



national research centre for  
environmental toxicology

**Gladstone Air Study 2009 to 2010:  
Monitoring for Polycyclic Aromatic  
Hydrocarbons (PAHs) and  
Polychlorinated Dibenzo-*p*-Dioxins  
(PCDDs) & -Furans (PCDFs), and  
Polychlorinated Biphenyls (PCBs).**

Karen Kennedy, Christie Bentley, Amy Heffernan, Chris  
Paxman, Gavin Stevenson, Jochen Mueller

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Report compiled by:

Dr. Karen Kennedy

Christie Bentley

Amy Heffernan

Chris Paxman

Gavin Stevenson

Prof. Jochen Mueller

---

Project Team

Dr Karen Kennedy - Entox

Gavin Stevenson – National Measurement Institute – Dioxin Section Manager

Jack Thompson – Entox

Laurence Hearn – Entox

Chris Paxman - Entox

Prof. Jochen Mueller - Entox

---

Report compiled for:

The Department of Environment & Resource Management, Queensland.

Dr. David Wainwright – Director Air Quality Sciences

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Direct enquiries to:

Karen Kennedy

National Research Centre for Environmental Toxicology (Entox)

39 Kessels Rd

Brisbane, Qld 4108

Phone: +61 7 32749113

Fax: +61 7 3274 9003

Email: [k.kennedy@uq.edu.au](mailto:k.kennedy@uq.edu.au)

Web: [www.entox.uq.edu.au](http://www.entox.uq.edu.au)

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### Staff from the Department of Environment & Resource Management, Gladstone, Queensland:

Dr. David Love - Principal Scientist, Central Coast Region, Environmental Services

Teegan Duckworth and the "CHAG" (Clean & Healthy Air for Gladstone) team

### Staff from the National Measurement Institute:

Dr Alan Yates - Quality Officer

Nino Piro - Senior Analyst

Robert Crough - Analyst

Cassandra Rauert - Analyst

Jesuina de Araujo - Technical Officer

Gerard Mamahit - Technical Officer

Luke Baker - Senior Chemist

Danny Slee - Organics Section Manager

Claire Edey - Technical Officer

Sowmya Ramakrishnan - Technical Officer

Gabriela Saveluc – Technical Officer

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## Abbreviations or symbols

<i>Abbreviation</i>	<i>Meaning</i>
B[a]P	Benzo[a]pyrene
B[a]P TEQ <sub>PAH</sub>	Benzo[a]pyrene toxic equivalent air concentration (ng.m <sup>-3</sup> )
CARB	California Air Resources Board
CHAG	Clean and Healthy Air for Gladstone (project)
DERM	Department of Environment & Resource Management
Flu	Fluoranthene
HAPs	Hazardous air pollutants (also referred to as “Air Toxics”)
HpCDD/F	Heptachlorodibenzo- <i>p</i> -dioxin/furan
HRGC	High Resolution Gas Chromatography
HxCDD/F	Hexachlorodibenzo- <i>p</i> -dioxin/furan
JECFA	Joint FAO/WHO expert committee on food additives
LOD	Limit of Detection
MS	Mass Spectrometry
NATA	National Association of Testing Authorities
NEPM	National Environmental Protection Measure (air toxics)
NHMRC	National Health and Medical Research Council
OCDD/F	Octachlorodibenzo- <i>p</i> -dioxin/furan
OEHHA	Office of Environmental Health Hazard Assessment
PAHs	Polycyclic aromatic hydrocarbons
PeCDD/F	Pentachlorodibenzo- <i>p</i> -dioxin/furan
PCBs	Polychlorinated biphenyls
PCDD/Fs	Polychlorinated dibenzo- <i>p</i> - dioxins/furans
∑PCDD/Fs	The sum of PCDD/Fs – excluding LODs



PCDFs	Polychlorinated dibenzo <i>-p-</i> furans
PEF	Potency equivalency factor for individual PAHs with respect to benzo[a]pyrene
PM <sub>10</sub>	Particulate matter with aerodynamic diameter < 10 µm
PUF	Polyurethane foam
QLD	Queensland
TEQ	Toxic equivalent air concentration with respect to the potency of a reference chemical
TEF	Toxic equivalency factor used to express the relative potency of a chemical with respect to a reference chemical (2,3,7,8-tetrachlorodibenzo- <i>p</i> -dioxin)
TCDD/F	Tetrachlorodibenzo- <i>p</i> -dioxin/furan
V <sub>A</sub>	The volume of air sampled (m <sup>3</sup> )
WHO <sub>05</sub> TEQ <sub>DF</sub>	2,3,7,8-tetrachlorodibenzo- <i>p</i> -dioxin equivalent air concentration derived using World Health Organization TEF values (2005) for individual PCDD/F congeners –middle bound (including half LODs)
WHO <sub>05</sub> TEQ <sub>P</sub>	2,3,7,8-tetrachlorodibenzo- <i>p</i> -dioxin equivalent air concentration derived using World Health Organization TEF values (2005) for individual “dioxin-like” PCB values- middle bound (including half LODs)
WHO <sub>98</sub> TEQ <sub>DF</sub>	2,3,7,8-tetrachlorodibenzo- <i>p</i> -dioxin equivalent air concentration derived using World Health Organization TEF values (1998) for individual PCDD/F congeners –middle bound (including half LODs)
WHO <sub>98</sub> TEQ <sub>P</sub>	2,3,7,8-tetrachlorodibenzo- <i>p</i> -dioxin equivalent air concentration derived using World Health Organization TEF values (1998) for individual “dioxin-like” PCB values- middle bound (including half LODs)

## EXECUTIVE SUMMARY

The Gladstone Air Study was initiated as part of the Clean & Healthy Air for Gladstone (CHAG) project established by Queensland Health and the Department of Environment and Resource Management. This project arose in response to community concern regarding the perceived cumulative impact of industrial growth in the Gladstone region on air quality and the consequences for human health. The Gladstone Air Study, as a component of CHAG, aimed to provide data which will profile the levels and types of specific hazardous air pollutants (HAPs) and allow for an assessment of the subsequent health risks they pose to humans living and working in the Gladstone region.

The specific HAPs, which were targeted in the Gladstone Air Study, included polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs). These HAPs were monitored over a twelve month period between February 2009 and January 2010. Monitoring was conducted on a monthly basis at two sites (South Gladstone and Targinie) and in winter (June/July 2009) and summer (December 2009) at an additional four sites (Boyne Island, Clinton, Auckland Point, and Boat Creek) within the Gladstone Air Monitoring Network. Some additional monthly monitoring occurred at Boyne Island in October and November.

Overall this monitoring for HAPs in the Gladstone region has found that the concentrations of PAHs, PCBs and PCDD/Fs in air:

- are within available health based guidelines (National Environmental Protection Measure (Air Toxics) monitoring investigation levels) established for benzo[a]pyrene as a marker for PAH exposure;
- do not contribute significantly to nor exceed available international exposure standards for intake of “dioxin-like” PCBs and PCDD/Fs recommended by the National Health and Medical Research Council within Australia; and
- are consistent with, or lower than the concentrations measured in other parts of Australia.

There was however considerable variation in the concentrations and profiles of specific HAPs within the Gladstone region. Overall the maximum concentrations of all PAH markers of exposure for the region occurred at the South Gladstone site and in summer. The maximum monthly and annual average concentrations of benzo[a]pyrene at this location were  $0.14 \text{ ng.m}^{-3}$  and  $0.046 \pm 0.045 \text{ ng.m}^{-3}$  respectively, while the regional average concentration (all data) was  $0.032 \pm 0.034 \text{ ng.m}^{-3}$ . These average concentrations are approximately an order of magnitude lower than the annual average monitoring investigation level of  $0.3 \text{ ng.m}^{-3}$  established under the National Environmental Protection Measure (Air Toxics). The concentrations of benzo[a]pyrene in the Gladstone region are similarly lower than the concentrations measured previously in ambient air in major cities in Australia.

The maximum monthly concentrations of PCDD/Fs and “dioxin-like” PCBs expressed as World Health Organization toxic equivalent air concentrations ( $\text{WHO}_{05} \text{ TEQ}_{\text{DF}}$  and  $\text{WHO}_{05} \text{ TEQ}_{\text{P}}$  respectively) occurred at South Gladstone in summer ( $12 \text{ fg.m}^{-3}$ ) and Boyne Island in winter ( $0.40 \text{ fg.m}^{-3}$ ). South Gladstone also had the highest annual average  $\text{WHO}_{05} \text{ TEQ}_{\text{DF}}$  ( $4.5 \text{ fg.m}^{-3}$ ) in the region while Auckland Point had the highest average  $\text{WHO}_{05} \text{ TEQ}_{\text{P}}$  ( $0.34 \text{ fg.m}^{-3}$ ). The regional average  $\text{WHO}_{05} \text{ TEQ}_{\text{DF}}$  and  $\text{WHO}_{05} \text{ TEQ}_{\text{P}}$  were  $2.3 \text{ fg.m}^{-3}$  and  $0.14 \text{ fg.m}^{-3}$  respectively. The regional average and range of  $2.3 \pm 2.4$  ( $0.24 - 12$ )  $\text{fg.m}^{-3}$  for  $\text{WHO}_{05} \text{ TEQ}_{\text{DF}}$  measured in the Gladstone region are very consistent with the finding of the *National Dioxin Program*

conducted in 2003 which indicated that the concentrations in ambient air in Australia are very low by world standards. For example WHO<sub>98</sub> TEQ<sub>DF</sub> average (and range) concentrations of 8.9 (0.73 – 41), 1.5 (0.27 – 4.04), 1.1 (0.11 – 121), 2.8 (0.29 – 13) fg.m<sup>-3</sup> were reported for Eagle Farm in Brisbane, Mutdapilly south west of Brisbane, Cape Grim in Tasmania and Berrimah in Darwin, respectively.

The dominant PCDD congener across the Gladstone region was octachlorodibenzo-p-dioxin (OCDD) which is approximately 10 000 times less potent than the reference dioxin congener 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD). Average OCDD concentrations ranged from 30 ± 24 fg.m<sup>-3</sup> at Boyne Island to 78 ± 57 fg.m<sup>-3</sup> at South Gladstone. 2,3,7,8-TCDD was only detected at the South Gladstone site in concentrations ranging from 0.50 fg.m<sup>-3</sup> to 2.9 fg.m<sup>-3</sup>. The highest concentrations of PCDF congeners occurred at Targinie and Boat Creek in the north of the region. These elevated PCDF profiles, where maximum concentrations were observed in winter, may reflect some preservation of wood smoke source profiles within the ambient profiles at these locations.

The dominant non-ortho PCB congener in the Gladstone region was PCB 77. The average concentrations for this congener ranged from 10 fg.m<sup>-3</sup> at Boat Creek and Targinie in the north of the region to 55 fg.m<sup>-3</sup> at Auckland Point. The most potent “dioxin-like” PCB monitored was the non-ortho congener PCB 126 which has an WHO<sub>05</sub> TEF of 0.1 (10 times less potent than 2,3,7,8-TCDD). This congener was present at relatively low concentrations across the region with average concentrations ranging from 0.75 – 2.8 fg.m<sup>-3</sup> at Clinton and Auckland Point respectively. The most dominant mono-ortho “dioxin-like” PCB was PCB 118 which was present at maximum values ranging from 517 fg.m<sup>-3</sup> at South Gladstone to 1321 fg.m<sup>-3</sup> at Auckland Point. It should be noted that this congener was not detected in any of the monitoring periods at sites to the north of Gladstone (Targinie and Boat Creek). While PCB 118 was detected at relatively high concentrations compared to many of the other “dioxin-like” PCBs, all of the mono-ortho PCBs exhibit a relatively low potency with respect to 2,3,7,8-TCDD.

## 1. INTRODUCTION

### 1.1 BACKGROUND

The Clean and Healthy Air for Gladstone (CHAG) project has been established by the Department of Environment and Resource Management (DERM) in collaboration with Queensland Health (QH) and local industry partners and community to better understand the current air quality in the Gladstone region. Gladstone is a major industrial hub in central Queensland with alumina refineries and smelters, a coal fired power station and Queensland's largest multi-commodity port (Gladstone Area Promotion & Development Ltd 2005). This project comes in response to community concern regarding the perceived cumulative impact that recent industrial growth has had on the air quality in the Gladstone region. These concerns initially related primarily to coal dust from coal loading facilities. In 2007 the Queensland (QLD) Parliament Member for Gladstone requested from the Minister for Health incidence data on asthma respiratory disease, miscarriages (stillbirths), cancer (all types) and leukaemia in the region. An apparent statistically significant excess of Chronic Lymphoid Leukaemia (CLL) notifications was found. A subsequent investigation by QLD Health found no evidence in the scientific literature for an environmental cause of elevated CLL rather that genetic factors (susceptibility) were more likely to partly explain this statistic (QH 2007). A "possible" causal link between exposure to the defoliant herbicides 2,4,5-T (2,4,5-trichlorophenoxyacetic acid) & 2,4-D (2,4-dichlorophenoxyacetic acid) and the polychlorinated dibenzo-*p*-dioxin (PCDD) congener 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) and CLL identified through literature review (Gaus et al. 2003) was noted but the evidence for a relationship was found to be inconsistent (QH 2007).

While monitoring of ambient air quality has been undertaken in the Gladstone region by the Queensland government since the 1980s, development in the area has lead to the need to review the locations of these monitoring stations and the range of chemicals and particulates that the samplers can monitor, in order to give the most representative data. The Gladstone Air Monitoring Network established as part of the CHAG project monitored a broad range of both criteria pollutants and hazardous air pollutants (HAPs) including:

- Nitrogen dioxide, sulphur dioxide, carbon monoxide, ozone
- Particulates
- Metals
- Volatile Organic Compounds (VOCs)
- Carbonyl compounds
- Polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzo-*p*-furans (PCDFs)

This was currently the largest scale air monitoring program to be implemented in Australia. The air monitoring data collected, in combination with public health data, will help to better understand the current air quality in the area and will assist local authorities to implement strategies aimed to reduce or eliminate key air pollutants that have been identified with the potential to cause adverse human health effects.

Overall, the Gladstone Air Study undertaken by Entox as part of the CHAG project aimed to provide data which will profile the levels and types of specific hazardous air pollutants (HAPs) and allow for an assessment of the subsequent health risks they pose to humans living and working in the Gladstone region. The specific HAPs which were targeted in the Gladstone Air Study as a component of the CHAG

project included PAHs, PCBs and PCDD/Fs over a twelve month period. The National Pollutant Inventory indicates that the dominant industrial sources for PCDD/Fs in the Gladstone region are electricity generation and basic non-ferrous metal manufacturing while for PAHs it is basic non-ferrous metal manufacturing industries. The Gladstone Air Study undertook air monitoring at six sites within the Gladstone Air Monitoring Network.

## 1.2 GLADSTONE AIR STUDY AIMS

The aim of this study was to measure and report ambient air concentrations of PAHs, PCBs and PCDD/Fs at between two to six sites in the Gladstone region. The air concentrations are reported as vapour plus particulate phase concentrations combined. All ambient concentration estimates were based on monthly sampling events within this twelve month period. In addition to reporting monthly ambient concentrations of these HAPs for specific locations in the Gladstone region within a twelve month period this study has several sub-aims. These sub-aims include conducting:

- A comparison of the levels of these compounds with other available data from Australia.
- A comparison of these levels with available health guidelines.
- An assessment of intake of PCDD/Fs and “dioxin-like” PCBs.

## 2. METHODS

### 2.1 SAMPLING SITES

Air monitoring for HAPs was conducted at South Gladstone, Targinie, Boat Creek, Clinton, Boyne Island and Auckland Point within the twelve month period from February 2009 to January 2010. The locations of these sampling sites within the Gladstone Region with respect to existing and proposed industry and residential areas are illustrated in Figure 1.

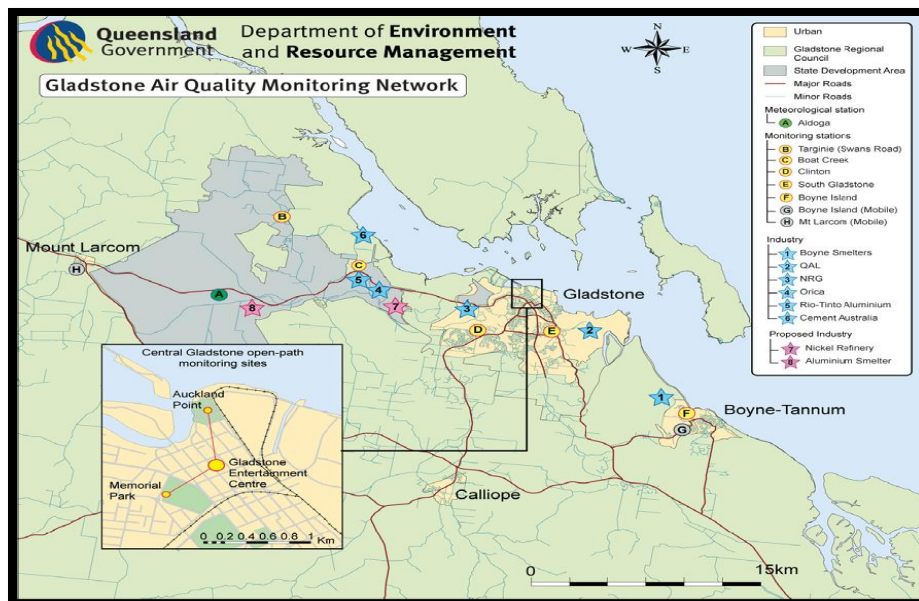








FIGURE 1 THE GLADSTONE AIR QUALITY MONITORING NETWORK SHOWING THE LOCATION OF SAMPLING SITES WITH RESPECT TO INDUSTRY AND RESIDENTIAL AREAS

**TABLE 1 A SUMMARY OF SAMPLING SITE INFORMATION FOR EACH MONITORING STATION INCLUDED IN THE GLADSTONE AIR QUALITY MONITORING NETWORK**

South Gladstone –“E”	Targinie – “B”	Boat Creek – “C”	Boyne Island – “F”	Clinton – “D”	Auckland Point – “inset on map”
					
<ul style="list-style-type: none"> <li>• South Gladstone State Primary School, Toolooa St.</li> <li>• Residential.</li> <li>• Proximity to alumina refinery</li> <li>• Queensland Alumina Limited (QAL) supplied monitoring equipment and contributes to running costs.</li> </ul>	<ul style="list-style-type: none"> <li>• Swans Rd</li> <li>• Established to monitor emissions from developing industrial area north of Gladstone</li> </ul>	<ul style="list-style-type: none"> <li>• Mt. Larcom-Gladstone Rd</li> <li>• Gladstone Area Water Board’s Boat Creek Pumping Station</li> <li>• Established to monitor emissions from industrial area north of Gladstone</li> </ul>	<ul style="list-style-type: none"> <li>• Beacon Ave.</li> <li>• Residential</li> <li>• South of Gladstone</li> <li>• Modelling indicates Boyne Island/Tannum Sands likely to be impacted by industrial air emissions</li> </ul>	<ul style="list-style-type: none"> <li>• Gladstone airport</li> <li>• Surrounded by residential areas. Proximity to the NRG Gladstone Power Station</li> <li>• NRG contributed to the establishment of the site and to on-going running costs.</li> </ul>	<ul style="list-style-type: none"> <li>• Central Gladstone</li> <li>• Port area with wharves handling a variety of cargoes</li> </ul>

Site photos obtained from DERM staff at Gladstone or site information and photos sourced from the DERM website on 12 May 2010:  
[http://www.derm.qld.gov.au/environmental\\_management/air/air\\_quality\\_monitoring/central\\_queensland\\_monitoring\\_stations.html](http://www.derm.qld.gov.au/environmental_management/air/air_quality_monitoring/central_queensland_monitoring_stations.html)

Auckland Point photo:  
<http://www.rgsq.org.au/24-151c.htm>



## 2.2 SAMPLING FREQUENCY & DURATION

TABLE 2 THE FREQUENCY & DURATION OF SAMPLING EVENTS FOR ALL SITES WITHIN THE GLADSTONE AIR QUALITY MONITORING NETWORK WHERE PAHS, DIOXINS, FURANS & PCBS WERE MONITORED. THE VOLUME OF AIR SAMPLED ( $V_A$  M<sup>3</sup>) AND THE NUMBER OF FILTER PAPER (FP) CHANGES WITHIN EACH PERIOD ARE ALSO INDICATED FOR EACH MONITORING EVENT.

