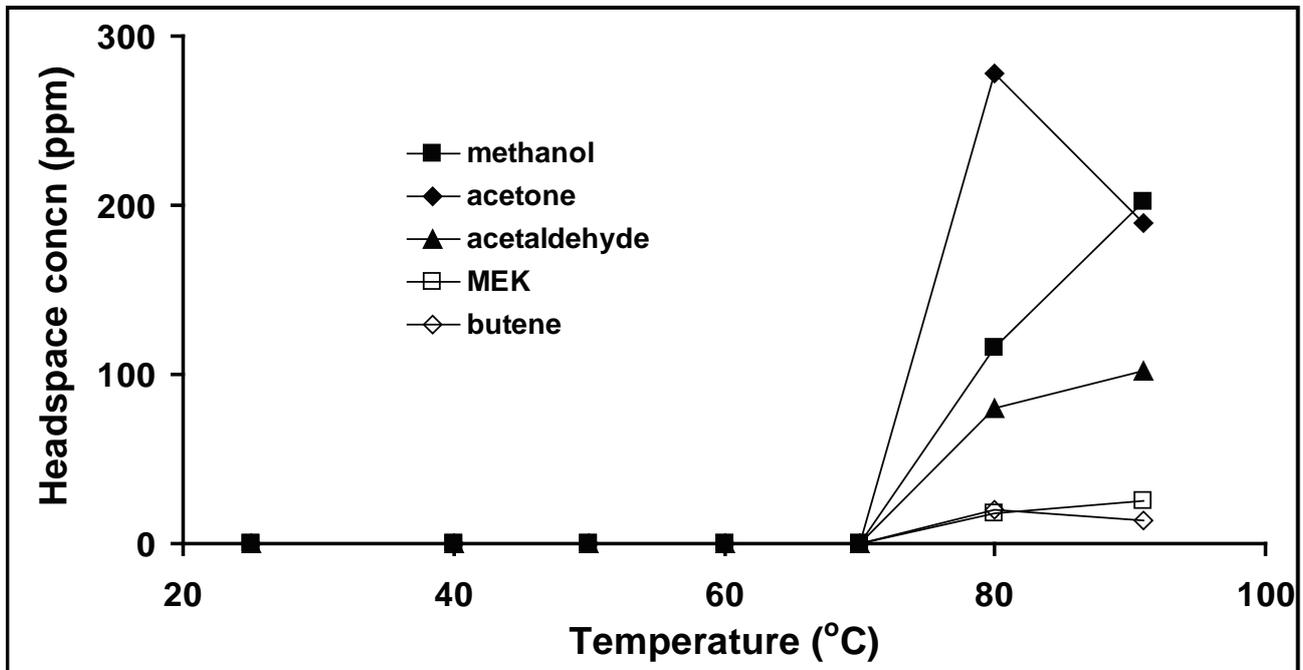


Figure 2. Headspace VOC concentrations for bauxite slurry in plant spent liquor as a function of temperature

