

Botany Groundwater Cleanup Project

Independent Monitoring Committee

Task 1

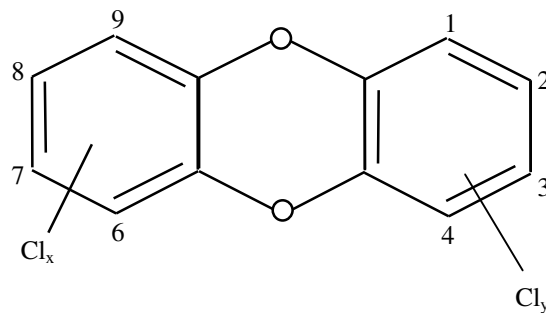
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1. What type of dioxins have been detected in emissions from the GTP stack?

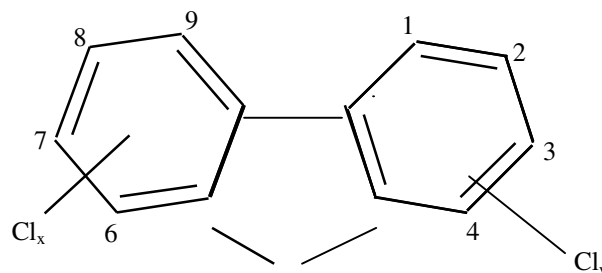
Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) are two families of organic compounds, related in chemical structure and biological properties, which are usually found together in the environment as complex mixtures. These compounds, commonly known as 'dioxins' or 'dioxins and furans', are found virtually everywhere on earth, with the main transport mechanism being atmospheric dispersion and deposition.

In molecular structure a dioxin consists of two benzene rings connected by a pair of oxygen bridges and a furan consists of two benzene rings connected by a single oxygen bridge and a C-C single bond. Chlorine atoms may be substituted at any or all of the positions assigned the numbers 1 - 4 and 6 - 9, as shown in Figures 1 and 2 below.



$$X = 0 \text{ to } 4, Y = 0 \text{ to } 4, X + Y \geq 1$$

Figure 1 Molecular Structure of Polychlorinated Dibenzop-Dioxins





$$X = 0 \text{ to } 4, Y = 0 \text{ to } 4, X + Y \geq 1$$

Figure 2 Molecular Structure of Polychlorinated Dibenzofurans

There are 75 possible chlorinated dioxin and 135 possible chlorinated furan congeners, resulting in a total of 210 possible congeners. In chemical notation, these congeners are referred to by the position of the chlorine atoms. For example, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, or 2,3,7,8-TCDD, is a dioxin congener with chlorine atoms located at the 2, 3, 7 and 8 positions, as depicted in Figure 3 below.

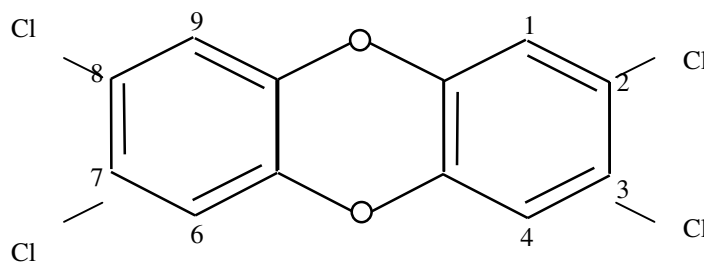


Figure 3 Molecular Structure of 2,3,7,8-TCDD

The toxicity of the 210 individual PCDD/F congeners varies widely, dependent upon the number and position of chlorine atoms within the molecules. 17 of these congeners have chlorine atoms in all of the 2, 3, 7 and 8 (lateral) positions, and are considered to be the most toxic. In 1989, the North Atlantic Treaty Organisation's (NATO) Committee on Challenges of Modern Society developed a procedure for assessing the total toxicity of a mixture of chlorinated dioxins and furans, such that consistency could be achieved in reporting of results. This procedure rated the toxicity of individual chlorinated dioxins and furans relative to 2,3,7,8-TCDD, the most toxic and widely studied congener.