SAMPLING MONTH-YEAR	South Gladstone	Targinie	Boyne Island	Clinton	Auckland Point	Boat Creek
FEB-09	3 <sup>rd</sup> Feb – 3 <sup>rd</sup> Mar ( $V_A = 3266$ m <sup>3</sup> ; FP = 4)	3 <sup>rd</sup> Feb – 3 <sup>rd</sup> Mar ( $V_A = 2409$ m <sup>3</sup> ; FP = 4)				
MAR-09	3 <sup>rd</sup> Mar – 3 <sup>rd</sup> Apr ( $V_A = 3329$ m <sup>3</sup> ; FP = 4)	3 <sup>rd</sup> Mar – 2 <sup>nd</sup> April ( $V_A = 2840$ m <sup>3</sup> ; FP = 4)				
APR-09	3 <sup>rd</sup> Apr – 2 <sup>nd</sup> May ( $V_A = 3582$ m <sup>3</sup> ; FP = 4)	2 <sup>nd</sup> Apr – 2 <sup>nd</sup> May ( $V_A = 2734$ m <sup>3</sup> ; FP = 4)				
MAY -09	2 <sup>nd</sup> May – 4 <sup>th</sup> Jun ( $V_A = 3874$ m <sup>3</sup> ; FP = 4)	2 <sup>nd</sup> May – 3 <sup>rd</sup> Jun ( $V_A = 2808$ m <sup>3</sup> ; FP = 4)				
JUN/JUL-09	4 <sup>th</sup> Jun – 28 <sup>th</sup> Jul ( $V_A = 5361$ m <sup>3</sup> ; FP = 3)	3 <sup>rd</sup> Jun – 28 <sup>th</sup> Jul ( $V_A = 4967$ m <sup>3</sup> ; FP = 3)	18 <sup>th</sup> Jun – 28 <sup>th</sup> Jul ( $V_A = 2454$ m <sup>3</sup> ; FP = 4)	17 <sup>th</sup> Jun – 28 <sup>th</sup> Jul ( $V_A = 3194$ m <sup>3</sup> ; FP = 4)	18 <sup>th</sup> Jun – 28 <sup>th</sup> Jul ( $V_A = 4467$ m <sup>3</sup> ; FP = 4)	17 <sup>th</sup> Jun – 28 <sup>th</sup> Jul ( $V_A = 3468$ m <sup>3</sup> ; FP = 4)
AUG-09	1 <sup>st</sup> Aug – 31 <sup>st</sup> Aug ( $V_A = 3066$ m <sup>3</sup> ; FP = 4)	1 <sup>st</sup> Aug – 31 <sup>st</sup> Aug ( $V_A = 2984$ m <sup>3</sup> ; FP = 4)				
SEP-09	31 <sup>st</sup> Aug – 28 <sup>th</sup> Sep ( $V_A = 3412$ m <sup>3</sup> ; FP = 4)	31 <sup>st</sup> Aug – 28 <sup>th</sup> Sep ( $V_A = 2486$ m <sup>3</sup> ; FP = 4)				
OCT-09	28 <sup>th</sup> Sep – 1 <sup>st</sup> Nov ( $V_A = 3891$ m <sup>3</sup> ; FP = 4)	28 <sup>th</sup> Sep – 1 <sup>st</sup> Nov ( $V_A = 2295$ m <sup>3</sup> ; FP = 4)	28 <sup>th</sup> Sep – 1 <sup>st</sup> Nov ( $V_A = 3818$ m <sup>3</sup> ; FP = 4)			
NOV-09	1 <sup>st</sup> Nov – 1 Dec ( $V_A = 3264$ m <sup>3</sup> ; FP = 4)	1 <sup>st</sup> Nov – 1 <sup>st</sup> Dec ( $V_A = 2795$ m <sup>3</sup> ; FP = 4)	1 <sup>st</sup> Nov – 1 <sup>st</sup> Dec ( $V_A = 3337$ m <sup>3</sup> ; FP = 4)			
DEC-09	1 <sup>st</sup> Dec – 31 <sup>st</sup> Dec ( $V_A = 2964$ m <sup>3</sup> ; FP = 4)	1 <sup>st</sup> Dec – 31 <sup>st</sup> Dec ( $V_A = 2600$ m <sup>3</sup> ; FP = 4)	1 <sup>st</sup> Dec – 31 <sup>st</sup> Dec ( $V_A = 3477$ m <sup>3</sup> ; FP = 4)	1 <sup>st</sup> Dec – 31 <sup>st</sup> Dec ( $V_A = 1733$ m <sup>3</sup> ; FP = 4)	1 <sup>st</sup> Dec – 31 <sup>st</sup> Dec ( $V_A = 3140$ m <sup>3</sup> ; FP = 4)	1 <sup>st</sup> Dec – 31 <sup>st</sup> Dec ( $V_A = 3526$ m <sup>3</sup> ; FP = 4)
JAN-10	31 <sup>st</sup> Dec – 5 Feb ( $V_A = 3781$ m <sup>3</sup> ; FP = 3)	31 <sup>st</sup> Dec – 5 <sup>th</sup> Feb ( $V_A = 3243$ m <sup>3</sup> ; FP = 2)				

Sampling duration and frequency for all sites in the Gladstone Region are indicated in Table 2. In summary sampling was conducted at the following sites as indicated:

- South Gladstone and Targinie: continuously for 12 months (February 2009 – January 2010).
- Boat Creek, Clinton, Boyne Island & Auckland Point: during winter (June-July 2009) and summer (December 2009).
- Boyne Island: also monitored during October and November 2009.

### 2.3 VAPOUR AND PARTICULATE PHASE AMBIENT AIR SAMPLING TECHNIQUES

Several thousand cubic metres of air (Table 2) was sampled monthly using low to medium volume pumps at each sampling site. Each pump was connected in series to a gas meter measuring the volume of air sampled  $V_A$  ( $m^3$ ). The air sampled by the pump was drawn through both a glass fibre filter paper (Whatman, GFA 90 mm) to trap particulate phase compounds and a glass cartridge containing 40 g Amberlite XAD-2 resin and a polyurethane foam (PUF) plug to trap vapour phase compounds. Exposed filter papers were exchanged for pre-cleaned filter papers (typically) on a weekly basis. The pump, gas meter and sampling train were housed in stainless steel deployment chambers protected from direct sunlight and rainfall. Each chamber was sited on the roof of an ambient air monitoring station by DERM staff at each location as illustrated in Figure 2.



FIGURE 2 A LOW VOLUME AIR SAMPLING CHAMBER SITED ON THE ROOF OF THE SOUTH GLADSTONE AIR MONITORING STATION



## 2.4 PREPARATION OF SAMPLERS

### 2.4.1 **Particulate Phase Samplers - Filter Papers**

Each filter paper was rinsed with acetone and toluene (Merck Suprasolv) and then furnaceed at 450 °C for 24 hours. Each filter paper was then stored in individual aluminium foil packets which were pre-folded and similarly solvent rinsed and furnaceed. Filter papers for each month were prepared, stored in labeled zip-lock bags and forwarded to Gladstone on a monthly basis. Individual clean foil packets were dispatched simultaneously for the retrieval and collection of exposed filter papers

### 2.4.2 **Vapour Phase Samplers – Amberlite XAD-2 resin and PUF plugs in glass cartridges.**

Glass cartridges were rinsed with acetone and toluene (Merck Suprasolv) and then furnaceed at 500 °C for 24 hours. Ground glass stoppers were treated similarly and used to seal each cartridge top and bottom. Both the XAD-2 resin and the PUF plugs were pre-extracted sequentially with acetone and then toluene (Merck Suprasolv) using an accelerated solvent extractor (ASE) in separate cells. The operating conditions used for the ASE were: 100 °C, 2 static cycles.solvent<sup>-1</sup>, 7 minute static, 60 % flush, 250 s purge. Once pre-extracted each glass cartridge was loaded with the pre-weighed (40 g) and pre-extracted XAD-2 using a pre-cleaned powder funnel. A pre-cleaned PUF plug was inserted on top of the XAD-2 resin and the cartridge was subsequently eluted with dichloromethane and dried under purified nitrogen to remove any residual toluene. Each cartridge was then sealed top and bottom with the glass stoppers and wrapped in pre-cleaned aluminium foil and stored in zip-lock bags for transport to Gladstone.

Two field blank samples were included over the course of the entire twelve month monitoring period. These samplers were prepared and dispatched to Gladstone, were transported to the field sites for the deployment but were not exposed to ambient air. These field blank samples were subsequently dispatched along with field exposed samples for that month to the National Measurement Institute (NMI) for chemical analysis. The total number of samples analysed from the monitoring period including blanks was thirty-four.

## 2.5 SAMPLER PROCESSING AT NMI

DERM staff dispatched (on ice packs) all monthly samples using chain of custody procedures to NMI for chemical analysis. The NMI is a NATA accredited laboratory (Laboratory # 198) compliant with ISO/IEC 17025:2005 (ISO 2005).

### 2.5.1 **Sample Extraction**

Each monthly sample was spiked with nine <sup>13</sup>C<sub>12</sub> isotopically labeled dioxin/furans, twelve <sup>13</sup>C<sub>12</sub> isotopically labeled PCBs, and fourteen deuterated PAHs as surrogate standards. Ambient air samples consisting of GFA filters, XAD-2 resin and PUF plugs were exhaustively solvent extracted using toluene. The extract was concentrated and split with 25 % each for PAH and Aroclor PCB analyses and 50 % for tetra- through to octa- PCDD/Fs and “dioxin-like” PCB analyses.

### 2.5.2 **PAH analysis**

This proportion of extract was treated in accordance with NMI method NGCM 11.27. Each extract was purified by column chromatography. Analysis was performed using high resolution gas chromatography (HRGC) with low resolution mass spectrometry (MS). The instrument was an Agilent 5975 GCMS run in single ion monitoring (SIM) mode. The column used was a DB5-ms (30 m x 0.25 mm x 0.25 µm). Results were corrected for the recovery of the labeled standards. The labeled standards (and target native

compounds) included: D<sub>8</sub>-naphthalene (naphthalene, 2-methylnaphthalene), D<sub>8</sub>-acenaphthylene (acenaphthylene), D<sub>10</sub>-acenaphthene (acenaphthene), D<sub>10</sub>-fluorene (fluorene), D<sub>10</sub>-phenanthrene (phenanthrene, anthracene), D<sub>10</sub>-fluoranthene (fluoranthene, pyrene), D<sub>12</sub>-benz[a]anthracene (benz[a]anthracene), D<sub>12</sub>-chrysene (chrysene), D<sub>12</sub>-benz[b]fluoranthene (benzo[b]fluoranthene), D<sub>12</sub>-benzo[k]fluoranthene (benzo[k]fluoranthene, benzo[e]pyrene), D<sub>12</sub>-benzo[a]pyrene (benzo[a]pyrene, perylene) , D<sub>12</sub>-indeno[1,2,3-c,d]pyrene (indeno[1,2,3-c,d]pyrene), D<sub>14</sub>-dibenz[a,h]anthracene (dibenz[a,h]anthracene, D<sub>12</sub>-benzo[g,h,i]perylene (benzo[g,h,i]perylene). The acceptable recovery range was set at 50 – 150 % but low recoveries were accepted as long as the signal/noise ratio of the standard was > 10.

### 2.5.3 Aroclor PCB analysis

This proportion of extract was treated in accordance with NMI method NR\_19. Clean up required partitioning with sulphuric acid, followed by alumina chromatography. Analysis was performed using dual column HRGC with electron capture detection (ECD). The instrument was an Agilent 6890 GC-ECD, and the columns used were a DB608 (15 m x 0.32 mm x 0.50 µm) and a DB1701 (15 m x 0.32 mm x 0.25 µm). The target analytes were Aroclor PCBs : 1016, 1221, 1232, 1242, 1248, 1254, 1260.

### 2.5.4 PCDD/Fs and “dioxin-like” PCBs analysis

This proportion of the extract was treated in accordance with NMI method AUTL\_01. Clean up was effected by partitioning with sulphuric acid then distilled water. Further purification was performed using FMS Power-Prep Automated column chromatography on acid and base modified silica gels, basic alumina and carbon dispersed on celite. Analysis was performed using HRGC (Agilent 6890) with HR (> 10,000) MS (Finnigan MAT 95XL) with isotopically labelled recovery standards added to each extract immediately prior to injection. Results were corrected for recovery of the <sup>13</sup>C<sub>12</sub> labelled surrogate standards. The target PCDD/F included tetra- (TCDD/F), penta- (PeCDD/Fs), hexa- (HxCDD/Fs), hepta- (HpCDD/Fs) and octa- (OCDD/F) congeners. The target “dioxin-like” PCBs included non-ortho (77, 81, 126, 169) and mono-ortho (105, 114, 118, 123, 156, 167, 189) substituted congeners. Two characteristic ions were selectively monitored for each congener group. Analyte identification was confirmed when target ions were detected in the correct abundance ratio within established retention time windows. The normal acceptance criteria for labelled standard recovery were 50 – 120 % for TCDD/Fs, PeCDD/Fs and HxCDD/Fs, 40 – 120 % for HpCDD/Fs and OCDD/Fs and 40 – 120 % for PCB congeners.

## 2.6 EXPRESSION OF RESULTS

NMI reported the levels of target analytes in each sample to Entox in certificates of analysis. In addition to the levels of target analytes in each sample results were also expressed in terms of toxic equivalencies (TEQ). TEQ are used to express the additive toxicity of a mixture of chemicals with the same mode of action with respect to an equivalent concentration of a reference chemical. The reference chemical is typically a well studied and potent chemical and it is assigned a potency of 1 and the relative potency of all other chemicals within the mixture are determined with respect to this reference chemical. The concentration of individual components of the mixture, are then weighted, using these relative potencies to derive the TEQ. Relative potencies for individual chemicals are referred to as either toxic equivalency factors (TEF) or as potency equivalency factors (PEF).

TEQ were reported as benzo[a]pyrene TEQ (B[a]P-TEQ<sub>PAH</sub> – Equation 1) for PAHs and as 2,3,7,8-TCDD TEQs according to the World Health Organization (WHO) for PCDD/Fs (WHO<sub>05</sub>-TEQ<sub>DF</sub> – Equation 2) and for “dioxin-like” PCBs (WHO<sub>05</sub>-TEQ<sub>P</sub> – Equation 3). PEF for individual PAHs with respect to benzo[a]pyrene were as defined by the California Air Resources Board and the United States Office of Environmental

Health Hazard Assessment (CARB & OEHHA 1994). TEF for individual PCDD/Fs and “dioxin-like” PCBs with respect to the most potent dioxin (2,3,7,8-TCDD) were as defined by Van den Berg et al. (2006). All TEQ were reported as lower bound (excluding limit of detection (LOD) values), middle bound (including half LOD values) and upper bound (including LOD values).

$$B[a]P \text{ TEQ}_{PAH} = \sum_{i=1}^7 [PAH_i \times B[a]P\text{-PEF}_i] \quad \text{Equation 1}$$

i = toxic PAH analyte index (1 – 7)

$$WHO_{05} \text{ TEQ}_{DF} = \sum_{i=1}^7 [PCDD_i \times \text{TEF}_i] + \sum_{j=1}^{10} [PCDF_j \times \text{TEF}_j] \quad \text{Equation 2}$$

i = PCDD congener index (1 – 7)

j = PCDF congener index (1 – 10)

$$WHO_{05} \text{ TEQ}_P = \sum_{k=1}^{12} [PCB_k \times \text{TEF}_k] \quad \text{Equation 3}$$

k = PCB congener index (1 – 12)

All results provided to Entox by NMI were subsequently converted to air concentrations for each location, using the total volume of air sampled within each monitoring period (Table 2). Complete data reports expressing all results for each monthly sampling period as air concentrations were then provided to DERM. In order to provide a regional assessment of the ambient concentrations of PAHs, PCDD/Fs and “dioxin like” PCBs a range of parameters have been selected for reporting purposes. In all cases both individual parameters for each sampling period, average values for each location, and overall regional and seasonal averages are provided for each parameter. The average values presented for the South Gladstone and

### 2.6.1 PAH parameters

Three parameters were selected to summarise the regional profile for PAH exposures in Gladstone. These included the ambient concentrations of benzo[a]pyrene (B[a]P), fluoranthene (Flu) and the B[a]P  $\text{TEQ}_{PAH}$  ( $\text{ng}\cdot\text{m}^{-3}$ ). Benzo[a]pyrene (B[a]P) is used as a marker for exposure to PAHs in the National Environmental Protection Measure (Air Toxics) with an annual average monitoring investigation level of  $0.3 \text{ ng}\cdot\text{m}^{-3}$  (NEPC 2004). In addition to B[a]P, an additional individual marker of PAH exposure has been used, which is the ambient concentration of fluoranthene (Flu). Fluoranthene, unlike benzo[a]pyrene, is a relatively abundant and hence consistently detected predominantly vapour phase PAH. Fluoranthene has been proposed as a complementary indicator to B[a]P previously (Bostrom et al. 2002). The middle bound B[a]P  $\text{TEQ}_{PAH}$  ( $\text{ng}\cdot\text{m}^{-3}$ ) has also been provided, since it is a parameter which quantifies the potency and presence of other PAHs (benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-c,d]pyrene, dibenz[a,h]anthracene) as components of a mixture to which exposure occurs (additivity assumed). “Middle Bound” B[a]P  $\text{TEQ}_{PAH}$  are reported for all locations.

### 2.6.2 PCDD/Fs and “dioxin-like” PCB parameters

WHO<sub>05</sub>-TEQ<sub>DF</sub> and WHO<sub>05</sub>-TEQ<sub>P</sub> (middle bound) air concentrations are used to compare all sampling events and the summer and winter sampling periods. In addition the sum of PCDD/F congeners (excluding LOD values) and the dominant congener OCDD are compared on a regional basis. Full congener profiles for the PCDD/Fs are illustrated and summary statistics provided for each congener at each location.

