Report on
IMC Task 17 - Dioxin Formation Investigation

Executive Summary

Although the dioxin monitoring shows that GTP stack emissions are now consistently less than the DECC limit, an unusual finding has been that there is an increase in dioxin concentrations (expressed as the TEQ, that is the toxic congeners only) between the quencher outlet and the stack of the GTP.

The aim of this task (IMC Task 17) was to determine if there is any change in the dioxin congener distribution (relative concentrations) between the quencher outlet and the stack of the GTP. It was hoped that knowing this might lead to a better understanding of which mechanism is at force in creating the very low concentrations of dioxins (i.e. de novo synthesis or desorption) after the quencher outlet.

NMI (National Measurement Institute) undertook additional analysis of existing sample sets collected from the quench outlet and stack of the GTP in 2006/2007. Because of difficulties with the analysis, the investigation was limited to just a few congeners and to 4 rather than the originally planned 8 sample sets.

The data analysis clearly showed an increase in the amount of toxic dioxin congeners over their low toxicity counterparts, and most importantly the presence of chlorinated dioxin congeners in the stack that weren't present at the quench outlet. It appears that chlorination of dioxin congeners is occurring between the quench outlet and the stack, possibly due to the presence of hydrochloric acid/chlorine in the scrubber liquor, resulting in the synthesis of more toxic congeners.

Due to the limited amount of data, it is not possible to investigate exactly what reactions were taking place. Thus no clear conclusions about formation mechanisms can be drawn from the results of this investigation.

Given that dioxin results for the GTP stack have been consistently below the NSW DECC stack emission limit of 0.1 ng/Nm^3, further work in this area would be purely academic and hence outside the scope of the IMC. We therefore recommend that no further work be undertaken in relation to this task.

Dr Chris Clunies Ross, Airlabs Environmental
Dr Mark Hibberd, CSIRO Marine and Atmospheric Research

19 May 2008

P (07) 3801 3762 F (07) 3801 4645

Scope of task

1. Develop a spreadsheet to extract the concentrations of the full suite of 210 dioxin congeners (rather than just the 17 toxic ones) from the analysis results already obtained by National Measurements Institute (NMI), for the purposes of undertaking a more detailed analysis of dioxin formation in the Orica Groundwater Treatment Plant (GTP).

2. Get NMI to use the above spreadsheet to extract results for the eight (8) most recent GTP dioxin sampling events (at both the stack and the quencher – a total of 16 samples), in order to list all the dioxin congeners present. These samples will include those taken by both Airlabs Environmental Pty Ltd (i.e. Dr Chris Clunies-Ross) and Stevenson's Environmental Management over the range of thermal oxidiser operating temperatures trialed earlier this year (900 – 1000 degrees Celsius).

3. Analysis by Dr Chris Clunies-Ross of the spreadsheet results to do determine which congener concentrations change between the quencher outlet and the stack of the GTP. Interpretation of the results by Dr Chris Clunies-Ross and Dr Mark Hibberd.

4. A brief report to the CLC outlining the findings of the investigation and any resulting recommendations.

Report

Results of dioxin testing conducted on the Orica Groundwater Treatment Plant (GTP) by both Stephenson Environmental and Airlabs Environmental consistently showed higher dioxin concentrations in the stack than at the outlet of the quench. This is very unusual. The dominant dioxin formation mechanism in combustion systems is generally accepted to be *de novo* synthesis. This occurs in the temperature range 250-450°C. Yet gas temperatures between the quench and the stack do not rise above 80°C, meaning that only minor dioxin formation is expected in this region. In addition, the wet scrubber located between the quench and the stack removes particulate matter (and hence dioxins) from the gas stream, meaning that a ***decrease*** in dioxin levels was actually anticipated.

To investigate this unusual phenomenon, the National Measurement Institute (NMI) was asked to develop a spreadsheet to extract the concentrations of the full suite of 210 dioxin congeners from the sample chromatograms, rather than just the 17 toxic ones usually reported. In this way, it would be possible to investigate whether the low-toxicity (non-2,3,7,8) dioxin congeners were converting to the toxic (2,3,7,8) forms between the quench and the stack due to processes such as additional chlorination or 'precursor' synthesis. This would lead to a better understanding of which mechanism is at force in creating the very low concentrations of dioxins (i.e. de novo synthesis or desorption) after the quencher outlet.

Unfortunately, it proved very difficult for NMI to determine non-2,3,7,8 chlorinated PCDDs and PCDFs. Originally, NMI believed that they would be able to determine all 210 dioxin congeners for about $200 per sample, but this was not the case. Therefore the investigation was restricted to 4 sample sets (quench outlet and stack) and only tetra, penta and hexa chlorinated congeners were quantified. The sample sets were those from 9 October 2006, 1 February 2007, 28 February 2007, and 28 June 2007.

The results obtained by NMI are summarised in the attached table (*IMC Task17 Congener Summary.pdf*). As noted by NMI, the table summarises "all native congener

peaks detected for Tetra, Penta and Hexa chlorinated dibenzo-p-dioxins and furans. A cut-off threshold of 5% of total homologue group peak area was used to eliminate minor peak contributions."

The data analysis clearly showed an increase in the amount of toxic dioxin congeners over their low toxicity counterparts, and most importantly the presence of chlorinated dioxin congeners in the stack that weren't present at the quench outlet. It appears that chlorination of dioxin congeners is occurring between the quench outlet and the stack, possibly due to the presence of hydrochloric acid/chlorine in the scrubber liquor, resulting in the synthesis of more toxic congeners.

Due to the limited amount of data, it is not possible to investigate what reformation reactions were taking place. Thus no clear conclusions about formation mechanisms can be drawn from the results of this investigation.

Given that dioxin results for the GTP stack have been consistently below the NSW DECC stack emission limit of 0.1 ng/Nm^3, further work in this area would be purely academic and hence outside the scope of the IMC. We therefore recommend that no further work be undertaken in relation to this task.

Dr Chris Clunies Ross, Airlabs Environmental
Dr Mark Hibberd, CSIRO Marine and Atmospheric Research

19 May 2008

Attachment: IMC Task17 Congener Summary.pdf

NMI chromatograms for the 8 samples are in the files:
N06_034591 Chromatograms.pdf
N06_034594 Chromatograms.pdf
N07_004647 Chromatograms.pdf
N07_004649 Chromatograms.pdf
N07_008243 Chromatograms.pdf
N07_008244 Chromatograms.pdf
N07_024198 Chromatograms.pdf