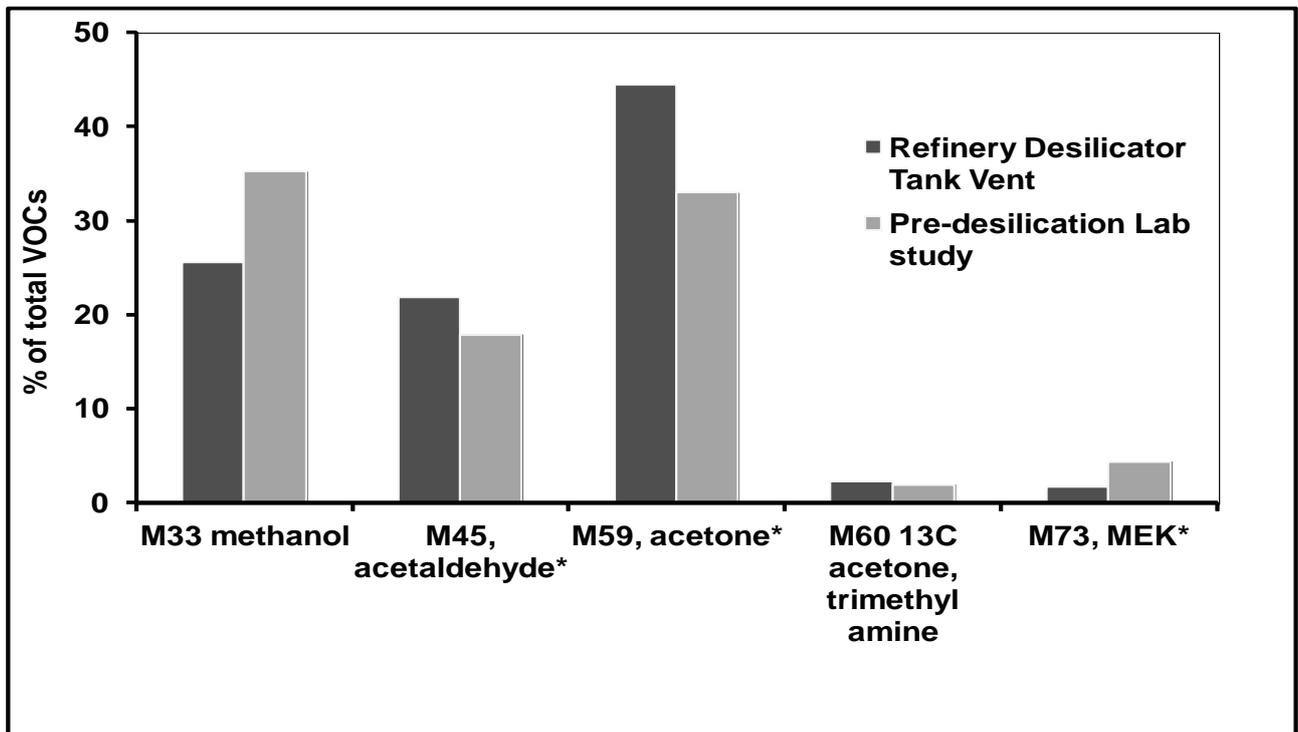


Figure 3. VOC generation in laboratory pre-desilication simulation compared with an equivalent refinery sample

This demonstrates the production in the Bayer process of the VOCs that are most commonly observed to be at concentrations above background downwind of the refinery. The asterisks indicate the possibility of another compound with the same mass; for example, the contribution of acetone containing the  $^{13}\text{C}$  isotope to the signal at mass 60 will be approximately 3% of the mass 59 signal.

#### Liquor burning

The results for the five most concentrated VOCs detected in the liquor burning simulation are shown in Figure 4, from which it can be seen that there is very little VOC production below 250°C. At about 270°C there is a rapid rise in the production of VOCs, primarily acetone, MEK and trimethyl benzene (TMB). The temperature was held at 350 °C for 25 minutes, during which time there was a rapid rise in VOC production to the extent that the

PRT-MS response saturated. There appeared to be a peak in VOC production at this temperature, followed by a drop presumably due to consumption of the organic starting materials. A further peak occurred upon raising the temperature to 450 °C as some more refractory organic compounds were pyrolysed. VOC production at these temperatures was dominated by trimethylbenzene and benzene with acetone and MEK making smaller contributions. Subsequently raising the temperature to 560 °C did not result in further VOC production; rather, the emissions tailed off as the starting materials were used up. The main emissions observed in this experiment, acetone, acetaldehyde, MEK, benzene and trimethylbenzene, are typical of liquor burning kiln emissions (Coffey et al. 2005). The results indicate that the main emissions are produced at temperatures likely to be found in the drying section of a liquor burner rather than in the high temperature kiln itself.