### 2.7 ESTIMATING INTAKE FOR PCDD/Fs & “DIOXIN-LIKE” PCBs

Average daily intake estimates within this report are derived for an average adult with a daily inhalation volume of 22 m<sup>3</sup>. This inhalation volume was based on 8-hour resting and 16-hours of light/non-occupational activity and is the default values for exposure assessment in the *Guidelines for assessing human health risks from environmental hazards* (Australian Government 2004). Similarly since exposure standards for human intake are typically based on a body weight basis an adult body weight of 64 kg has been assumed, which is the average of the adult male and adult female default values in these guidelines. It has furthermore been assumed that 100 % of the combined vapour plus particulate phase ambient exposure is available for intake and that the indoor and outdoor ambient concentrations of these contaminants are the same. The average daily intakes derived for the sum of PCDD/Fs and “dioxin-like” PCBs as TEQ are then expressed on a monthly basis (30 days) and compared with the JECFA exposure standard (2001) of 70 pg.kg<sup>-1</sup> body weight.month<sup>-1</sup> recommended by the NHMRC (NHMRC & TGA 2002). JECFA is the Joint FAO/WHO Expert Committee on Food Additives which evaluated dioxins at their 57<sup>th</sup> meeting at Rome, in 2001.

### 3. RESULTS

#### 3.1 EXPOSURE TO POLYCYCLIC AROMATIC HYDROCARBONS IN THE GLADSTONE REGION

##### 3.1.1 Regional summary of PAH exposure markers

A regional summary of the markers for PAH exposure (fluoranthene (Flu), benzo[a]pyrene (B[a]P) and B[a]P TEQ<sub>PAH</sub>) are provided in Table 3. All regional summary statistics were derived from the concentration in air (ng.m<sup>-3</sup>) determined for all locations across the region in all monthly sampling periods.

**TABLE 3 SUMMARY STATISTICS FOR MARKERS OF EXPOSURE TO POLYCYCLIC AROMATIC HYDROCARBONS BASED ON MONTHLY ASSESSMENTS OF CONCENTRATION IN AIR AT SIX LOCATIONS WITHIN THE GLADSTONE REGION.**

Marker	Summary Statistics of Monthly Concentration in Air (ng.m <sup>-3</sup> ) across the Gladstone Region				
	Minimum	Maximum	Average	Summer Average <sup>a</sup>	Winter Average <sup>b</sup>
Fluoranthene	0.069	1.5	0.52 ± 0.37	0.42 ± 0.39	0.46 ± 0.16
	DEC-09 Boyne Island	FEB-09 South Gladstone			
Benzo[a]pyrene	0.0068	0.14	0.032 ± 0.034	0.034 ± 0.047	0.0021
	<LOD at all sites or JAN-10 Targinie	JAN-10 South Gladstone			
B[a]P TEQ <sub>PAH</sub> <sup>c</sup>	0.012	0.26	0.045 ± 0.051	0.051 ± 0.071	0.027 ± 0.013
	JUN/JUL-09 Targinie	JAN-10 South Gladstone			

<sup>a</sup> The summer average was derived from all concentration in air estimates within FEB-09, DEC-09 and JAN-10 monitoring periods;

<sup>b</sup> The winter average was derived from all concentration in air estimates within JUN/JUL-09 and AUG-09;

<sup>c</sup> This is the middle bound TEQ

The ranges for the vapour phase PAH marker Flu are approximately an order of magnitude higher than for the predominantly particulate phase PAH marker B[a]P. This result is typical for PAH exposures with the PAH profiles for all sites in the Gladstone region being dominated by the two-ring vapour phase PAHs naphthalene and 2-methylnaphthalene. For example, the levels of 2-methylnaphthalene ranged from 1.0 ng.m<sup>-3</sup> (DEC-09 Boat Creek) to 15 ng.m<sup>-3</sup> (SEP-09 South Gladstone). The other vapour phase PAHs which dominated these profiles were fluorene, phenanthrene, Flu and pyrene. Of these PAHs phenanthrene was the most dominant with concentrations in air ranging from 0.32 ng.m<sup>-3</sup> (DEC-09 Boyne Island) to 5 ng.m<sup>-3</sup> (SEP-09 South Gladstone). For all markers of PAH exposure (Table 3) the maximum regional exposure occurred at the South Gladstone site. All of these maximum concentrations occurred in summer sampling periods. There were however limited detections of the particulate bound PAH marker B[a]P in winter, with detectable levels only being determined for the South Gladstone site (0.021 ng.m<sup>-3</sup>) in the AUG-09 monitoring period. Given the variation in these markers within the region it is not surprising that no distinct seasonal pattern is evident in the exposure to these PAH markers on a regional basis. However the summer averages are higher by a factor of 16 for B[a]P (limited data in winter), while the B[a]P TEQ<sub>PAH</sub> are higher by a factor of 2. The concentration of the vapour phase PAH marker Flu is relatively consistent between seasons and similarly unlikely to be significantly different given the regional variation.

The regional summary statistics for the PAH markers Flu, B[a]P and B[a]P TEQ<sub>PAH</sub> are illustrated in comparison with the averages for each of these PAH markers for all locations in Figure 3. Ambient concentrations in all sampling periods and averages for each sampling site for all marker PAHs (and 2-methylnaphthalene and phenanthrene) are summarised in Tables in Appendix 1. It should be noted that averages for each sampling site are based on more monitoring periods for South Gladstone and Targinie (annual averages) which were continuously monitored on a monthly basis within the 12 month period and also Boyne Island which was monitored along with all other locations in both winter (JUN/JUL-09) and summer (DEC-09) but also in OCT-09 and NOV-09 (together with South Gladstone and Targinie). The sites,

which were only monitored in winter (JUN/JUL-09) and summer (DEC-09), included Clinton, Auckland Point and Boat Creek. The average concentration from these sites, are therefore based on a maximum of two concentration estimates when detected.

The lowest and highest average concentrations for Flu were determined at Boyne Island ( $0.26 \pm 0.17 \text{ ng.m}^{-3}$ ) and South Gladstone ( $0.83 \pm 0.43 \text{ ng.m}^{-3}$ ) respectively. No average B[a]P concentrations could be determined for Boyne Island and Auckland Point since B[a]P was not detected at these sites. South Gladstone was however the location with the highest annual averages for both B[a]P ( $0.046 \pm 0.045 \text{ ng.m}^{-3}$ ) and B[a]P TEQ<sub>PAH</sub> ( $0.078 \pm 0.077 \text{ ng.m}^{-3}$ ). Boyne Island had the lowest average B[a]P TEQ<sub>PAH</sub> with  $0.017 \pm 0.0034 \text{ ng.m}^{-3}$ .

### **3.1.2 Comparison of average concentrations of benzo[a]pyrene in air with NEPM monitoring investigation level**

The average ambient air concentrations determined indicate that the NEPM monitoring investigation level of  $0.3 \text{ ng.m}^{-3}$  for benzo[a]pyrene as a marker for PAH exposures (NEPC 2004) is unlikely to be exceeded on an annual basis for the sites at which consistent data has been obtained across a twelve month period (South Gladstone and Targinie) as illustrated in Figure 3 B. The MIL in Australia is equivalent to an annual average criterion of  $0.30 \text{ ng.m}^{-3}$  adopted under the New Zealand Ambient Air Quality Guidelines (2002) and is similar to the exposure standard for B[a]P of  $0.25 \text{ ng.m}^{-3}$  (averaging time one year) recommended by the United Kingdom Expert Panel on Air Quality Standards (1999). These criteria were reviewed by the Environment Protection and Heritage Council which incorporates the NEPC prior to the establishment of the NEPM MIL for B[a]P (EPHC 2003).

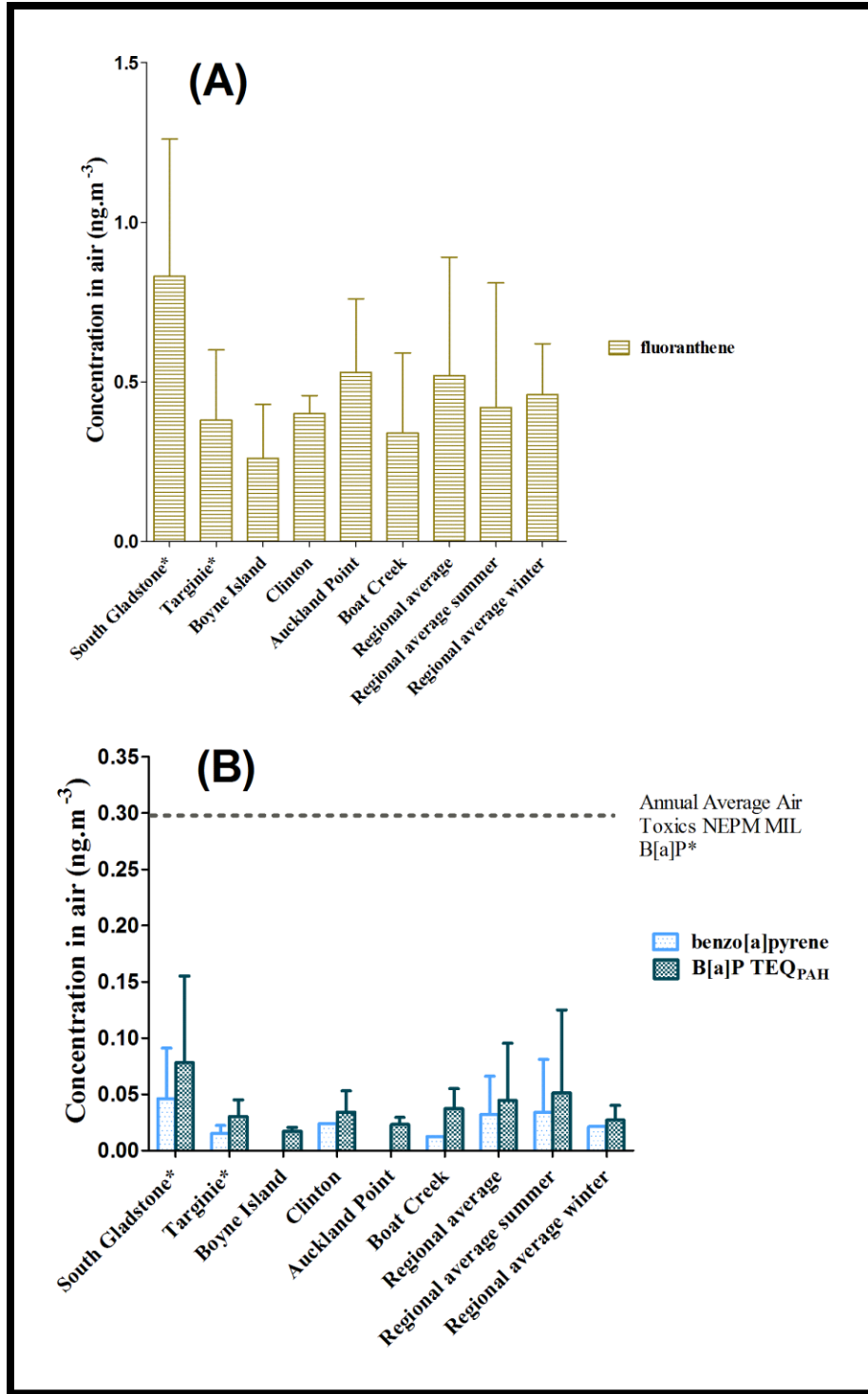


FIGURE 3 AVERAGE CONCENTRATIONS FOR EACH SAMPLING LOCATION AND GLADSTONE REGIONAL SUMMARY CONCENTRATIONS FOR (A) FLUORANTHENE AND (B) BENZO(A)PYRENE AND B[A]P TEQ<sub>PAH</sub>

\*Average concentrations at South Gladstone and Targinie represent annual averages and are comparable to annual average NEPM MIL for B[a]P. Note: the NEPM MIL refers to B[a]P concentrations only, not B[a]P TEQ<sub>PAH</sub>.

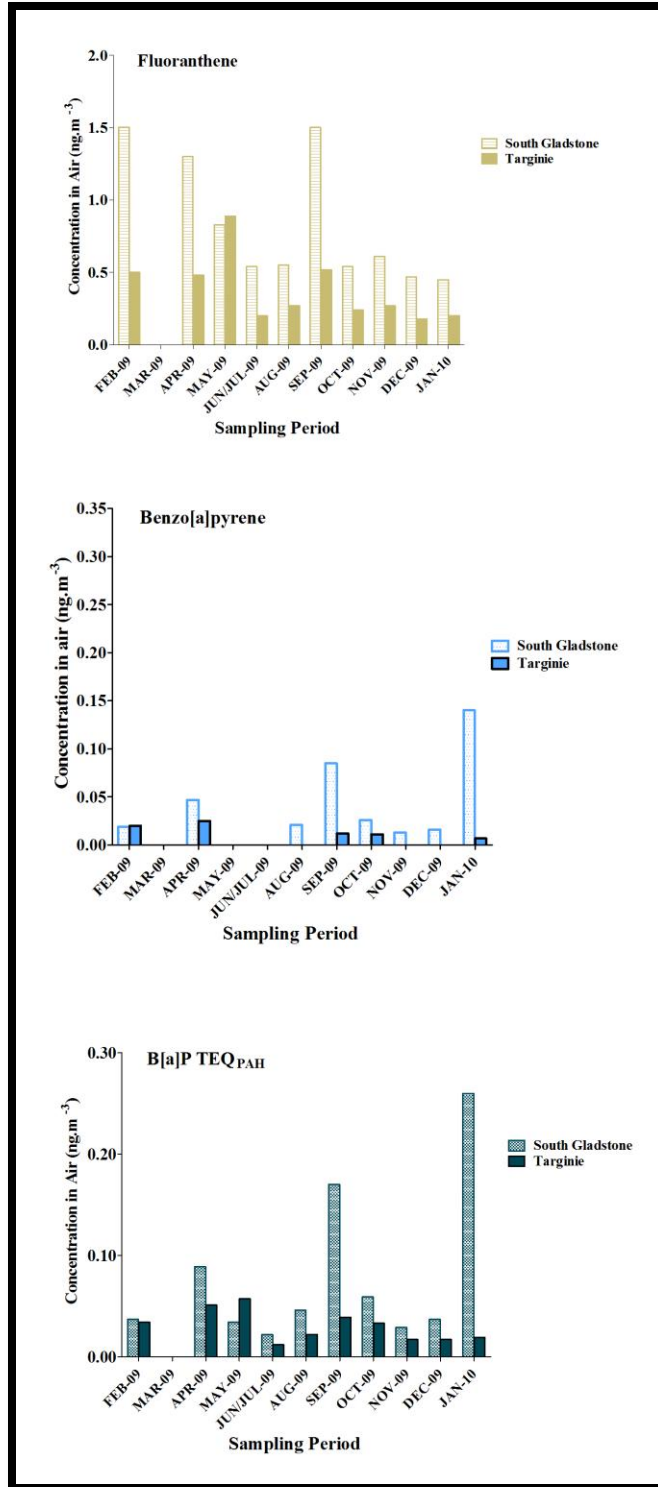


FIGURE 4 MONTHLY PAH EXPOSURE MARKER CONCENTRATIONS BETWEEN FEB-09 AND JAN-10 AT SOUTH GLADSTONE AND TARGINIE.



### 3.1.3 Comparison of the average concentrations of PAHs in the Gladstone region with other recent Australian data

Polycyclic aromatic hydrocarbons as a class of compounds are not routinely monitored as air toxics in Australia. Since the introduction of the NEPM (Air Toxics) and the establishment of a monitoring investigation level for B[a]P each State has focused more efforts on monitoring these by-products of incomplete combustion processes. Apart from the current study, the most recent (reported) monitoring of PAH levels in Queensland was that undertaken between 2003-2004 during sampling of PM<sub>10</sub> in Brisbane (Rocklea and Springwood) as part of the Fine Particle Composition in Four Major Australian Cities project. The cities included Melbourne, Sydney, Brisbane and Adelaide. Five PAHs were consistently detected (> 30 % of samples) in this study and these were all predominantly particulate phase compounds including benzo[b+k]fluoranthene (“b” & “k” quantified together), benzo[e]pyrene, benzo[a]pyrene, indeno[1,2,3-c,d]pyrene and benzo[g,h,i]perylene. The average “urban” and “suburban” site averages for benzo[a]pyrene were  $0.18 \pm 0.37 \text{ ng.m}^{-3}$  and  $0.11 \pm 0.18 \text{ ng.m}^{-3}$  respectively (Chan et al. 2008).

The average concentration of B[a]P reported in this study for the Gladstone region arranged in descending order were:  $0.046 \pm 0.045 \text{ ng.m}^{-3}$  (South Gladstone),  $0.024 \text{ ng.m}^{-3}$  (Clinton),  $0.015 \pm 0.007 \text{ ng.m}^{-3}$  (Targinie),  $0.012 \text{ ng.m}^{-3}$  (Boat Creek). It is notable that benzo[a]pyrene was less than the LOD in both winter (JUN/JUL-09) and summer (DEC-09) sampling periods at both Boyne Island and Auckland Point. No average concentrations are therefore available for these sites. The average concentrations in the Gladstone region were lower by an order of magnitude than the average levels for major Australian cities in the previous study. The concentrations of B[a]P in the Gladstone region are similarly lower than annual average data compiled recently for the *Air Toxics NEPM Mid-Term Review* from 2004-2009 for roadside, CBD, industrial and residential areas, which range from  $0.11 - 0.15 \text{ ng.m}^{-3}$  (NEPC 2010).

More recent monitoring conducted using polyurethane foam (PUF) passive air samplers in 2007 at the South Gladstone site reported summer and winter levels of B[a]P of  $0.025 \pm 0.0096 \text{ ng.m}^{-3}$  and  $0.060 \pm 0.023 \text{ ng.m}^{-3}$  (Kennedy et al. 2010) respectively which is consistent with the data for South Gladstone in this current study except that a summer maximum was not observed for the 2007 data. This work also found that the concentrations of PAH exposure markers B[a]P and B[a]P TEQ were lower in regional areas such as Gladstone compared with capital cities such as Perth, Brisbane and Adelaide which is to be expected when the dominant sources for these combustion byproducts can be vehicular emissions and wood smoke. In spite of other sources for PAHs which exist in the Gladstone region due to the presence of industries such as alumina refineries and fossil fuel power plants, the region remains within current health based guideline values.

### 3.1.4 Continuous monthly monitoring for PAHs at South Gladstone and Targinie over twelve months (FEB-09 to JAN-10)

The monthly concentration estimates for PAH exposure markers (Flu, B[a]P and B[a]P TEQ<sub>PAH</sub>) at these two continuously monitored sites are illustrated in Figure 4. The average factor between monthly concentration ratios for South Gladstone and Targinie were 2 (Flu), 7 (B[a]P) and 3 (B[a]P TEQ<sub>PAH</sub>) which is indicative of higher monthly concentrations at South Gladstone. The monthly profiles across a twelve month period illustrate the potential for elevated levels in both summer and spring (SEP-09). It also illustrates that the peak monthly concentrations for predominantly vapour phase compounds like Flu do not necessarily coincide with the peak monthly concentrations for predominantly particulate phase PAHs like benzo[a]pyrene (i.e. JAN-10). It should be noted that MAR-09 concentration estimates have been excluded from these plots but are reported in Tables in Appendix 1. This was due to particularly high

baseline levels in this month in samples from both sites. Since there was no field blank prepared in this period it is not possible to exclude contamination issues in the preparation of samplers for this month.

