Sampling and analyses of polychlorinated dibenzo dioxins (PCDDs) and polychlorinated dibenzo furans (PCDFs) emissions in South Africa: A practitioner's guide

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Abstract
Dioxins and furans are toxic chemicals. A draft report released for public comment in September 1994 by the US Environmental Protection Agency clearly describes dioxin as a serious public health threat. The public health impact of dioxins may rival the impact that dichlorodiphenyltrichloroethane (DDT) had on public health in the 1960's. According to the United States Environmental Protection Agency(USEPA) report, not only does there appear to be no "safe" level of exposure to dioxin, but levels of dioxin and dioxin-like chemicals have been found in the general US population that are "at or near levels associated with adverse health effects." With this in mind the purpose of this paper is to provide an overview of the current dioxin and furan emissions from industry in South Africa, in terms of compliance with the relevant emission limit values (ELVs) and the current challenges faced with the monitoring and analysis thereof.

Keywords
dioxins, furans

Introduction
"The term Dioxin is commonly used to refer to a family of toxic chemicals that share a similar chemical structure and induce harm through a similar mechanism. Dioxins have been characterized by the USEPA as likely human carcinogens and are anticipated to increase the risk of cancer at background levels of exposure. Examples of dioxin include polychlorinated biphenyls (PCBs), polychlorinated dibenzo dioxins (PCDDs), and polychlorinated dibenzo furans (PCD/Fs)" (Energy Justice Network, 2014; USGS, 2014).

PCDD/F's are by-products of incineration, uncontrolled burning and certain industrial processes. Industrial sources of PCDD/F's to the environment include incinerators, metal smelters, cement kilns, paper and pulp industry, manufacture of chlorinated organics, and coal burning power plants (DOW, 2014). Dioxin is also produced by non-industrial sources (now considered by the U.S. Environmental Protection Agency (USEPA) to be the greatest source in the USA (US EPA, 2014), like residential wood burning, backyard burning of household waste, oil heating, and emissions from diesel vehicles.

South African legislation, Government Notice 893 of 22 November 2013 – Listed Activities and Associated Minimum Emission Standards Identified In Terms Of Section 21 of the National Environmental Management: Air Quality Act, 2004 (Act No. 39 of 2004), sets out PCDD/F emission limits for new and existing plants. The emission limit that is set for all dioxin regulated processes is 0.1 ng I-(Toxic equivalence) TEQ/m^3 (Normalised to a temperature of 0°C, pressure of 101.3 kPa, dry and at specified oxygen (O_2) concentration).

The method prescribed in government notice 893 for PCDD/F monitoring is US EPA Method 23 - Determination of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans from Municipal Waste Combustors (US EPA, no date).

There are no laboratories available in South Africa that can perform the analytical work prescribed in US EPA Method 23. All the collected samples are therefore exported to other countries where these facilities are available. As a consequence significant logistical and analytical costs are incurred.

Samples have to be collected, stored, transported and analysed following the requirements of US EPA Method 23 in order to obtain valid, reliable and accurate data.

The results of PCDD/F data are expressed in terms of toxic equivalent factors (TEQ) which provides an estimate of the toxicity of a sample (Keika Ventures, 2014). The total TEQ value is used in risk assessment studies and regulations in the US and Europe set acceptable TEQ levels for PCDD/F in air emissions. Using the TEQ approach, each individual 2,3,7,8-substituted PCDD/F (there are 17) is assigned a Toxicity Equivalency

Factor(TEF). The TEF factor correlates the toxicity of each 2,3,7,8-substituted PCDD/F to 2,3,7,8-TCDD which is considered to be the most toxic of all PCDD/F's.

There are different sets of TEF's that can be used to calculate TEQ, however, the most commonly used set is the International Toxicity Equivalency Factors (I-TEF). I-TEF is the TEFs referenced in US EPA Method 23 and also the TEF's to be used for South African reporting. The World Health Organization (WHO) TEFs also have wide use in risk assessment study data.

To calculate a sample's TEQ, you multiply the concentration of each specific analyte by its corresponding TEF which gives you the TEQ for each 2,3,7,8-substituted D/F. Sum the TEQ for each 2,3,7,8-substituted analyte to get the Total TEQ for the sample.

$$TEQ_{sample} = \sum (\text{concentration} \times TEF)_{2,3,7,8\text{-substituted analyte}}$$

Table 1 details the two commonly used types of TEF's.