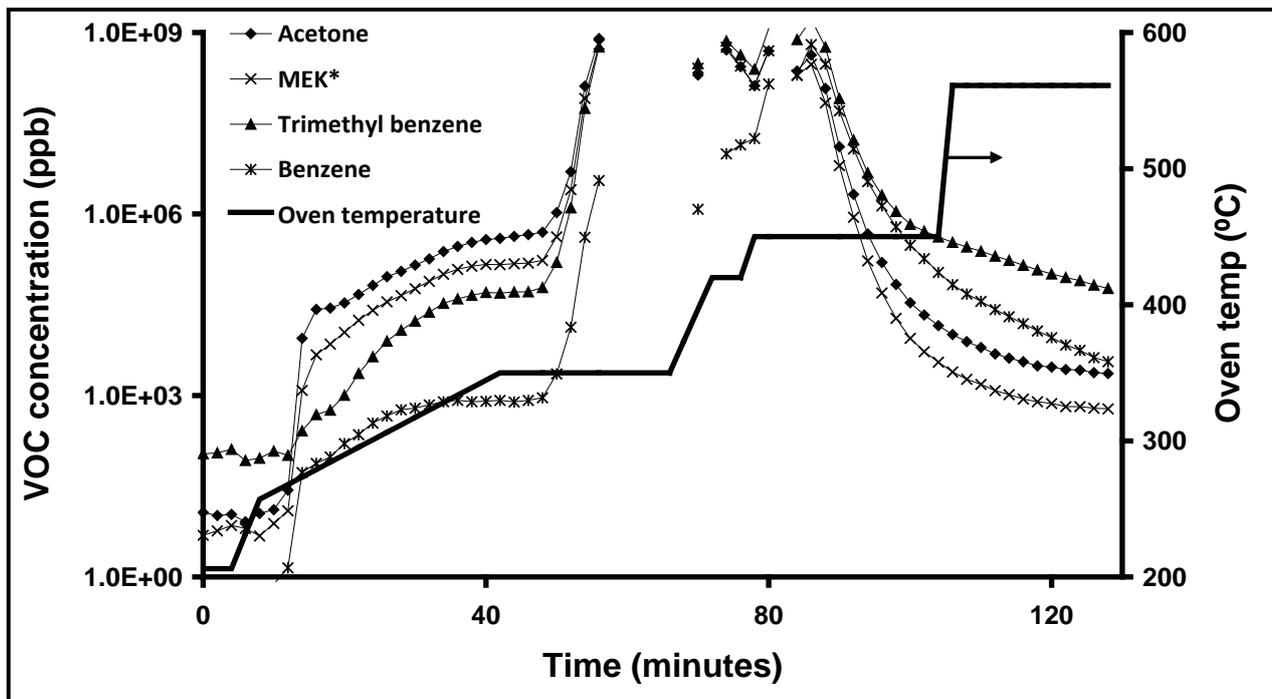


Figure 4. Concentrations of the main 5 VOCs produced in the simulated liquor burning experiment.

#### 4. Linking the measurements to Bayer process chemistry

VOCs are produced in the Bayer process from the degradation of more complex organic compounds which primarily originate from the bauxite. For example, humic compounds react with

caustic soda to yield amino-acid fragments that release ammonia and amines, and hydroxycarboxylic acids which are also produced from the degradation of lignins and carbohydrates (Power and Loh, 2010).