### 3.1.5 A comparison of seasonal monitoring results at all six location for all PAH markers

All six sites were monitored simultaneously in both winter (JUN/JUL-09) and summer (DEC-09). A comparative assessment of these seasonal deployments is illustrated in Figure 5. No distinct seasonal pattern was evident on a regional basis as discussed previously. However monitoring at individual sites within the region does reveal some differences between summer and winter concentrations of PAH markers. Boyne Island, Auckland Point and Boat Creek were similarly higher in winter for both Flu and B[a]P TEQ<sub>PAH</sub>. South Gladstone, Targinie and Clinton are higher in summer for B[a]P TEQ<sub>PAH</sub> but the levels of Flu are either relatively equivalent or slightly higher in winter.

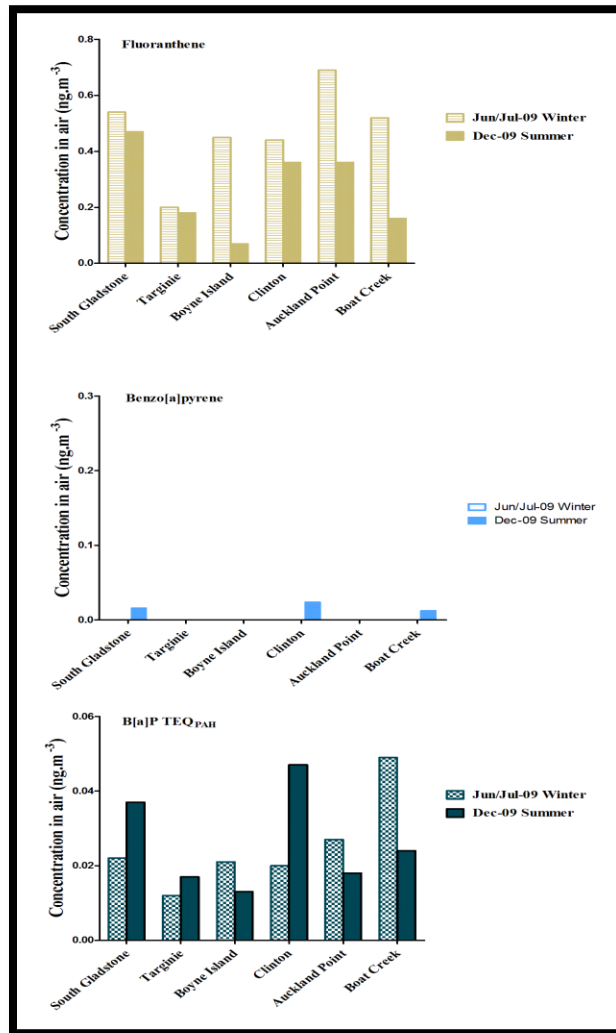


FIGURE 5 SEASONAL MONITORING AT SIX SITES IN THE GLADSTONE REGION

### 3.2 EXPOSURE TO AROCLOR PCBs IN THE GLADSTONE REGION

Aroclor PCBs were only detected in two monthly sampling periods in November (South Gladstone) and December (Boyne Island). The PCB detected in both cases was Aroclor 1254 with concentration in air estimates of 0.31 ng.m<sup>-3</sup> and 0.11 ng.m<sup>-3</sup> respectively. It is likely that larger air volumes are required to quantitatively estimate the regional profiles of Aroclor PCBs in the Gladstone region and that the 25 % of extract retained for these purposes was insufficient.

### 3.3 EXPOSURE TO POLYCHLORINATED -DIOXINS (PCDDs), -FURANS (PCDFs) AND -BIPHENYLS (“DIOXIN-LIKE” PCBs)

#### 3.3.1 A regional summary of markers of PCDD/F and “dioxin-like” PCB exposure

A regional summary of the markers for PCDD/F and dioxin-like PCB exposure (WHO<sub>05</sub> TEQ<sub>DF</sub> – middle bound, WHO<sub>05</sub> TEQ<sub>p</sub> – middle bound, ΣPCDD/Fs - excluding LODs, OCDD) are provided in Table 4. All regional summary statistics were derived from the concentration in air (fg.m<sup>-3</sup>) determined for all locations across the Gladstone region in all monthly sampling periods.

**TABLE 4 SUMMARY STATISTICS FOR MARKERS OF EXPOSURE TO PCDD/FS AND “DIOXIN-LIKE” PCBs BASED ON MONTHLY ASSESSMENTS OF CONCENTRATION IN AIR AT SIX LOCATIONS WITHIN THE GLADSTONE REGION.**

Marker	Summary Statistics of Monthly Concentration in Air (fg.m <sup>-3</sup> ) across the Gladstone Region				
	Minimum	Maximum	Average	Summer Average <sup>c</sup>	Winter Average <sup>d</sup>
WHO <sub>05</sub> TEQ <sub>DF</sub> <sup>a</sup>	0.24	12	2.3 ± 2.4	2.8 ± 3.7	2.3 ± 1.2
	OCT-09 Boyne Island	JAN-10 South Gladstone			
WHO <sub>05</sub> TEQ <sub>p</sub> <sup>a</sup>	0.011	0.40	0.14 ± 0.11	0.13 ± 0.11	0.22 ± 0.11
	DEC-09 Targinie	JUN/JUL-09 Boyne Island			
ΣPCDD/Fs <sup>b</sup>	18	439	152 ± 122	114 ± 133	214 ± 133
	DEC-09 Boyne Island	JUN/JUL-09 Targinie			
OCDD	9.5	243	62 ± 45	41 ± 26	78 ± 38
	DEC-09 Boyne Island	SEP-09 South Gladstone			

<sup>a</sup>middle bound TEQ (half LOD)

<sup>b</sup>excluding LODs

<sup>c</sup>The summer average was derived from all concentration in air estimates within FEB-09, DEC-09 and JAN-10 monitoring periods;

<sup>d</sup>The winter average was derived from all concentration in air estimates within JUN/JUL-09 and AUG-09;

These regional profiles again reveal relatively high variation in the levels of these exposure markers across the Gladstone region. This is evident in the range for each marker covering over an order of magnitude within the region. Because of this variation it is difficult to infer seasonal patterns on a regional basis although winter WHO<sub>05</sub> TEQ<sub>p</sub>, ΣPCDD/Fs and OCDD concentrations are all higher than summer levels by an approximate factor of 2.

The regional summary statistics for these markers (Table 4) of exposure are illustrated in comparison to the averages for each location in Figure 6 A (WHO TEQ) and B (ΣPCDD/Fs and OCDD). Ambient concentrations for all sampling periods and average concentrations for each sampling site are provided in Tables in Appendix 2.

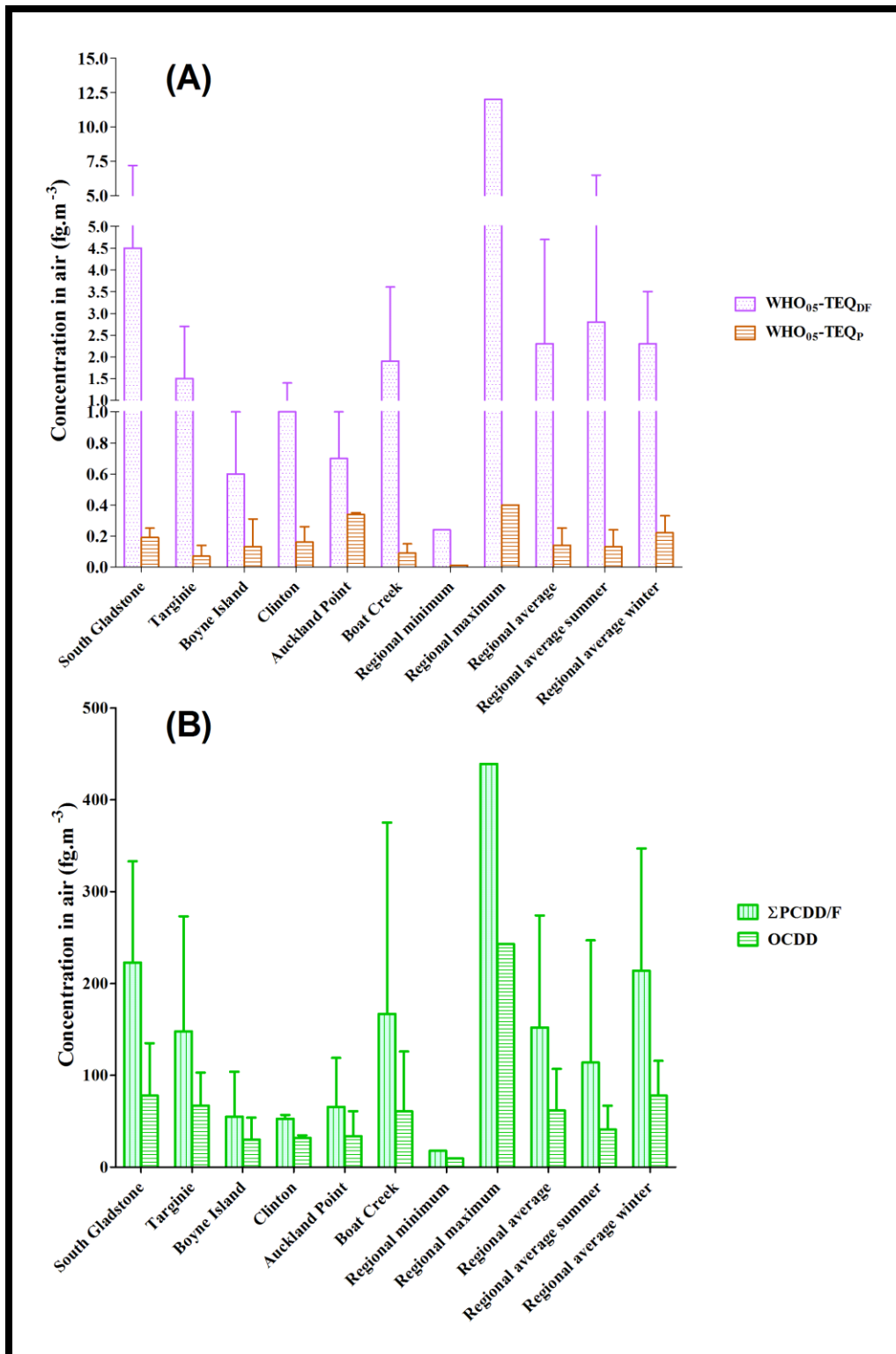


FIGURE 6 AVERAGE CONCENTRATIONS FOR EACH SITE AND REGIONAL SUMMARY STATISTICS FOR MARKERS OF EXPOSURE TO PCDD/Fs AND "DIOXIN-LIKE" PCBs

Average WHO<sub>05</sub> TEQ<sub>DF</sub> for individual sites ranged from 0.59 ± 0.39 fg.m<sup>-3</sup> at Boyne Island, 0.74 ± 0.28 fg.m<sup>-3</sup> at Auckland Point), and 1.0 ± 0.41 fg.m<sup>-3</sup> at Clinton to 1.5 ± 1.2 fg.m<sup>-3</sup> (Targinie) and 1.9 ± 1.7 fg.m<sup>-3</sup> (Boat Creek) in the north of the region and were highest (4.5 ± 2.7 fg.m<sup>-3</sup>) at the South Gladstone site. It should be noted that the potent reference dioxin congener 2,3,7,8-TCDD (TEF = 1) was only detected at the South Gladstone site at concentrations ranging from 0.50 fg.m<sup>-3</sup> (JUN/JUL-09) to 2.9 fg.m<sup>-3</sup> (JAN-10). The dominant PCDD/F congener detected across all sites was OCDD (Figure 6B) with average concentrations ranging from 30 ± 24 fg.m<sup>-3</sup> at Boyne Island, 32 ± 2.8 fg.m<sup>-3</sup> at Clinton and 34 ± 27 fg.m<sup>-3</sup> at Auckland Point to 61 ± 65 fg.m<sup>-3</sup> at Boat Creek and 67 ± 36 fg.m<sup>-3</sup> at Targinie in the north of the region to a maximum of 78 ± 57 fg.m<sup>-3</sup> at South Gladstone. The TEF for OCDD is 0.0003 which is approximately 1000 times less potent than 2,3,7,8-TCDD.

Given that the sources of PCDD/Fs and “dioxin-like” PCBs are quite unique it is not surprising that the regional profiles for these compound classes are different. The annual average WHO<sub>05</sub> TEQ<sub>P</sub> for individual sites ranged from 0.072 ± 0.066 fg.m<sup>-3</sup> and 0.095 ± 0.062 fg.m<sup>-3</sup> at Targinie and Boat Creek respectively in the north of the region to 0.13 ± 0.18 fg.m<sup>-3</sup> (Boyne Island), 0.16 ± 0.10 fg.m<sup>-3</sup> (Clinton) and 0.19 ± 0.060 fg.m<sup>-3</sup> at South Gladstone, with a maximum average concentration of 0.34 ± 0.010 for the port site at Auckland Point. The concentrations for Auckland Point were relatively consistent in the two periods monitored with 0.34 fg.m<sup>-3</sup> in winter (JUN/JUL-09) and 0.35 fg.m<sup>-3</sup> in summer (DEC-09).

### 3.3.2 A comparison of human intake from air of PCDD/Fs and “dioxin-like” PCBs at each site in the Gladstone region with the human intake standard proposed by JECFA and recommended by the NHMRC

The annual average WHO<sub>05</sub> TEQ<sub>DF</sub> and WHO<sub>05</sub> TEQ<sub>P</sub> were converted to monthly average adult intakes (pg.kg<sup>-1</sup> body weight.month<sup>-1</sup>) using the default values indicated in Section 3.7 (Estimating Intake of PCDD/Fs and “dioxin-like” PCBs). These intake estimates were then expressed as a proportion of the JECFA (2001) exposure standard (70 pg.kg<sup>-1</sup> body weight.month<sup>-1</sup>) recommended by the NHMRC (NHMRC & TGA 2002). All of these estimates are provided in Table 5.

**TABLE 5 MONTHLY AVERAGE INTAKE ESTIMATES FOR WHO<sub>05</sub> TEQ<sub>DF</sub> (PCDD/Fs) AND WHO<sub>05</sub> TEQ<sub>P</sub> (“DIOXIN-LIKE” PCBs) AND TOTAL INTAKE ESTIMATES FOR ALL SITES WITHIN THE GLADSTONE REGION. EACH INTAKE ESTIMATE IS ALSO EXPRESSED AS A PERCENTAGE OF THE JECFA (2001) EXPOSURE STANDARD.**

	South Gladstone	Targinie	Boyne Island	Clinton	Auckland Point	Boat Creek
<b>WHO<sub>05</sub> TEQ<sub>DF</sub> intake (pg.kg<sup>-1</sup> bw.month<sup>-1</sup>)</b>	<b>0.046</b>	<b>0.015</b>	<b>0.0061</b>	<b>0.010</b>	<b>0.0076</b>	<b>0.020</b>
% of exposure standard	0.07	0.02	0.01	0.01	0.01	0.03
<b>WHO<sub>05</sub> TEQ<sub>P</sub> intake (pg.kg<sup>-1</sup> bw.month<sup>-1</sup>)</b>	<b>0.0019</b>	<b>0.0007</b>	<b>0.0014</b>	<b>0.0016</b>	<b>0.0035</b>	<b>0.0010</b>
% of exposure standard	0.003	0.001	0.002	0.002	0.005	0.001
<b>Total intake (pg.kg<sup>-1</sup> bw.month<sup>-1</sup>)</b>	<b>0.048</b>	<b>0.016</b>	<b>0.0074</b>	<b>0.012</b>	<b>0.011</b>	<b>0.021</b>
% of exposure standard	0.07	0.02	0.01	0.02	0.02	0.03

In all cases the intake via air is less than 0.1 % of the JECFA exposure standard. The dominant contributors to intake at all locations on a TEQ basis are the PCDD/Fs and not the “dioxin-like” PCBs. This is to be expected given that the regional average WHO<sub>05</sub> TEQ<sub>DF</sub> and WHO<sub>05</sub> TEQ<sub>P</sub> were 2.3 ± 2.4 fg.m<sup>-3</sup> and 0.14 ± 0.11 fg.m<sup>-3</sup> respectively. On a regional basis the total intake via air using these average TEQ values is 0.026 pg.kg<sup>-1</sup> bw.month<sup>-1</sup> which is 0.04 % of the 70 pg.kg<sup>-1</sup> bw.month<sup>-1</sup> exposure standard.

### 3.3.3 Comparison of the average concentrations of PCDD/Fs and “dioxin-like” PCBs with other recently reported Australian levels

The Australian Government (Department of the Environment & Heritage) funded the *National Dioxins Program* in 2003. One component of the *National Dioxins Program* was the assessment of the concentration of PCDD/Fs and “dioxin-like” PCBs in air. The levels of these compounds were measured at 10 sites across Australia and the results reported in *Technical Report # 4 Dioxins in Ambient Air in Australia* (Gras et al. 2004). The concentrations in air determined for the Gladstone region are consistent with these previously reported Australian levels. For example Eagle Farm in Brisbane and Mutdapilly (South West of Brisbane) had WHO<sub>98</sub> TEQ<sub>DF</sub> (middle bound) averaging 8.9 (0.73 – 41) fg.m<sup>-3</sup> and 1.5 (0.27 – 4.04) fg.m<sup>-3</sup> respectively. The “pristine remote” site of Cape Grim in Tasmania meanwhile had an average WHO<sub>98</sub> TEQ<sub>DF</sub> of 1.1 (0.11 – 121) fg.m<sup>-3</sup>. The only site north of Brisbane in the *National Dioxin Program* (Air) was situated at Berrimah in Darwin (Northern Territory). This site had average WHO<sub>98</sub> TEQ<sub>DF</sub> of 2.8 (0.29 – 13) fg.m<sup>-3</sup> which is consistent with the average (and range) determined for the Gladstone region in this present study (2.3 (0.24 – 12) fg.m<sup>-3</sup>). The concentrations reported in Australia are considered very low by world standards (Gras et al. 2004). The concentrations of “dioxin-like” PCBs in the Gladstone region (WHO<sub>05</sub> TEQ<sub>p</sub>) are again consistent with Australian levels although somewhat lower than the WHO<sub>98</sub> TEQ<sub>p</sub> reported in the *National Dioxin Program*. For example, Berrimah in the Northern Territory averaged 0.53 (0.11 – 1.2) fg.m<sup>-3</sup> and Cape Grim averaged 0.11 (0.02 – 0.41) fg.m<sup>-3</sup> while Gladstone averaged 0.14 (0.011 – 0.40) fg.m<sup>-3</sup>. It should be noted that results reported in the Gladstone Air Study and the *National Dioxins Program* were derived using different WHO TEF schemes (WHO TEF revised in 2005 versus WHO TEF 1998 values respectively). A review of the effect of the change in TEF on the TEQ calculation in air samples collected during the NDP study resulted in a 17 % decrease of the TEQ using the WHO<sub>05</sub> TEFs (Mueller 2007).

### 3.3.4 “Dioxin-like” PCB and PCDD/F congener profiles throughout the monitoring periods

Complete congener profiles for “dioxin-like” PCBs and PCDD/Fs for all sites in the Gladstone region are provided in Figures 7 - 18 in Appendix 3.