The I-TEFs/89 scheme, which has been adopted as an interim procedure for assessing dioxin risk by the USEPA and the majority of western countries, assigns a non-zero value to the 17 dioxins and furans with chlorine substituted in the 2, 3, 7 and 8 positions. A zero value is given to all other congeners.

To date, three reports have been received for dioxin testing conducted on the GTP stack; two from SGS Australia Pty Ltd and one from Stephenson Environmental Management Australia. All three reports relate to testing conducted on the GTP plant emissions prior to shutdown. In each case, all 17 toxic congeners were found.

2. What is the level of accuracy for the dioxin sampling and analysis?

The major sources of sampling uncertainty are related to:

- the stability and character of the stack gas flow,
- the consistency of the process being monitored,
- the size, shape and character of the particles, and
- the breakthrough of PCDD/Fs retained by the sample resin trap.

The effect of resin trap breakthrough is minimised by the use of internal surrogate standards. The isotope dilution technique employed for dioxin analysis effectively divides the concentration of ^{12}C emission PCDD/Fs retained by the resin by the fraction of ^{13}C surrogates recovered. This in effect compensates for any breakthrough. While the measurement uncertainty of the sampling will vary according to the above parameters, it is expected to be $\pm 15\%$.

The National Measurement Institute in Sydney estimates the analytical measurement uncertainty to be $\pm 10\%$. Hence the overall measurement uncertainty for dioxin monitoring is approximately $\pm 25\%$.

3. Why does dioxin monitoring take so long?

Although sampling can be completed in a day, PCDD/F extraction, cleanup and analysis typically takes 3-4 weeks to complete. The procedure required to determine the PCDD/F concentration is quite complex. Firstly, it is necessary to extract the sample from the sampling media and then to isolate the dioxins and furans from all the other compounds present in the extract. This extraction and cleanup process normally requires at least a week in the laboratory. It should be remembered that PCDD/F congeners are measured in picograms, or millionth of a millionth (trillionth) of a gram. This is like finding an individual grain of salt in an Olympic sized pool filled with salt.

PCDD/Fs are separated and quantified using high resolution gas chromatography with high resolution mass spectrometry (HRGC/HRMS). Multiple sample injections are required, as PCDD/F fractions must be separated on both a polar and non-polar capillary column to allow an isomer specific determination of all 2,3,7,8-substituted isomers. This process typically takes 2-3 days to complete. Finally, interpretation and reporting of results can take a further 2 days.

As dioxin laboratories are always busy, there can be a 1-2 week delay prior to commencing the analytical procedure. As a result, routine dioxin analysis takes 3-4 weeks, although urgent samples can be analysed in 10 days with payment of a premium (typically 100%).

4. What recommendations could be made to improve the monitoring of dioxins or surrogates (such as temperature) in the GTP?

Temperature is a critical parameter in the formation of chlorinated dioxins and furans in combustion systems. PCDD/Fs are formed as combustion gases are cooled through a process known as *de novo* synthesis. This phenomenon has been observed in the temperature range 250 – 450°C, and predominantly occurs in the temperature range 300 – 400°C.

To minimise *de novo* synthesis in the GTP system, a 'rapid-quench' design was used. With this, combustion gases are cooled down to approximately 460°C in the heat exchanger, and then rapidly quenched with liquid to instantly drop the temperature below 70°C, ensuring that PCDD/Fs have minimal opportunity to form. Although the plant pyrometer indicated that the temperature of gases leaving the heat exchanger was at least 450°C during dioxin testing, this was based on a single point measurement and it is believed that 'cold spots' may have been present in the system due to inadequate mixing of gases.

During the recent shut-down, baffles were installed in the heat exchanger to improve the mixing of gases and additional thermocouples were installed to ensure that the gas temperature was measured across a representative cross-sectional area. These modifications enable the minimum temperature of gases in the heat exchanger to be more effectively determined, and as such enhance the ability to monitor a parameter likely to influence PCDD/F formation.