Table 1: *TEF Factors*

Compound	I-TEF	WHO (Mammals/Humans)
2,3,7,8-TCDD	1	1
1,2,3,7,8-PeCDD	0.5	1
1,2,3,4,7,8-HxCDD+	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.01
OCDD	0.001	0.001
2,3,7,8-TCDF	0.1	0.1
1,2,3,7,8-PeCDF	0.05	0.05
2,3,4,7,8-PeCDF	0.5	0.5
1,2,3,4,7,8-HxCDF	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01
OCDF	0.001	0.001

Sampling methodology

US EPA Method 23 requires specialised sampling equipment including skilled and trained test personnel. All the glass components/sample exposed components upstream of and including the XAD resin trap shall be cleaned following prescribed cleaning protocols. Filters need to be pre-cleaned following solvent extraction procedure as detailed in the method. XAD resin traps are prepared and spiked prior to usage. The absorbent trap must be used within 4 weeks of cleaning. The XAD traps should also be clearly labelled with expiration date and a unique number.

Careful consideration should therefore be given to timelines when ordering and preparing traps. Traps need to be ordered in advance to allow the laboratory to prepare, spike and courier the components in time for the sampling campaign. New traps should be ordered in the event that the traps surpass the expiration date.

It is important that the XAD-2 adsorbent resin temperature do not exceed 50°C because thermal decomposition will occur. During testing, the XAD-2 temperature must not exceed 20°C for the efficient capture of the PCDD/F's to take place. Consideration should be given to the transportation, storage and handling of reagents on site. High ambient temperatures found in South Africa could easily have an effect on the traps if not stored away from sources of heat or direct sunlight.

Recovery of the sample train should take place immediately after the test is completed. All sample-exposed surfaces (the stack gas is exposed to sampling components (glass liners, nozzles, filter holders, etc) prior to being trapped on the filter and XAD resin) should be sealed and transported to a suitable location for the clean-up/recovery process once the probe is cool enough to handle. The recovery area should be free of dust, smoke and other potential sources of contamination.

A rigorous sample clean-up/recovery procedure is detailed in the method and should be adhered to. The solvents used have to be pesticide grade and only Teflon wash bottles should be utilised for recoveries.

All samples must be extracted within 30 days of collection and analysed within 45 days of extraction. Samples could be detained in customs or redirected and may not be received and extracted within the allowed time window. Samples also need to be stored at temperatures ≤ 4°C.

Figure 1 is a schematic of the EPA method 23 sampling train.

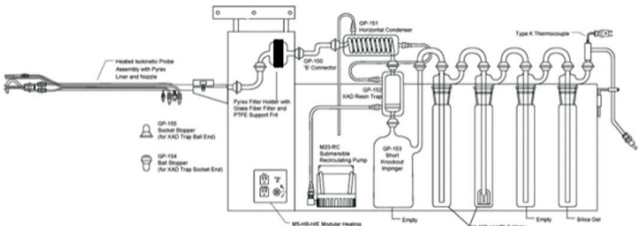

Figure 1: *Schematic of sampling system*

In Figures 2 and 3, sampling equipment in use is shown.

Figure 2: *Typical sample train set up*

Figure 3: *Glass nozzle, pitot tube and thermocouple*

Reporting criteria

It is important to understand the analytical data and reporting criteria. The report should detail the criteria utilised from the analytical reports.

Symbols are used in the analytical report and also in the presentation of the test results. The symbols indicate results that have special significance and require different procedures in calculations and data interpretation. The data reporting procedures outlined in US EPA Method 23 are used in presenting all analytical results. Any values flagged should be considered and addressed in the final report as the reported values may have statistical significance.

Analytical results that are below detection limits (ND) need special mention as the results could be interpreted differently and therefore reports could vary from one test report/test house to another.

The US EPA has different ways of reporting the data, depending on the intended use of the results. Users may decide to substitute ND with zero, 0.5x ND or use the ND value depending on the intended use of the results.

The following example could be used to demonstrate the above,

- Risk analyses from specific plants – Substitute the ND result with the limit of detection (DL) value. This approach will provide the worst case or highest value. This will generally be indicated on the report as ITEF TEQ (ND=DL; EMPC=EMPC)
- Developing emission factors – Substitute the ND results with half the limit of detection value. This approach may provide an average emission. This will generally be indicated on the report as ITEF TEQ (ND=DL/2; EMPC=EMPC/2)
- Setting emission limits and compliance testing – Substitute ND result with zero. This will generally be indicated on the report as ITEF TEQ (ND=0; EMPC=0). EPA also make mention that applying zero should only be done for tests with a sample time of more than 4 hours

Table 2: *Example of certain laboratory reporting qualifiers/attributes*

Data Qualifiers/Data Attributes	
>	Indicates high recoveries. Shown with the numeric value at the top of the range
B	The analyte is found in the method blank, at a level that is <=10x the sample concentration
C	Two or more congeners co-elute. In EDDs C denotes the lowest IUPAC congener in a coelution group and additional co-eluters for the group are shown with the number of the lowest IUPAC co-eluter
E	The reported concentration exceeds the calibration range (upper point of the calibration curve)
EMPC	Represents an Estimated Maximum Possible Concentration. EMPC's arise in cases where the signal/noise ratio is not sufficient for peak identification (the determined ion-abundance ratio is outside the allowed theoretical range), where there is co-eluting interference, or where a single ion is utilised for quantification due to PFK interference)
J	Indicates that an analyte has a concentration below the reporting limit (lowest point of the calibration curve)
ND	Indicates a non-detect

Table 3 represents an example of a laboratory report showing the difference in concentration levels adopting the aforementioned criteria.