#### “DIOXIN-LIKE” PCB CONGENERS

Summary statistics for each “dioxin-like” PCB congener (non-ortho and mono-ortho) for all sites in the Gladstone region are provided in Table 6. The dominant non-ortho PCB congener in the region was PCB 77. This congener was more frequently present at maximum concentrations in summer for most locations except for Boyne Island which had a winter maximum concentration of 106 fg.m<sup>-3</sup>. The average concentrations for this congener ranged from 10 fg.m<sup>-3</sup> at Boat Creek and Targinie in the north of the region to 37 fg.m<sup>-3</sup> (South Gladstone), 40 fg.m<sup>-3</sup> (Boyne Island), 46 fg.m<sup>-3</sup> (Clinton) and 55 fg.m<sup>-3</sup> at Auckland Point. The most potent “dioxin-like” PCB monitored was the non-ortho congener PCB 126 which has an WHO<sub>05</sub> TEF of 0.1 (10 times less potent than 2,3,7,8-TCDD). This congener was present at relatively low concentrations across the region with average concentrations ranging from 0.75 – 2.8 fg.m<sup>-3</sup> at Clinton and Auckland Point respectively. Maximum concentrations within the region of were 3.4 fg.m<sup>-3</sup> at Boyne Island and 2.9 fg.m<sup>-3</sup> at Auckland Point. The most dominant mono-ortho “dioxin-like” PCB was PCB 118 which was present at maximum values ranging from 517 fg.m<sup>-3</sup> at South Gladstone to 1321 fg.m<sup>-3</sup> at Auckland Point. It should be noted that this congener was not detected in any of the monitoring periods at sites to the north of Gladstone (Targinie and Boat Creek). While PCB 118 was detected at relatively high concentrations compared to many of the other “dioxin-like” PCBs, all of the mono-ortho PCBs exhibit a relatively low potency with respect to 2,3,7,8-TCDD with WHO<sub>05</sub> TEFs of 0.00003. WHO<sub>05</sub> TEFs for all of the “dioxin-like” PCBs and PCDD/F congeners are provided in Table 7.

TABLE 6 SUMMARY STATISTICS (FG.M<sup>3</sup>) FOR INDIVIDUAL NON-ORTHO AND MONO-ORTHO "DIOXIN-LIKE" PCB CONGENERS FOR EACH LOCATION

	South Gladstone				Targinie				Boat Creek			
	Average	Min	Max	Max Occurrence <sup>a</sup>	Average	Min	Max	Max Occurrence	Average	Min	Max	Max Occurrence
<b>Non-ortho</b>												
<b>PCB 77</b>	<b>37</b>	26	58	SUMMER	<b>10</b>	6.0	21	SUMMER	<b>10</b>	9	12	SUMMER
PCB 81	1.3	0.78	1.9	SUMMER	0.80	0.36	1.7	WINTER	0.72	0.72	0.72	WINTER
PCB 126	1.9	1.4	2.3	WINTER	1.2	0.35	2.2	WINTER	1.3	1.3	1.3	WINTER
PCB 169	-	-	-		0.48	0.23	0.72	WINTER	-	-	-	
<b>Mono-ortho</b>												
<b>PCB 105</b>	<b>128</b>	90	178	SUMMER	<b>29</b>	24	36	AUTUMN	<b>40</b>	40	40	WINTER
PCB 114	8.2	6.2	12	AUTUMN	2.5	2.5	2.5	AUTUMN	-	-	-	
<b>PCB 118</b>	<b>384</b>	270	517	SUMMER	-	-	-		-	-	-	
PCB 123	6.1	4.6	7.2	WINTER	1.5	1.5	1.5	WINTER	-	-	-	
<b>PCB 156</b>	<b>34</b>	27	40	SUMMER	-	-	-		-	-	-	
PCB 157	4.7	4.2	5.6	SUMMER	1.9	1.9	1.9	SUMMER	-	-	-	
PCB 167	10	7.1	13	AUTUMN	5.5	4.0	6.9	SUMMER	7.0	6.9	7.1	SUMMER
PCB 189	1.4	1.4	1.4	SPRING	1.5	0.81	2.3	SPRING	-	-	-	
<b>Non-ortho</b>	Boyne Island				Clinton				Auckland Point			
<b>PCB 77</b>	<b>40</b>	15	106	WINTER	<b>46</b>	17	75	SUMMER	<b>55</b>	40	70	SUMMER
PCB 81	2.5	0.55	4.5	WINTER	1.7	1	2.4	SUMMER	1.9	1.8	2.0	SUMMER
PCB 126	2.0	0.69	3.4	WINTER	0.75	0.75	0.75	WINTER	2.8	2.8	2.9	WINTER
PCB 169	-	-	-		-	-	-		-	-	-	
<b>Mono-ortho</b>												
<b>PCB 105</b>	<b>193</b>	45	342	WINTER	<b>218</b>	85	352	SUMMER	<b>372</b>	235	509	SUMMER
PCB 114	12	4.5	19	WINTER	18	18	18	SUMMER	26	16	35	SUMMER
<b>PCB 118</b>	<b>532</b>	196	868	WINTER	<b>524</b>	188	860	SUMMER	<b>1100</b>	878	1321	SUMMER
PCB 123	18	18	18	WINTER	-	-	-		15	12	18	SUMMER
<b>PCB 156</b>	<b>65</b>	65	65	WINTER	<b>75</b>	75	75	SUMMER	<b>69</b>	49	89	SUMMER
PCB 157	13	13	13	WINTER	-	-	-		14	9.4	19	SUMMER
PCB 167	13	8.1	23	WINTER	19	7	31	SUMMER	26	17	35	SUMMER
PCB 189	3.0	1.5	4.5	WINTER	-	-	-		2.9	2.9	2.9	WINTER

<sup>a</sup> indicates the season in which the maximum concentration was observed for this congener (for Boat Creek, Clinton and Auckland Point monitoring was only conducted in winter and summer; Boyne Island was monitored only during winter, spring and summer); All summary statistics do not include LOD values.

TABLE 7 TOXIC EQUIVALENCY FACTORS (WHO<sub>05</sub> TEF<sub>p</sub>) FOR INDIVIDUAL “DIOXIN-LIKE” PCB CONGENERS

<b>Non-ortho PCBs</b>	<b>WHO<sub>05</sub> TEF</b>
PCB 77	0.0001
PCB 81	0.0003
PCB 126	0.1
PCB 169	0.03
<b>Mono-ortho PCBs</b>	
PCB 105	0.00003
PCB 114	0.00003
PCB 118	0.00003
PCB 123	0.00003
PCB 156	0.00003
PCB 157	0.00003
PCB 167	0.00003
PCB 189	0.00003

The *National Dioxin Program* previously found that the “dioxin-like” PCBs were typically higher in warmer seasons unlike the PCDD/Fs (Gras et al 2003). In this study of sites in the Gladstone region this was the case only for Clinton and Auckland Point which typically recorded the maximum concentrations of individual congeners in summer, except for PCB 126 at both locations and PCB 189 which was only detected in winter at Auckland Point. In addition, Boyne Island consistently recorded maximum concentrations for all congeners during winter sampling. No clear seasonal profile was evident for “dioxin-like” PCB congeners at South Gladstone, Targinie or Boat Creek. The winter average of the WHO<sub>05</sub> TEQ<sub>p</sub> for the region was approximately a factor of 2 times higher in winter at  $0.22 \pm 0.11 \text{ fg.m}^{-3}$  compared with  $0.13 \pm 0.11 \text{ fg.m}^{-3}$  in summer (Table 4). This study illustrates the potential for variable seasonal congener profiles within sites in the same region and that higher concentrations in warmer periods may not be the norm for this location.

#### PCDD/F CONGENERS

Summary statistics for each PCDD/F congener for all sites in the Gladstone region are provided in Table 8. Individual PCDD/F congeners are identified by numbers which indicate the position where chlorines are substituted on the dibenzo rings and by the level of chlorine substitution (refer footnote Table 8). The maximum concentrations for the PCDD/Fs typically occur in winter as was found previously during monitoring for the *National Dioxin Program*. However it is very apparent that this trend of elevated winter concentrations is not the case for the PCDDs at the South Gladstone site. The maximum dioxin concentrations at this site either all occur in summer or, in the case of the dominant congener OCDD, in spring. The next most abundant congener across the Gladstone region is 1,2,3,4,6,7,8,-HpCDD which is 100 times less potent than 2,3,7,8-TCDD with a TEF of 0.01. The WHO<sub>05</sub> TEF for the individual PCDD/F congeners are provided in Table 9.

It is worth noting again that the potent dioxin congener 2,3,7,8-TCDD, which is the reference chemical for determining TEF, was only detected at the South Gladstone site. Furthermore this site has the highest concentration of each PCDD congener within the region, which would account for the maximum WHO<sub>05</sub> TEQ<sub>DF</sub> level of  $12 \text{ fg.m}^{-3}$  concentration occurring at South Gladstone in summer. There is however one other PCDD (1,2,3,7,8-PeCDD) which has a TEF of 1 (as potent as 2,3,7,8-TCDD) and this congener was detected at South Gladstone, Targinie, Boat Creek and Auckland Point at average concentrations of 2.5, 0.74, 0.75, and  $0.47 \text{ fg.m}^{-3}$  respectively.



TABLE 8 SUMMARY STATISTICS (FG.M<sup>-3</sup>) FOR INDIVIDUAL PCDD/F CONGENERS FOR EACH LOCATION

Furans (PCDFs)	South Gladstone				Targinie				Boat Creek			
	Average	Min	Max	Max Occurrence*	Average	Min	Max	Max Occurrence	Average	Min	Max	Max Occurrence
2,3,7,8-TCDF	0.56	0.17	0.88	WINTER	1.2	0.5	1.6	WINTER	1.4	1.4	1.4	WINTER
1,2,3,7,8-PeCDF	0.47	0.38	0.56	WINTER	1.2	0.8	1.7	WINTER	1.9	1.9	1.9	WINTER
2,3,4,7,8-PeCDF	0.63	0.56	0.71	WINTER	2.1	0.8	3.2	WINTER	2.6	2.6	2.6	WINTER
1,2,3,4,7,8-HxCDF	0.25	0.25	0.25	SPRING	1.7	1.1	2.4	WINTER	3.2	3.2	3.2	WINTER
1,2,3,6,7,8-HxCDF	0.31	0.26	0.35	WINTER	1.9	1.0	3.0	WINTER	2.4	2.4	2.4	WINTER
2,3,4,6,7,8-HxCDF	0.24	0.24	0.24	WINTER	2.5	0.9	5.4	WINTER	1.7	1.7	1.7	WINTER
1,2,3,7,8,9-HxCDF												
1,2,3,4,6,7,8-HpCDF	0.92	0.4	1.7	SPRING	3.5	0.8	13	WINTER	5.5	5.5	5.5	WINTER
1,2,3,4,7,8,9-HpCDF	0.40	0.2	0.57	SPRING	1.0	0.4	1.6	WINTER	1.1	1.1	1.1	WINTER
OCDF	0.66	0.3	0.91	WINTER	2.5	0.8	4.2	WINTER	1.9	1.9	1.9	WINTER
<b>Dioxins (PCDDs)</b>												
2,3,7,8-TCDD	1.2	0.5	2.9	SUMMER	-	-	-	-	-	-	-	-
1,2,3,7,8-PeCDD	2.5	0.9	6.1	SUMMER	0.74	0.43	0.93	WINTER	0.75	0.75	0.75	WINTER
1,2,3,4,7,8-HxCDD	1.6	0.8	3.7	SUMMER	0.81	0.67	0.95	WINTER	0.81	0.81	0.81	WINTER
1,2,3,6,7,8-HxCDD		1.0	7.4	SUMMER	1.2	0.43	2.0	WINTER	1.1	1.1	1.1	WINTER
1,2,3,7,8,9-HxCDD	4.1	1.7	10	SUMMER	1.7	1.7	1.7	WINTER	-	-	-	-
1,2,3,4,6,7,8-HpCDD	<b>19</b>	8.6	42	SUMMER	<b>5.1</b>	1.6	12	WINTER	<b>10</b>	10	10	WINTER
OCDD	<b>78</b>	39	243	SPRING	<b>67</b>	28	154	WINTER	<b>61</b>	15	107	WINTER
<b>Furans (PCDFs)</b>												
	Boyne Island				Clinton				Auckland Point			
2,3,7,8-TCDF	0.61	0.61	0.61	WINTER	0.47	0.47	0.47	WINTER	-	-	-	-
1,2,3,7,8-PeCDF	0.37	0.37	0.37	WINTER	-	-	-	-	-	-	-	-
2,3,4,7,8-PeCDF	-	-	-	-	0.59	0.59	0.59	WINTER	0.49	0.49	0.49	WINTER
1,2,3,4,7,8-HxCDF	-	-	-	-	-	-	-	-	-	-	-	-
1,2,3,6,7,8-HxCDF	-	-	-	-	-	-	-	-	0.31	0.31	0.31	-
2,3,4,6,7,8-HxCDF	-	-	-	-	-	-	-	-	-	-	-	-
1,2,3,7,8,9-HxCDF	-	-	-	-	-	-	-	-	-	-	-	-
1,2,3,4,6,7,8-HpCDF	0.73	0.52	0.94	WINTER	0.82	0.58	1.1	WINTER	1.0	1.0	1.0	WINTER
1,2,3,4,7,8,9-HpCDF	-	-	-	-	-	-	-	-	0.19	0.19	0.19	WINTER
OCDF	-	-	-	-	-	-	-	-	-	-	-	-
<b>Dioxins (PCDDs)</b>												
2,3,7,8-TCDD	-	-	-	-	-	-	-	-	-	-	-	-
1,2,3,7,8-PeCDD	-	-	-	-	-	-	-	-	0.47	0.47	0.47	WINTER
1,2,3,4,7,8-HxCDD	-	-	-	-	-	-	-	-	-	-	-	-
1,2,3,6,7,8-HxCDD	-	-	-	-	0.54	0.27	0.81	SUMMER	0.31	0.31	0.31	WINTER
1,2,3,7,8,9-HxCDD	-	-	-	-	-	-	-	-	-	-	-	-
1,2,3,4,6,7,8-HpCDD	<b>2.3</b>	1.2	4.9	WINTER	<b>1.9</b>	1.9	1.9	WINTER	<b>4.7</b>	4.7	4.7	WINTER
OCDD	<b>30</b>	9.5	65	WINTER	<b>32</b>	30	34	SUMMER	<b>34</b>	15	54	WINTER

<sup>a</sup> indicates the season in which the maximum concentration was observed for this congener (for Boat Creek, Clinton and Auckland Point monitoring was only conducted in winter and summer; Boyne Island was monitored only during winter, spring and summer); All summary statistics do not include LOD values; TCDD/F = tetrachlorodibenzo-*p*-dioxin/furan; PeCDD/F = pentachlorodibenzo-*p*-dioxin/furan; HxCDD/F = hexachlorodibenzo-*p*-dioxin/furan; HpCDD/F = heptachlorodibenzo-*p*-dioxin/furan; OCDD = octachlorodibenzo-*p*-dioxin/furan

TABLE 9 TOXIC EQUIVALENCY FACTORS (WHO<sub>05</sub> TEF<sub>Df</sub>) FOR INDIVIDUAL PCDD/F CONGENERS

<b>Furans (PCDFs)</b>	<b>WHO<sub>05</sub> TEF</b>
2,3,7,8-TCDF	0.1
1,2,3,7,8-PeCDF	0.03
2,3,4,7,8-PeCDF	0.3
1,2,3,4,7,8-HxCDF	0.1
1,2,3,6,7,8-HxCDF	0.1
2,3,4,6,7,8-HxCDF	0.1
1,2,3,7,8,9-HxCDF	0.1
1,2,3,4,6,7,8-HpCDF	0.01
1,2,3,4,7,8,9-HpCDF	0.01
OCDF	0.0003
<b>Dioxins (PCDDs)</b>	
2,3,7,8-TCDD	1
1,2,3,7,8-PeCDD	1
1,2,3,4,7,8-HxCDD	0.1
1,2,3,6,7,8-HxCDD	0.1
1,2,3,7,8,9-HxCDD	0.1
1,2,3,4,6,7,8-HpCDD	0.01
OCDD	0.0003

It is interesting to compare the relative concentrations of furans and dioxins at South Gladstone and the two sites in the north of the Gladstone region (Targinie and Boat Creek) which appear to have relatively similar profiles. PCDF congeners (furans) were higher at Targinie and Boat Creek by factors of 2 to 10 and 2 to 12 respectively. These factors were relatively consistent for individual congeners across these two locations. Conversely PCDD congeners (dioxins) were higher at South Gladstone compared to Targinie and Boat Creek by factors of between 2 to 4 and 2 to 3 respectively except for OCDD which was higher by a factor of 1.2 and 1.3 respectively. Toxic congener profiles determined for wood smoke (eucalypt) suggest that a pattern of elevated furans with a decrease with increasing chlorination and a slight peak at 1,2,3,4,6,7-HpCDF may be preserved to an extent in observed profiles (Gras et al. 2004 and Gras et al. 2002 in previous reference). Some elevation of PCDF concentrations are evident at these two locations, however a decrease in these levels with increasing chlorination is not apparent in these profiles. There is however a peak in the levels of 1,2,3,4,6,7-HpCDF which is typically the dominant PCDF congener at all locations.

#### 4. SUMMARY OF FINDINGS

This component of the CHAG project monitored and reported on the concentrations of PAHs, PCBs and PCDD/Fs at up to six sites over a twelve month period (February 2009 – January 2010). The regional averages for markers of exposure to PAHs and PCDD/Fs and “dioxin-like” PCBs were determined and these are summarised in Table 10.

TABLE 10 A SUMMARY OF REGIONAL AVERAGES OF MARKERS OF EXPOSURE TO PAHS, “DIOXIN-LIKE” PCBs AND PCDD/FS

Marker	Regional average
<b>PAHs</b>	(ng.m <sup>-3</sup> )
<i>Fluoranthene</i>	0.52 ± 0.37
<i>Benzo[a]pyrene</i>	0.032 ± 0.034
<i>B[a]P TEQ<sub>PAH</sub></i>	0.045 ± 0.051
<b>PCDD/Fs &amp; "dioxin-like" PCBs</b>	(fg.m <sup>-3</sup> )
<i>WHO<sub>05</sub> TEQ<sub>DF</sub></i>	2.3 ± 2.4
<i>WHO<sub>05</sub> TEQ<sub>P</sub></i>	0.14 ± 0.11
<i>ΣPCDD/Fs</i>	152 ± 122
<i>OCDD</i>	62 ± 45

Benzo[a]pyrene is used as a marker of PAH exposure in Australia with an annual average monitoring investigation level of 0.3 ng.m<sup>-3</sup> established under the NEPM Air Toxics (2004). With limited detections of B[a]P particularly in winter in the region, the average concentrations determined for South Gladstone, Targinie, Clinton and Boat Creek were all under the MIL by at least an order of magnitude. The concentrations determined in Gladstone appear consistent with other regional areas of Australia and well under the concentrations measured in urban capital cities such as Brisbane previously. All maximum occurrences of these markers of PAH exposure occurred at South Gladstone during summer. Boyne Island, Auckland Point and Boat Creek had higher concentrations of B[a]P TEQ<sub>PAH</sub> in winter while South Gladstone, Targinie and Clinton were higher in summer.