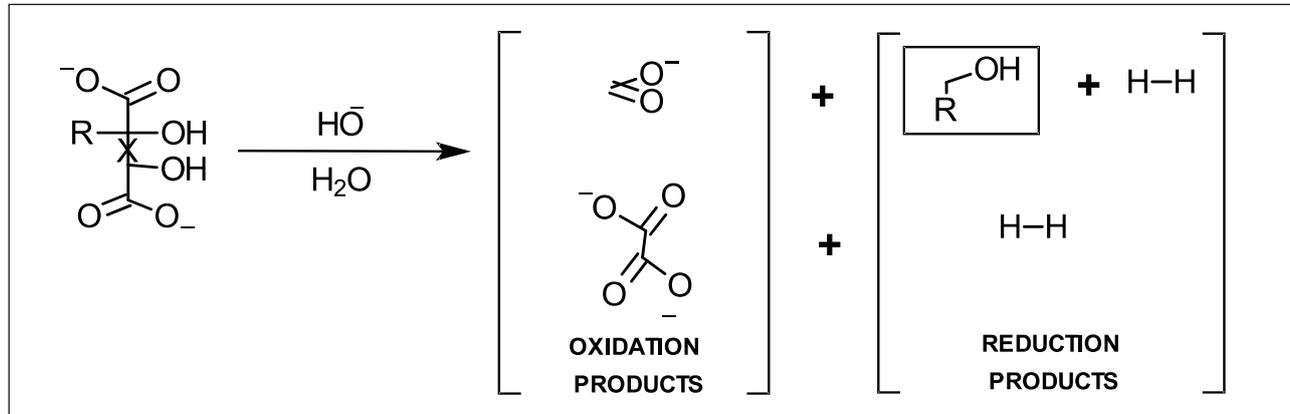


Figure 5. Schematic summarising the mechanism proposed for the formation of volatile alcohols (see box) and hydrogen as reduction products, and simpler carboxylic acids including formaldehyde as oxidation products, in the base-catalysed oxidation by water of polyhydroxy carboxylic acids.

Hydroxycarboxylic acids can further degrade to produce hydrogen and a range of VOCs, for example alcohols as shown in Figure 5, which illustrates the formation of volatile alcohols through the base-catalysed oxidation of polyhydroxy carboxylic acids. In this example, an initial cleavage occurs at the point marked "X", and the products of that cleavage are oxidized by water to produce hydrogen and an alcohol as the reduction products. Where R = H, the product is methanol, R = CH<sub>3</sub> produces ethanol, and so-on, according to the mechanism proposed by Loh et al (2010).

By analogy it is proposed that other starting compounds may, by similar redox mechanisms, give rise to formaldehyde, acetone and acetaldehyde, all of which are present in refinery volatile emissions. Allowing for other oxidants, it may further be proposed that these VOCs are in general the reduction products of base-catalysed redox reactions in which water, other organic compounds, or oxygen may be the oxidant, and the oxidation products of which are simpler carboxylic acids or carbonate.

## 5. Summary and Conclusions

The sources and composition of VOCs from alumina refining has been investigated through four studies on different scales:

- Real time measurements of VOCs in air approximately 2 km away from an alumina refinery showed methanol, acetone and acetaldehyde have sources in the direction of the refinery;
- Measurements of VOCs and odour from refinery point samples revealed many compounds of which methanol, acetone and acetaldehyde occurred at the highest concentrations;
- A laboratory study which measured VOC emissions from slurry mixtures simulating pre-desilication and liquor burning generated VOCs consistent with those found in the field study and point sampling; and
- The chemical mechanisms by which VOCs may be generated have been investigated.

For odour intensities that were measured in the field, in point source samples, and in the laboratory, in no case could the compounds responsible be fully determined. Also, (consistent with previous studies) it was found that odour was not directly related to the total VOC concentration in the samples.

The PTR-MS technique has been demonstrated to be capable of detecting individual VOCs and following them with high time resolution at very low concentrations, which makes it an excellent technique for tracking VOCs in the ambient environment as a tool for source attribution. It does however require support from

other techniques to enable definitive identification of VOCs in some cases.

For the first time to our knowledge, methanol has been confirmed as a major component of refinery emissions. The PTRMS was the key to this achievement, because methanol is difficult to quantify by many of the standard techniques used in ambient VOC analysis, and because it is generally present at a significant background concentration in the atmosphere, so that excellent time-resolution is required to enable source attribution.

Investigations of the mechanisms of the degradation of organic material in the Bayer process indicates that the VOCs evolved are in general the reduction products of base-catalysed redox reactions in which organic compounds from the bauxite are oxidized, and in which water may be the oxidant.

This study has combined field observations, point source analyses and laboratory studies, unified by fundamental chemical knowledge, to provide the basis of a comprehensive explanation of VOC production in the Bayer process, a current and emerging environmental issue concerning alumina refining.

## Acknowledgements

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