In terms of actual source monitoring for dioxins, a common concern is that sampling is only conducted over short, discrete periods. Although the GTP stack is currently being monitored each month, most licensed premises are only required to collect a PCDD/F sample over a 6 hour period every 6 or 12 months.

Unfortunately, dioxins are not well suited to continuous monitoring. This is because:

- there are 17 toxic PCDD/F congeners that would have to be individually determined at part per trillion levels, and
- PCDD/Fs have both a particulate and a gaseous fraction.

The particulate fraction would have to be extracted prior to analysis, making true continuous monitoring impossible.

Chemical surrogates of dioxins and furans can be continuously monitored. These indicator compounds are easier to measure than PCDD/Fs and tend to mimic their formation, ie, an increase in the surrogate concentration indicates a potential increase in PCDD/F formation. The simplest surrogate compound to monitor is carbon monoxide, however, as this is not present at significant concentrations in the GTP emissions it is not well suited to this application.

Other dioxin surrogates, known as pre-cursors, actually participate in the chemical formation process, and as such are considered to be more reliable as indicators of formation. Such compounds include chlorophenols and chlorobenzenes. They can be continuously measured on-line using a Proton Transfer Reaction – Mass Spectrometer (PTR-MS). The use of a PTR-MS to monitor dioxin surrogates has been successfully demonstrated at incinerator plants in Japan.

There is an on-line system that can continuously analyse for dioxins and furans themselves at parts per trillion levels in real time (minutes) using a time-of-flight mass spectrometer. The main advantage of such a system is that the operator is immediately informed that a licence excursion is occurring, and can shut down the plant and/or take corrective action. However, there are several limitations of this system. As discussed above, continuous monitors can only determine gas phase dioxins, filtering out the particulate phase. And secondly, it can not simultaneously monitor all 17 toxic congeners. Both of these limitations mean that the determined PCDD/F concentration is an estimate at best. Additionally, at 3 – 4 million dollars it is cost prohibitive.

Another approach is to continuously sample PCDD/Fs and analyse them later. There is a commercially produced system that can sample a stack emission continuously over an extended period, eg, weekly, bi-weekly or monthly, so that the emission can be monitored 100% of the time. By continuously measuring the flue gas velocity and temperature the extraction rate can be continuously adjusted to ensure accurate sampling. Special conditions, such as plant shut down, are detected by the control unit and the measurement paused if necessary.

The system contains a filter unit for the collection of dioxins and furans. This can be quickly replaced and sent to the laboratory for the standard HRGC/HRMS analysis.

The main disadvantages of a continuous sampling system are:

- the result is an average over the week, fortnight or month, and peak concentrations can not be determined, and
- as with normal discrete stack testing, the result is not available until a month after the completion of sampling.

The problem of time delays encountered with dioxin monitoring is further exacerbated by this system, due to the length of time taken to collect the sample. As such, the operator may not be aware of licence excursions for up to 2 months after the event.

5. How could sampling and analysis be undertaken by the various labs in order to provide the community with confidence in the results in the long-term?

The results of testing undertaken by the SGS and Stephenson/NMI laboratories are reasonably consistent, with similar congener profiles present in all 3 cases. All NATA/ISO accredited dioxin laboratories use isotopically labelled surrogate standards as part of their internal quality control. They also participate in proficiency testing programs. Unfortunately, this is restricted to matrices such as soil, biological matter and food. Proficiency testing programs do not include emission samples as there are no certified reference materials available.

One way to improve the community's confidence in dioxin monitoring would be to establish a proficiency testing program for emission samples. Certified reference materials could be prepared from herbicide manufacturing residues, which typically contain all PCDD/F congeners at high levels. Dioxin sampling modules could be spiked with a known amount of this material and sent to a number of laboratories for comparison.

Obviously, if consistent results were not obtained the matter would have to be investigated. The results of these proficiency testing programs could be made available to the community, increasing their confidence through the transparency of the process.