Relatively extensive monitoring of “dioxin-like” PCBs and PCDD/Fs in Australia has been previously undertaken as part of the *National Dioxins Program*. The concentrations of these compounds in the Gladstone region are consistent with the very low (by world standards) levels of these compounds in air in Australia. The monthly intakes of these compounds through air exposure in the Gladstone region were less than 0.1 % of the JECFA exposure standard of 70 pg.kg<sup>-1</sup> bw.month<sup>-1</sup> recommended by the NHMRC. South Gladstone had higher levels of PCDDs than all other locations in the Gladstone region which is reflected in the maximum WHO<sub>05</sub> TEQ<sub>DF</sub> of 12 fg.m<sup>-3</sup> being measured for this site in the January 2010 monitoring period. Maximum concentrations of PCDD/F congeners were more likely to occur in winter in the Gladstone region except for at the South Gladstone site where PCDD maximum concentrations occurred in summer. The *National Dioxin Program* previously found that “dioxin-like” PCBs were typically higher in warmer seasons *unlike the PCDD/Fs*. However in this study of the Gladstone region summer maximum concentrations of all “dioxin-like” PCB congeners were only measured at Clinton and Auckland Point.

## 5. REFERENCES

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## 6. APPENDIX 1: PAH EXPOSURE MARKERS

TABLE 11 MONTHLY CONCENTRATIONS IN AIR AND AVERAGES FOR 2-METHYLNAPHTHALENE (NG.M<sup>-3</sup>)

### 2-methylnaphthalene (ng.m<sup>-3</sup>) - one of the most abundant PAHs monitored

	South Gladstone	Targinie	Boyne Island	Clinton	Auckand Point	Boat Creek
FEB-09	10	3.6				
MAR-09	20*	1.2*				
APR-09	11	2.5				
MAY-09	9.3	3				
JUN/JUL-09	6.5	1.8	6.5	5.9	6.5	4.6
AUG-09	7.2	1.5				
SEP-09	15	3.7				
OCT-09	12	2.4	6.3			
NOV-09	8	2.5	2.6			
DEC-09	7.8	1.6	1.6	6.3	5.1	1.0
JAN-10	6.1	1.6				
<b>Average</b>	<b>9.3</b>	<b>2.4</b>	<b>4.3</b>	<b>6.1</b>	<b>5.8</b>	<b>2.8</b>
Std. Dev.	2.8	0.81	2.5	0.28	0.99	2.5

\* excluded-refer section 3.1.4

TABLE 12 MONTHLY CONCENTRATIONS IN AIR AND AVERAGES FOR FLUORANTHENE (NG.M<sup>-3</sup>)

### Fluoranthene - marker of exposure to vapour phase PAHs

	South Gladstone	Targinie	Boyne Island	Clinton	Auckand Point	Boat Creek
FEB-09	1.5	0.50				
MAR-09	1.4*	0.35*				
APR-09	1.3	0.48				
MAY-09	0.83	0.89				
JUN/JUL-09	0.54	0.20	0.45	0.44	0.69	0.52
AUG-09	0.55	0.27				
SEP-09	1.5	0.52				
OCT-09	0.54	0.24	0.34			
NOV-09	0.61	0.27	0.17			
DEC-09	0.47	0.18	0.069	0.36	0.36	0.16
JAN-10	0.45	0.20				
<b>Average</b>	<b>0.83</b>	<b>0.38</b>	<b>0.26</b>	<b>0.40</b>	<b>0.53</b>	<b>0.34</b>
Std. Dev.	0.43	0.22	0.17	0.057	0.23	0.25

\* excluded - refer section 3.1.4

TABLE 13 MONTHLY CONCENTRATIONS IN AIR AND AVERAGES FOR PHENANTHRENE (NG.M<sup>-3</sup>)

**Phenanthrene - relatively abundant vapour phase PAH marker**

	South Gladstone	Targinie	Boyne Island	Clinton	Auckland Point	Boat Creek
FEB-09	4.9	1.9				
MAR-09	4.5*	1.2*				
APR-09	3.3	1.5				
MAY-09	2.8	2.6				
JUN/JUL-09	2.2	1.0	2.0	1.7	2.5	2.5
AUG-09	1.9	1.1				
SEP-09	5.0	1.9				
OCT-09	2.0	1.0				
NOV-09	2.2	1.3				
DEC-09	2.0	0.92	0.32	1.7	1.7	0.85
JAN-10	0.77	0.93				
<b>Average</b>	<b>2.7</b>	<b>1.4</b>	<b>1.2</b>	<b>1.7</b>	<b>2.1</b>	<b>1.7</b>
<b>Std. Dev.</b>	<b>1.3</b>	<b>0.56</b>	<b>1.2</b>	<b>0.0000</b>	<b>0.57</b>	<b>1.2</b>

\* excluded -refer section 3.1.4

TABLE 14 MONTHLY CONCENTRATIONS IN AIR AND AVERAGES FOR BENZO[A]PYRENE (NG.M<sup>-3</sup>)

**Benzo[a]pyrene - marker for PAH exposure in Australia with a monitoring investigation level established for NEPM air toxics**

	South Gladstone	Targinie	Boyne Island	Clinton	Auckland Point	Boat Creek
FEB-09	0.019	0.020				
MAR-09	<0.11	<0.14				
APR-09	0.047	0.025				
MAY-09	<0.026	<0.036				
JUN/JUL-09	<0.019	<0.020	<0.041	<0.031	<0.022	<0.029
AUG-09	0.021	<0.017				
SEP-09	0.085	0.012				
OCT-09	0.026	0.011	<0.0052			
NOV-09	0.013	<0.013	<0.010			
DEC-09	0.016	<0.013	<0.010	0.024	<0.011	0.0121
JAN-10	0.14	0.0068				
<b>Average</b>	<b>0.046</b>	<b>0.015</b>		<b>0.024</b>		<b>0.0121</b>
<b>Std dev.</b>	<b>0.045</b>	<b>0.007</b>		-		-

TABLE 15 MONTHLY CONCENTRATIONS IN AIR AND AVERAGES FOR BENZO[A]PYRENE TOXIC EQUIVALENTS (NG.M<sup>-3</sup>)

<b>B[a]P TEQ<sub>PAH</sub> (ng.m<sup>-3</sup>)</b>						
	<b>South Gladstone</b>	<b>Targinie</b>	<b>Boyne Island</b>	<b>Clinton</b>	<b>Auckland Point</b>	<b>Boat Creek</b>
FEB-09	0.037	0.034				
MAR-09	0.14*	0.14*				
APR-09	0.089	0.051				
MAY-09	0.034	0.057				
JUN/JUL-09	0.022	0.012	0.021	0.02	0.027	0.049
AUG-09	0.046	0.022				
SEP-09	0.17	0.039				
OCT-09	0.059	0.033	0.017			
NOV-09	0.029	0.017	0.015			
DEC-09	0.037	0.017	0.013	0.047	0.018	0.024
JAN-10	0.26	0.019				
<b>Average</b>	<b>0.078</b>	<b>0.030</b>	<b>0.017</b>	<b>0.034</b>	<b>0.023</b>	<b>0.037</b>
<b>Std. Dev.</b>	<b>0.077</b>	<b>0.015</b>	<b>0.0034</b>	<b>0.019</b>	<b>0.0064</b>	<b>0.018</b>

\* excluded refer section 3.1.4

## 7. APPENDIX 2: "DIOXIN-LIKE" PCB & PCDD/F EXPOSURE MARKERS

TABLE 16 MONTHLY CONCENTRATIONS IN AIR AND AVERAGES FOR WHO<sub>05</sub> TEQ<sub>DF</sub> (FG.M<sup>-3</sup>)



WHO<sub>05</sub>-TEQ<sub>DF</sub> middle bound (fg.m<sup>-3</sup>)

	South Gladstone	Targinie	Boyne Island	Clinton	Auckland Point	Boat Creek
FEB-09	3.7	1.4				
MAR-09	2.8	0.81				
APR-09	3.6	0.88				
MAY-09	3.6	1.4				
JUN/JUL-09	2.2	4.0	1.1	0.69	0.94	3.2
AUG-09	2.6	3.2				
SEP-09	3.8	0.48				
OCT-09	5.9	0.57	0.24			
NOV-09	2.7	2.2	0.48			
DEC-09	6.7	0.46	0.49	1.3	0.54	0.71
JAN-10	12	0.68				
Average	<b>4.5</b>	<b>1.5</b>	<b>0.59</b>	<b>1.0</b>	<b>0.74</b>	<b>1.9</b>
Std dev.	2.7	1.2	0.39	0.41	0.28	1.7

TABLE 17 MONTHLY CONCENTRATIONS IN AIR AND AVERAGES FOR WHO<sub>05</sub> TEQ<sub>P</sub> (FG.M<sup>-3</sup>)

WHO<sub>05</sub>-TEQ<sub>P</sub> (fg.m<sup>-3</sup>)

	South Gladstone	Targinie	Boyne Island	Clinton	Auckland Point	Boat Creek
FEB-09	0.17	0.075				
MAR-09	0.24	0.074				
APR-09	0.23	0.095				
MAY-09	0.16	0.046				
JUN/JUL-09	0.19	0.24	0.40	0.088	0.34	0.14
AUG-09	0.26	0.12				
SEP-09	0.20	0.017				
OCT-09	0.23	0.021	0.037			
NOV-09	0.06	0.061	0.078			
DEC-09	0.11	0.011	0.022	0.22	0.35	0.051
JAN-10	0.22	0.025				
Average	<b>0.19</b>	<b>0.072</b>	<b>0.13</b>	<b>0.16</b>	<b>0.34</b>	<b>0.095</b>
Std dev.	0.060	0.066	0.18	0.10	0.010	0.062

TABLE 18 MONTHLY CONCENTRATIONS IN AIR AND AVERAGES FOR ΣPCDD/FS (FG.M<sup>-3</sup>)

Sum of PCDD/F congeners excluding LOD values

	South Gladstone	Targinie	Boyne Island	Clinton	Auckland Point	Boat Creek
FEB-09	159	54				
MAR-09	173	92				
APR-09	140	91				
MAY-09	142	150				
JUN/JUL-09	162	439	126	56	103	314
AUG-09	179	332				
SEP-09	428	113				
OCT-09	262	65	42			
NOV-09	126	157	33			
DEC-09	260	35	18	50	28	20
JAN-10	423	96				
Average	<b>223</b>	<b>148</b>	<b>55</b>	<b>53</b>	<b>66</b>	<b>167</b>
Std dev.	110	125	49	4	53	208

TABLE 19 MONTHLY CONCENTRATIONS IN AIR AND AVERAGES FOR OCDD (FG.M<sup>-3</sup>)

OCDD - dominant congener (fg.m<sup>-3</sup>)

	South Gladstone	Targinie	Boyne Island	Clinton	Auckland Point	Boat Creek
FEB-09	55	38				
MAR-09	62	85				
APR-09	39	55				
MAY-09	44	75				
JUN/JUL-09	62	87	65	30	54	107
AUG-09	68	154				
SEP-09	243	80				
OCT-09	87	40	26			
NOV-09	43	35	19			
DEC-09	64	28	9.5	34	15	15
JAN-10	93	59				
Average	<b>78</b>	<b>67</b>	<b>30</b>	<b>32</b>	<b>34</b>	<b>61</b>
Std dev.	57	36	24	2.8	27	65

## 8. APPENDIX 3: "DIOXIN-LIKE" PCB & PCDD/F CONGENER PROFILES FOR EACH SITE

### 8.1 SOUTH GLADSTONE

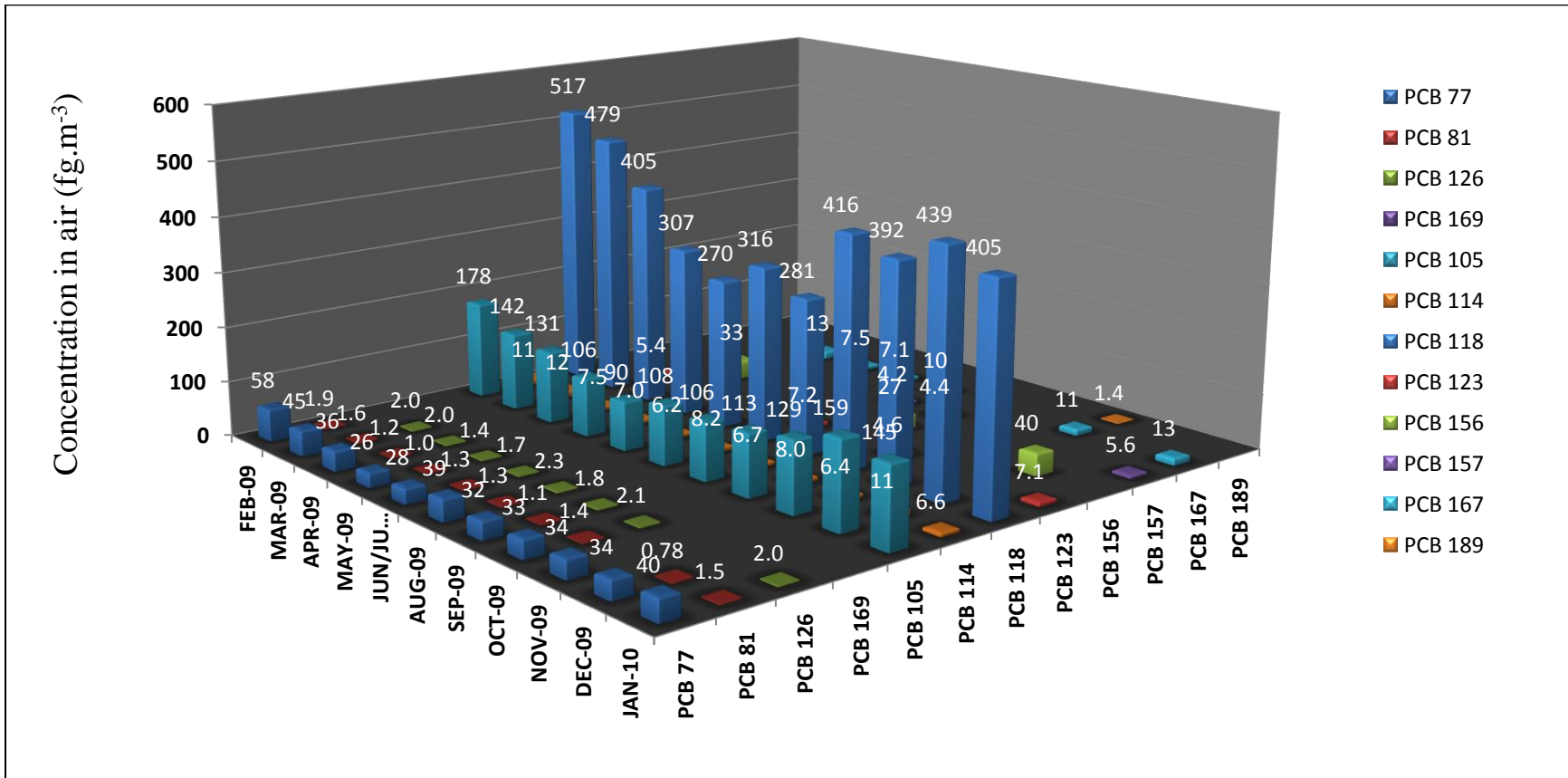


FIGURE 7 SOUTH GLADSTONE "DIOXIN-LIKE" PCB CONGENER PROFILES

\*Please note that the scale of the y-axis varies in each of the figures in Appendix 3