Table 3: *Example of laboratory data*

Compound/Analyte	**Method Blank (picogram)**	**Sample 1 (picogram)**	**Sample 2 (picogram)**
2,3,7,8-TCDD	(1.37)	22.1	(2.19)
1,2,3,7,8-PeCDD	(1.36)	62.1	(2.36)
1,2,3,4,7,8-HxCDD	(1.27)	55.6	(2.19)
1,2,3,6,7,8-HxCDD	(1.26)	93.7	(2.17)
1,2,3,7,8,9-HxCDD	(1.37)	84.8	(2.44)
1,2,3,4,6,7,8-HpCDD	(1.54)	755	[2.6]
OCDD	6.04	1650	[8.15]
2,3,7,8-TCDF	(0.868)	167	(1.89)
1,2,3,7,8-PeCDF	(0.996)	234	(1.87)
2,3,4,7,8-PeCDF	(0.969)	311	(1.7)
1,2,3,4,7,8-HxCDF	(0.758)	347	2.26
1,2,3,6,7,8-HxCDF	(0.725)	366	1.86
2,3,4,6,7,8-HxCDF	(0.739)	428	[1.77]
1,2,3,7,8,9-HxCDF	(0.961)	56.2	(1.6)
1,2,3,4,6,7,8-HpCDF	(0.931)	1480	[3.24]
1,2,3,4,7,8,9-HpCDF	(1.51)	243	(2.29)
OCDF	(2.92)	1340	(5.24)
ITEF TEQ (ND=0; EMPC=0)	0.00604	408	0.412
ITEF TEQ (ND=0; EMPC=EMPC)	0.00604	408	0.656
ITEF TEQ (ND=DL/2; EMPC=0)	1.72	408	3.18
ITEF TEQ (ND=DL/2; EMPC=EMPC)	1.72	408	3.34
ITEF TEQ (ND=DL; EMPC=EMPC)	3.43	408	6.02

Current legislation does not specify the criteria for reporting PCDD/F results other than that I-TEQ should be utilised. In the end, the licensing authority must decide on the most suitable way to consider results reported as ND and detail the requirement in the respective air emissions licence.

In the United Kingdom the worst case scenario is applied to their results and their sampling time stipulation for PCDD/F is six (6) hours per test. Each country will establish its own criteria for sampling and reporting.

Not all laboratories use the same criteria as detailed in Table 2 and Table 3. Certain laboratories will only report ND=0 and ND=DL.

Actual emissions data

Table 4 details actual PCDD/F emission concentrations measured by Levego at various South African processes; Concentration @10% oxygen.

Table 4: *PCDD/F emission concentrations at various South African processes*

Different Industry Types	Concentration; ng/Nm³ (dry) #
Type A - Medical waste without cleaning	4533.70
Type A - Medical waste with poor pollution abatement	3.19
Type A - Medical waste with good pollution abatement	0.04
Type B - Cement	0.0012 or 1.2E-03
Type C - Drum reconditioning	101.67
Type D - Metal industry	1.57

ITEF TEQ (ND=DL;EMPC=EMPC)

The industry types are made up of various processes within each industry. The industry types are limited to the listed activities requiring PCDD/F emission measurements.

From the above it is evident that most emitters are well above the allowable limits. The average concentrations reported above were based on the worst case scenario. Referring to Table 3, sample 2, it becomes clear how many different concentration levels could have been reported.

Conclusion

Considering the toxicity of PCDD/F's, emission concentration levels in South Africa and the various possibilities of reporting PCDD/F concentration it becomes imperative to establish a national format for reporting.

In South Africa, we should as a minimum report both the worst case scenario (ND=DL) as well as the lower bound (ND=0) for reporting PCDD/F emissions. Testing laboratories in South Africa cannot decide on their own reporting criteria. The regulator need to adopt specific criteria to report to and all the testing laboratories need to apply the same criteria when reporting.

Failure to establish common reporting criteria will create significant inconsistences in terms of legal compliance demonstration, environmental impact assessment studies, and toxicology studies to name a few.

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