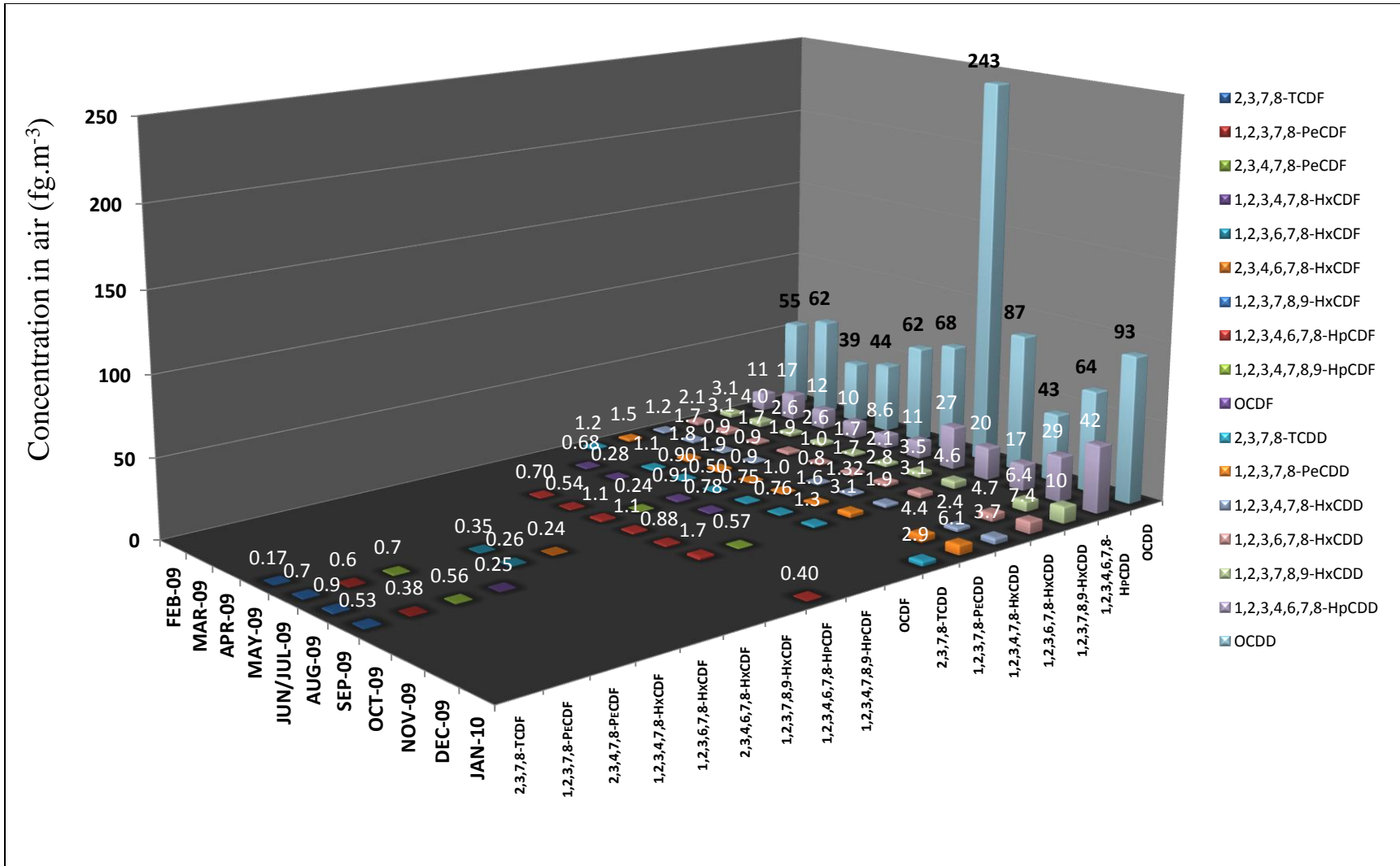


FIGURE 8 SOUTH GLADSTONE PCDD/F CONGENER PROFILES

8.2 TARGINIE

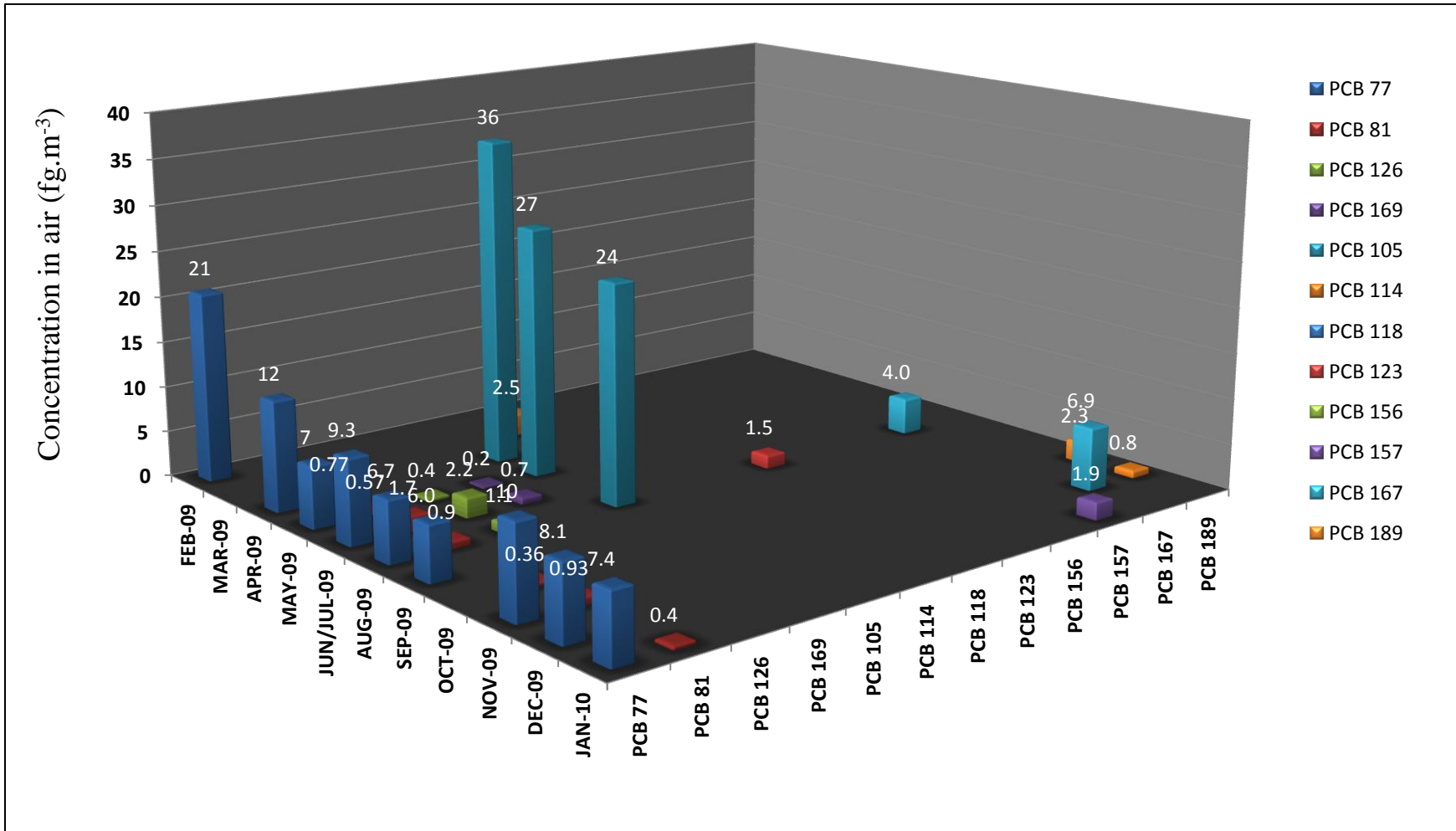


FIGURE 9 TARGINIE "DIOXIN-LIKE" PCB CONGENER PROFILES

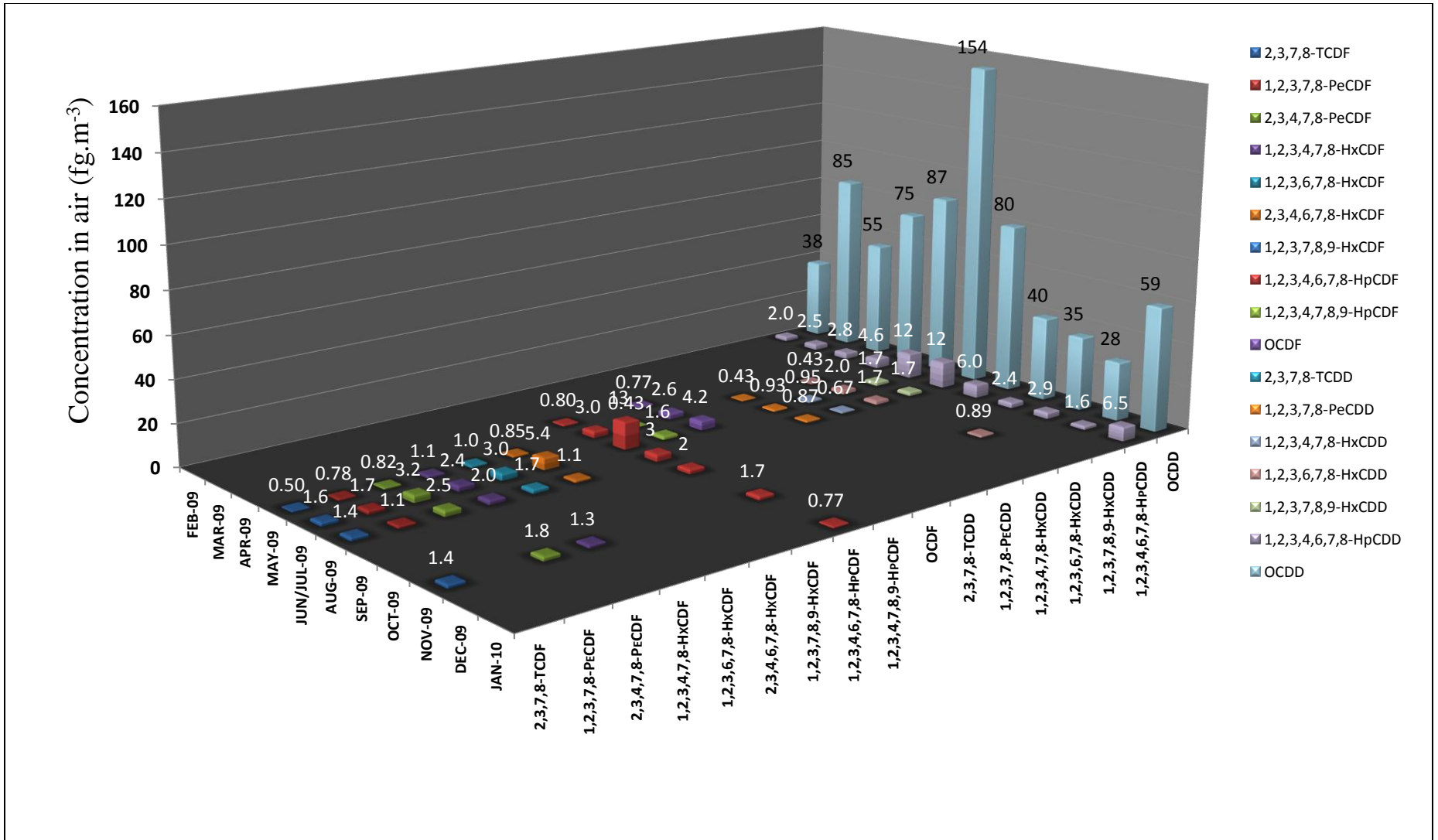


FIGURE 10 TARGINIE PCDD/F CONGENER PROFILES

8.3 BOYNE ISLAND

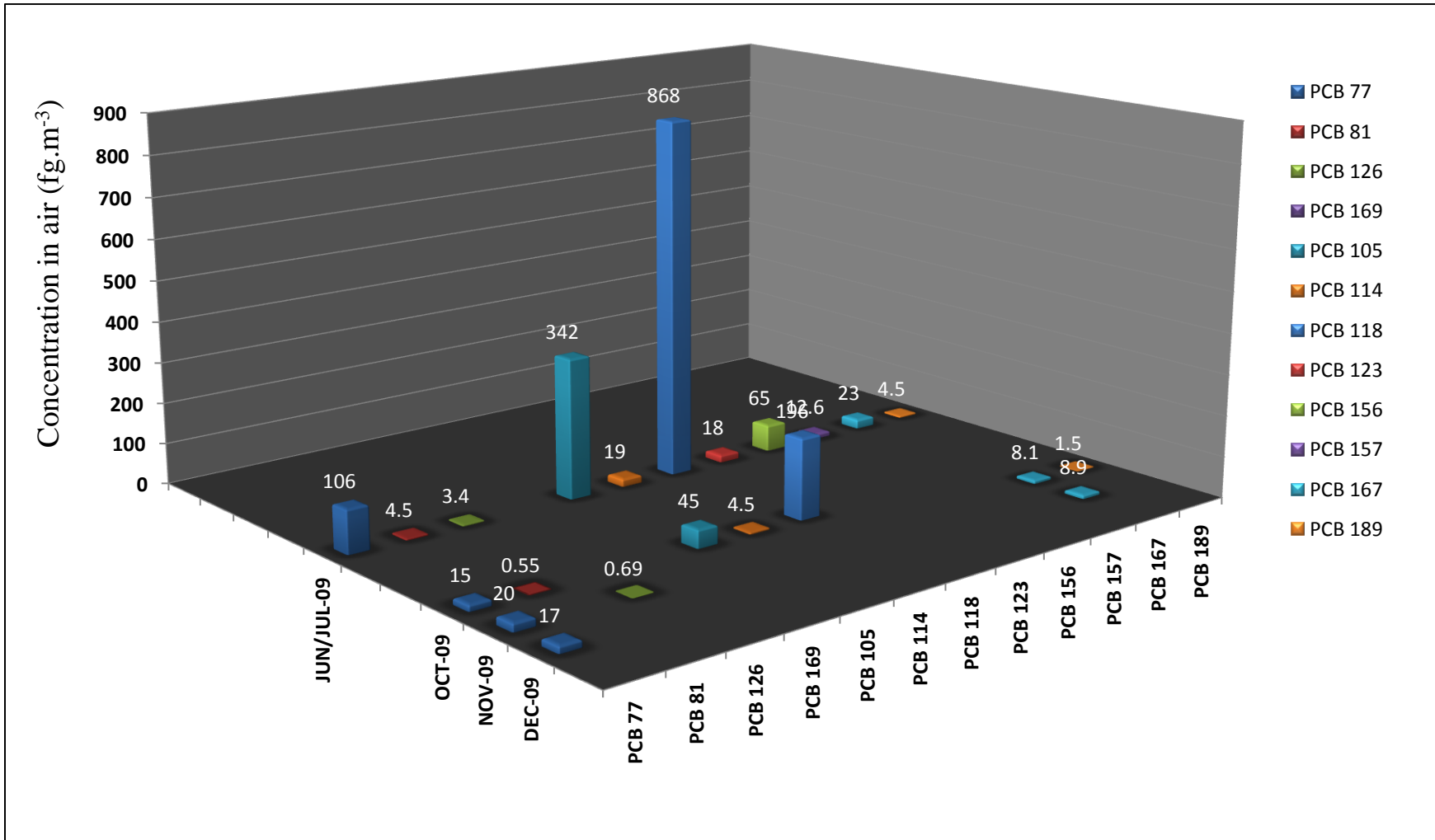


FIGURE 11 BOYNE ISLAND "DIOXIN-LIKE" PCB CONGENER PROFILES

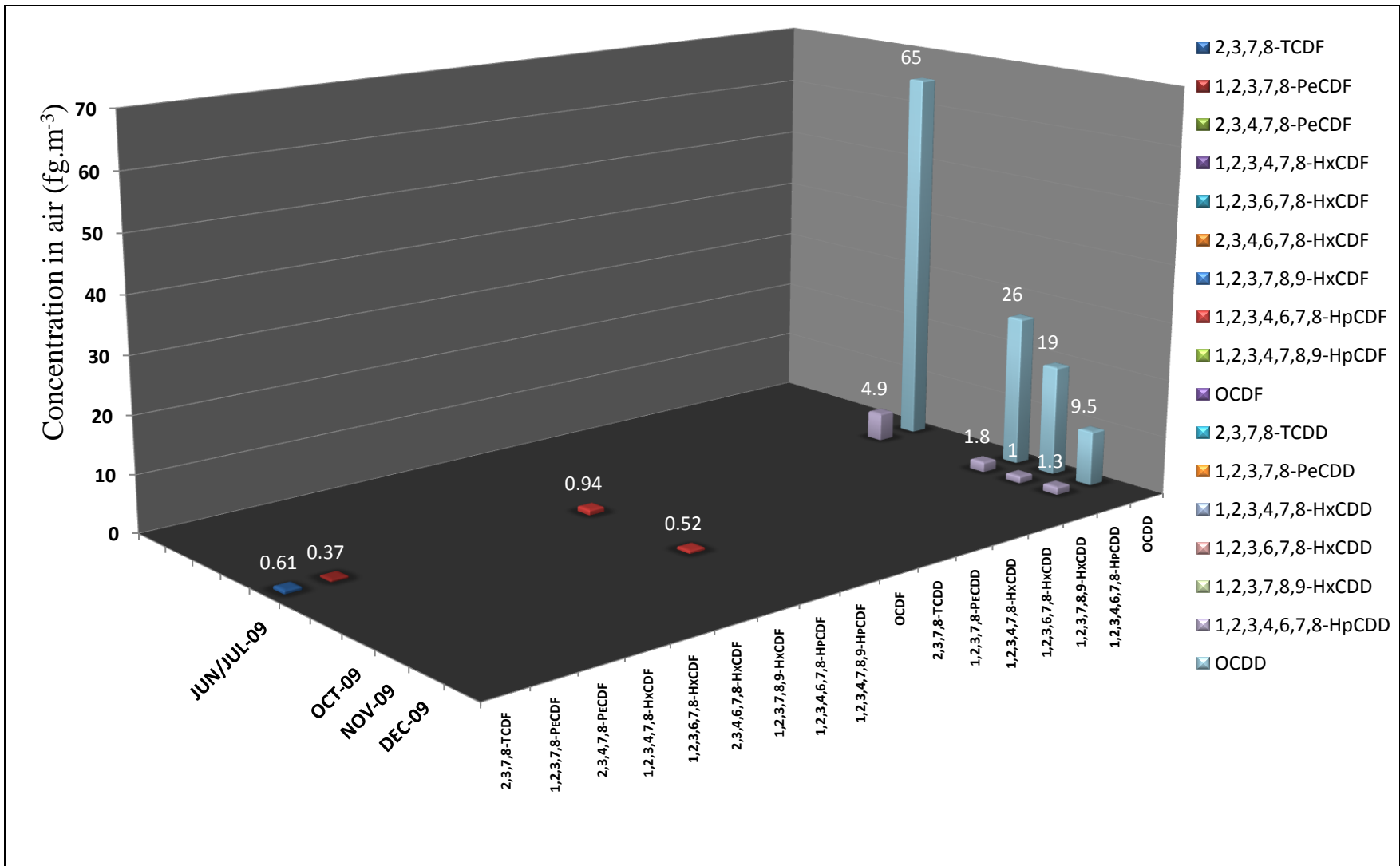


FIGURE 12 BOYNE ISLAND PCDD/F CONGENER PROFILES



8.4 CLINTON

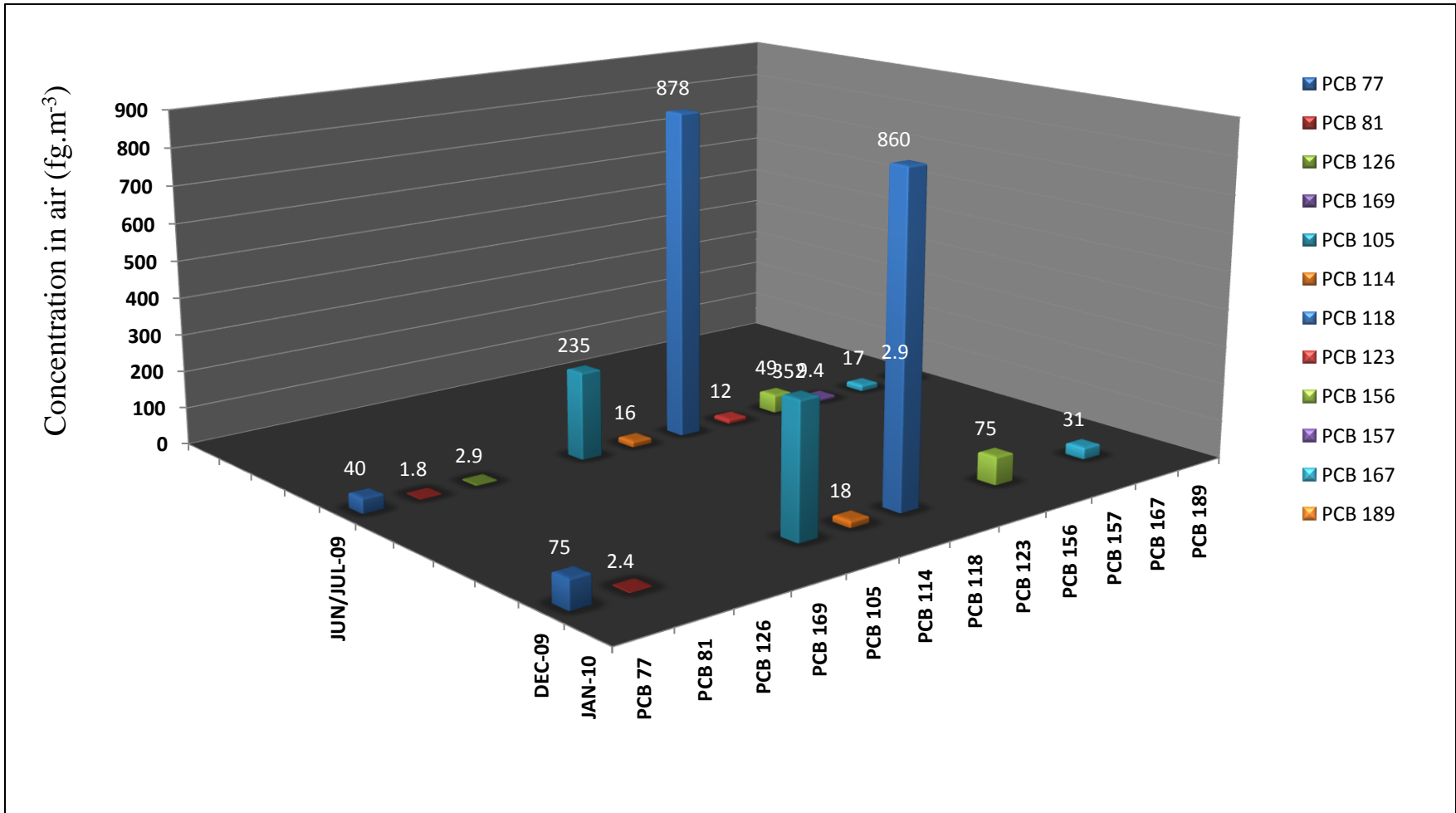


FIGURE 13 CLINTON "DIOXIN-LIKE" PCB CONGENER PROFILES

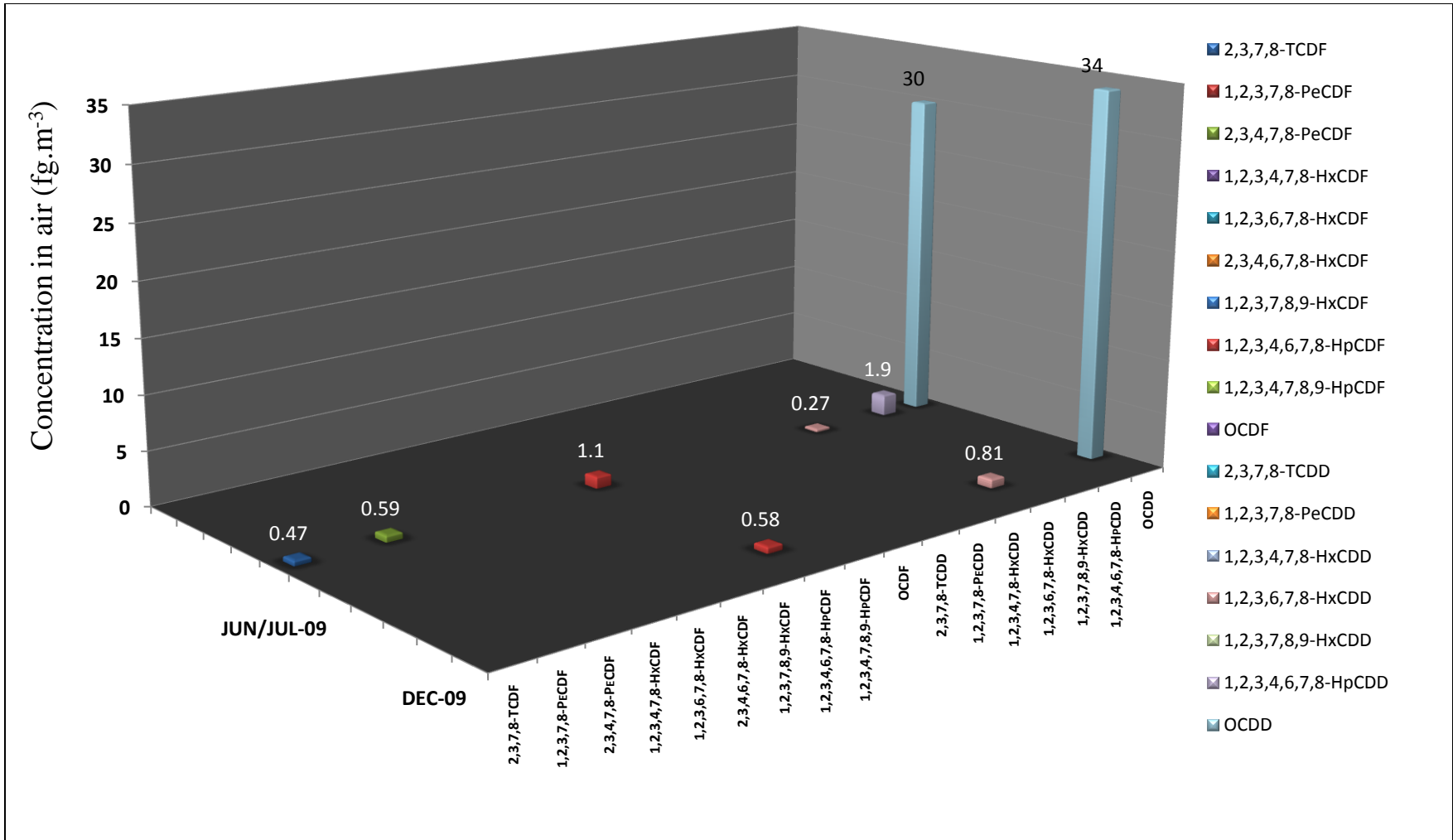


FIGURE 14 CLINTON PCDD/F CONGENER PROFILES

8.5 AUCKLAND POINT

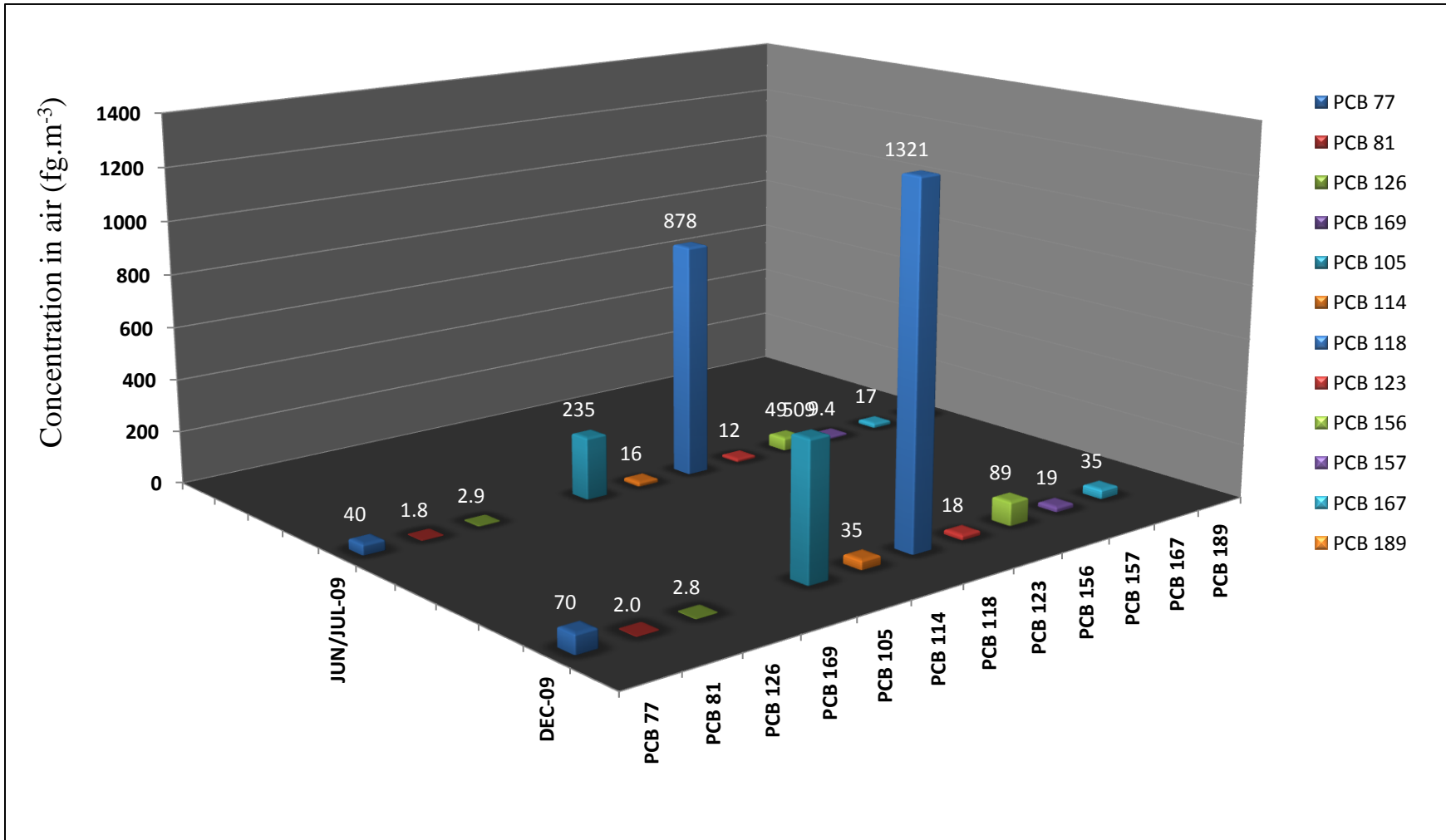


FIGURE 15 AUCKLAND POINT "DIOXIN-LIKE" PCB CONGENER PROFILES

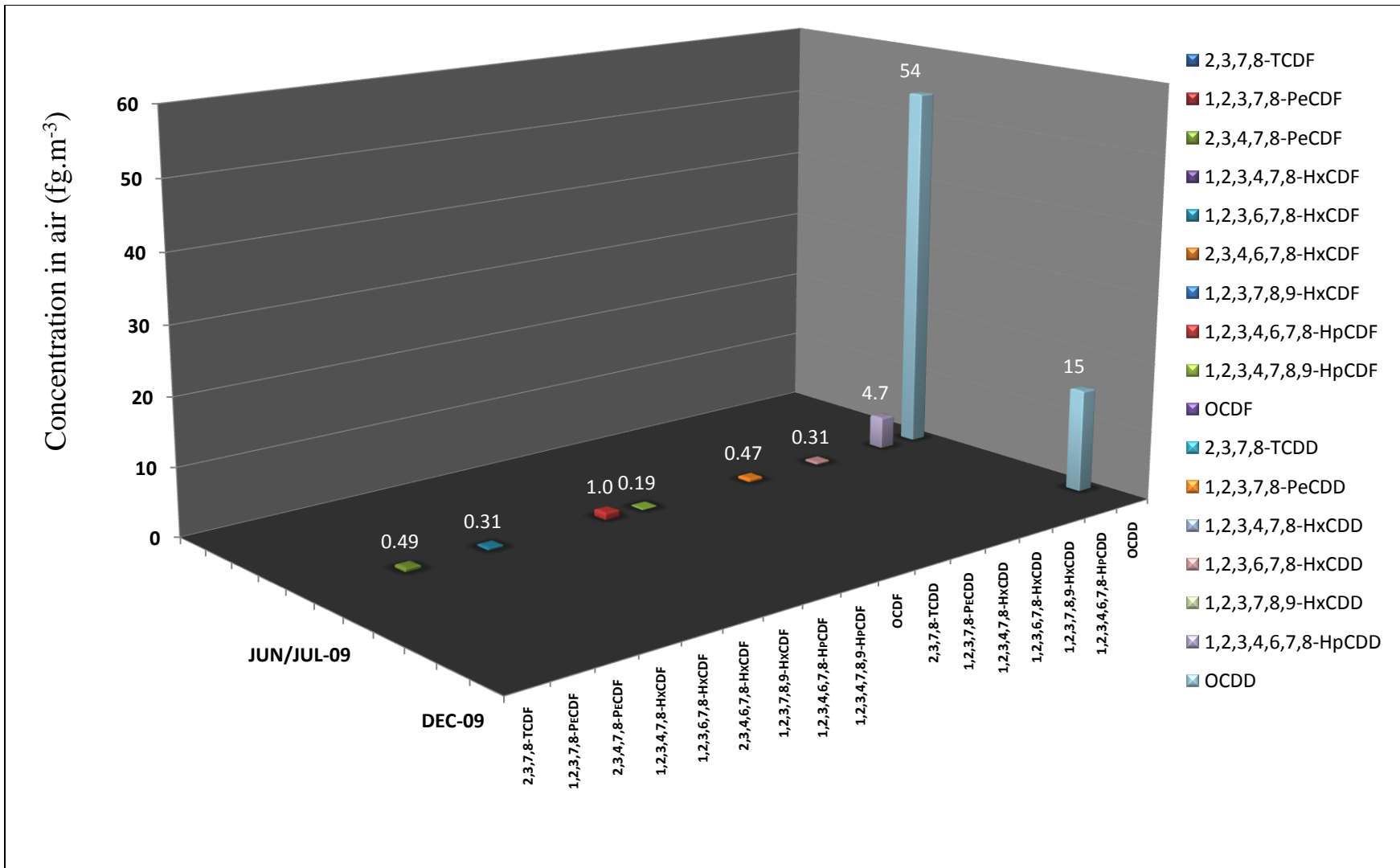


FIGURE 16 AUCKLAND POINT PCDD/F CONGENER PROFILES

8.6 BOAT CREEK

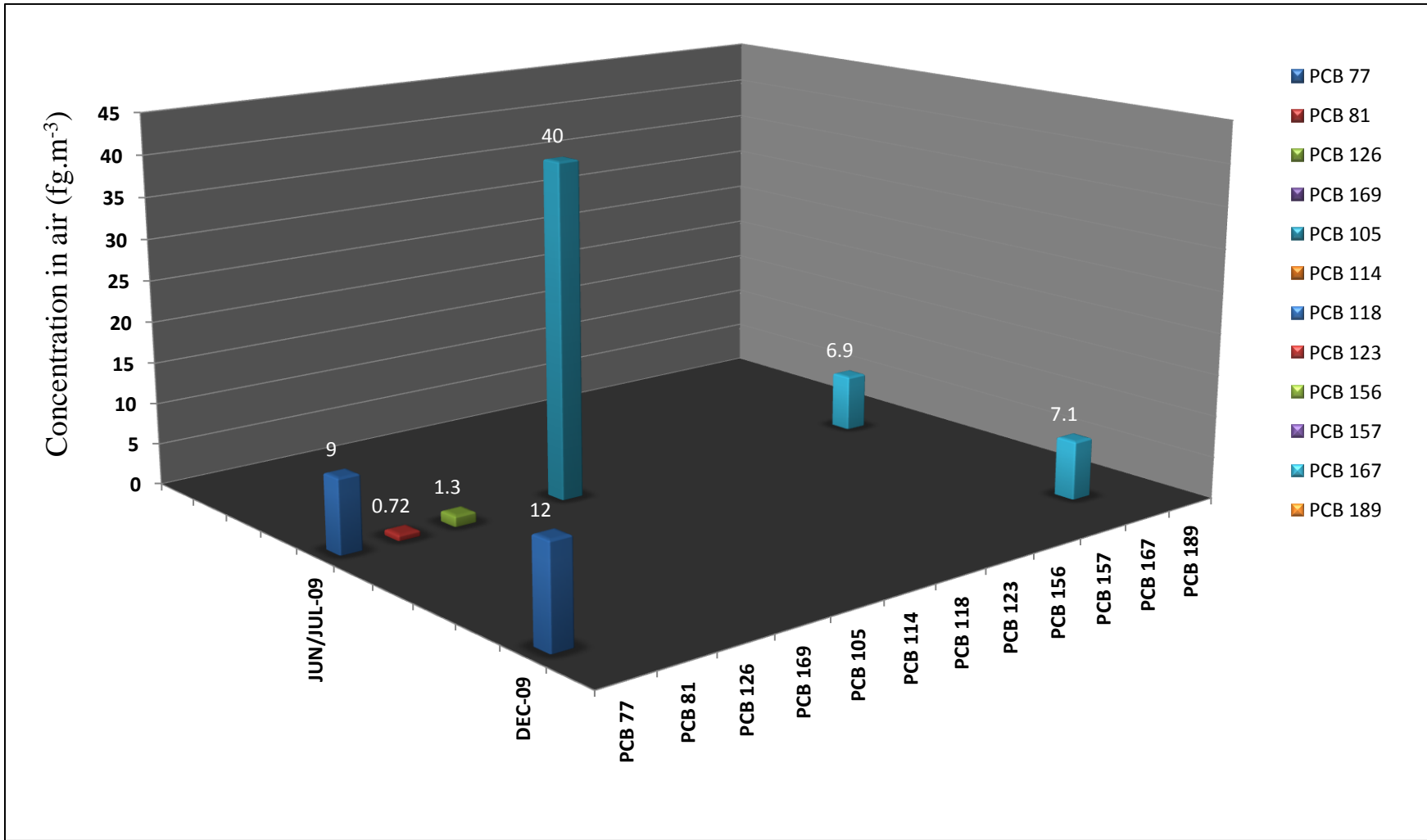


FIGURE 17 BOAT CREEK “DIOXIN-LIKE” PCB CONGENER PROFILES

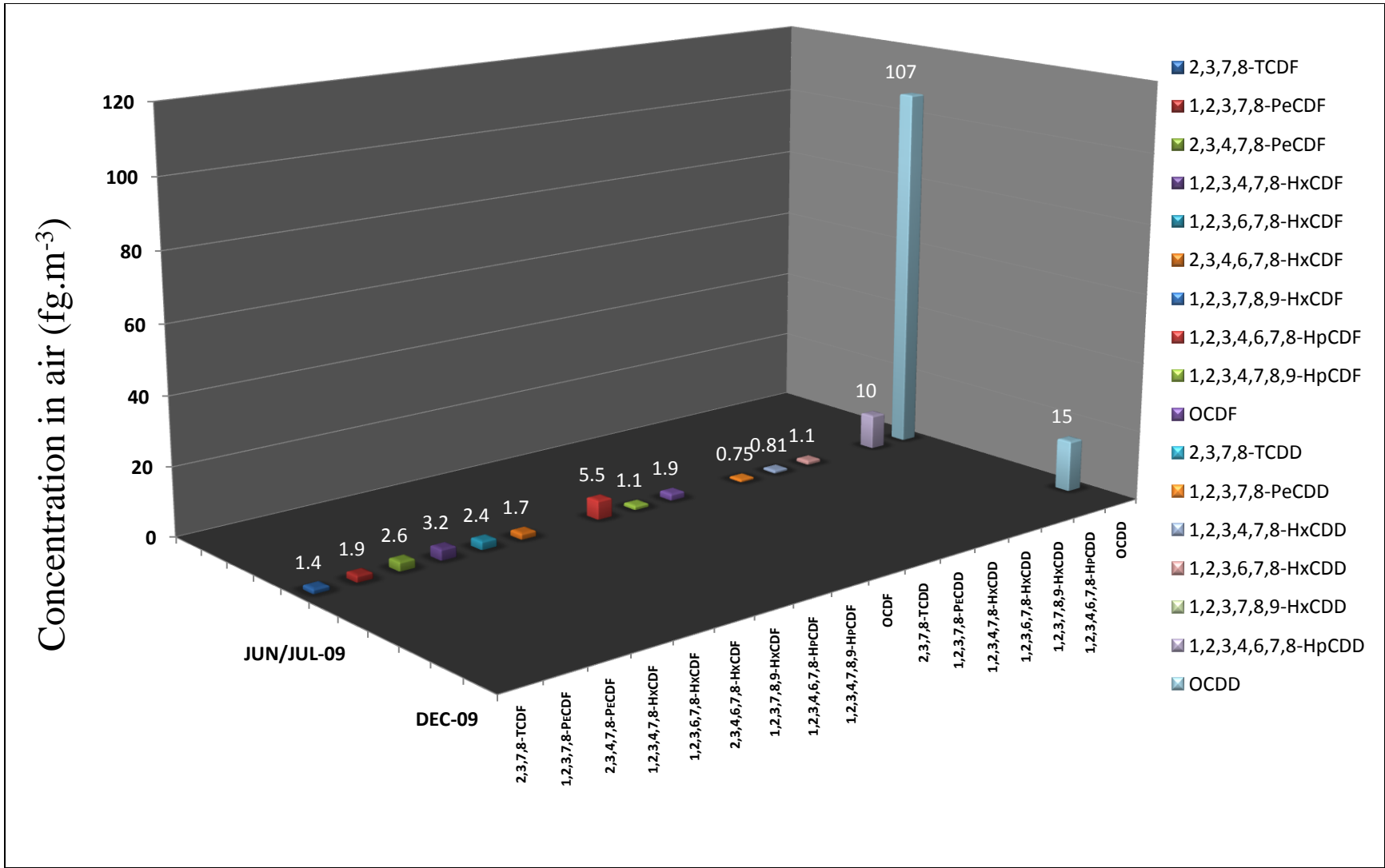


FIGURE 18 BOAT CREEK PCDD/F CONGENER PROFILES