Appendices

Appendix A—Sources of dioxins

Dioxins are released into the environment in a variety of ways and in varying quantities, depending on the source.

Dioxins have recently been found in clay deposits in the USA. No definitive experimental evidence has been brought forward to account for the presence of the dioxins from known anthropogenic sources or to explain the selective chemical synthesis of dioxins under the conditions inherent to the formation of clays some 40 million years ago (Ferrario 2000).

Studies of sediment deposits from freshwater lakes in the United States have generally shown CDD and CDF concentrations began to rise in the 1930s and 1940s, and then began to decline in some lakes in the 1960s and 1970s (Cleverly 1996).

Although these compounds are released from a variety of sources, the congener profiles of dioxins found in sediments have been linked to combustion sources (Hites 1991).

Dioxins have never been intentionally produced, other than on a laboratory-scale basis for use in chemical analyses. Rather, they are produced as the unintended by-products of some human activities (mostly processes involving combustion) or from some natural activities such as bushfires and volcanic activity. A recent study has also found that production of OCDD and HpCDD from pentachlorophenol in clouds and rain droplets is an important contributor to dioxin concentrations in air (Baker and Hites 2000).

A report by UNEP on dioxin and furan inventories categorised anthropogenic sources of dioxins and furans into nine major sectors (UNEP 1999):

- iron and steel—iron and steel plants including foundries, sinter and coke plants
- non-ferrous metals—primary and secondary plants for the generation of copper, aluminium, zinc and lead
- power plants—fuelled with coal, gas, crude oil and wood
- industrial combustion plants—industrial units fuelled with coal, gas, crude oil, sewage sludge and biomass for use on-site
- small combustion units—mostly domestic stoves and chimneys fired with coal, oil and gas
- waste incineration—includes incineration of municipal solid waste, hazardous waste, sewage sludge, hospital waste, waste wood and crematoria
- road transport—passenger cars, buses, trucks run on leaded petrol, unleaded petrol or diesel
- mineral products production—generation of cement, lime, glass and brick
- others—shredder plants, asphalt mixing, drying of green fodder, wood chips, chemical industry, accidental fires and prescribed burnings.

A study to investigate the sources of polychlorinated dibenzo-p-dioxin (PCDD) and polychlorinated dibenzofuran (PCDF) emissions in Australia was conducted based on international inventory studies and the application of emission factors. For most sources the emission estimates were presented as a range and were indicative only as they were subject to considerable uncertainties. Based on the upper bound of each range, it was found that biomass combustion from prescribed burning and bushfires was potentially the most significant source of PCDD and PCDF in Australia, contributing approximately 75% to the total estimates. The next most significant sources in decreasing order were: cement production, residential wood combustion, coal combustion, sinter production, industrial wood combustion and lime production. These sources combined with prescribed burning and bushfires, accounted for approximately 95% of total emissions. Motor vehicles were estimated to contribute less than 1% of total emissions (Environment Australia 1998).

Appendix B—Toxic equivalents

In most environmental media, dioxins occur as complex mixtures of congeners. To enable the toxicity of a complex mixture to be expressed as a single number, the concept of toxic equivalents (TEQs) has been developed. Due to their structure these congeners cause health effects in organisms by way of an interaction with a receptor inside cells known as the Ah receptor. Different congeners interact with the receptor with different potencies and the concentration at which a particular congener will cause health effects is related to its ability to interact with this receptor. This common mechanism of action has enabled an approach to be developed to assess the possible health effects from exposure to mixtures of these congeners based on toxic equivalent factors (TEFs). Of the 210 possible congeners, only those with chlorine atoms in the 2, 3, 7 and 8 positions (i.e. 17 possible congeners in total) exhibit toxic effects through interaction with the Ah receptor.

The TEFs are based on assessments of the potency of each congener to interact with the Ah receptor relative to 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), the most toxic member of the group. The TEFs are essentially a set of weighting factors, each of which expresses the toxicity of a specific congener in terms of the mass of TCDD that would cause an equivalent toxic response. Multiplication of the concentration of the congener by its TEF yields the corresponding TEQ. The total toxicity of any mixture is then simply the sum of the individual congener TEQs.

The most widely adopted system of TEFs is that proposed by the North Atlantic Treaty Organisation/Committee on the Challenges of Modern Society (Kutz et al 1990) and known as the International Toxic Equivalents Factor (I-TEFs) scheme. This scheme has been expanded by the World Health Organisation (WHO) (Van den Berg et al 1998) to include factors for mammals (who are used as surrogates for humans), birds and fish. Table B1 lists the I-TEFs and WHO-TEFs for the 17 2,3,7,8-congeners. The most toxic congener—2,3,7,8-tetrachlorodibenzo-para-dioxin (2,3,7,8-TCDD)—is rated as 1. Other congeners are rated between 0 and 1, depending on their relative toxicity. The remaining 193 congeners have TEFs of zero.

Table 4: Toxic equivalent factors for dioxins

Dioxin congener (a)	I-TEF (Kutz et al1990)	WHO-TEF (humans/mammals) (Van den Berg et al 1998)
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	0.0001
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	0.0001

Notes
The name of each congener takes the form: [z,]-XxCDY
Where Xx can take the values T meaning tetra (i.e. 4)
Pe meaning penta (i.e. 5)
Hx meaning hexa (i.e. 6)
Hp meaning hepta (i.e. 7) or
O meaning octa (i.e. 8)
CD means chlorodibenzo
and Y can take the values D meaning dioxin; or
F meaning furan

Thus HpCDD means heptachlorodibenzodioxin
and PeCDF means pentachlorodibenzofuran

and further, the prefix digits (z) indicate the positions on the central molecule (dibenzo-p-dioxin or dibenzofuran—see Figure 1) to which the chlorine atoms are attached.

Appendix C—Air flow determination

C1. Introduction

Figure 14 overleaf indicates the nature of the sampling instrument. Apart from the sampling head, which holds the filter and absorbent canister, much of the detail of the instrument is associated with control and measurement of the air flow rate so total air flow volume through the canister/filter can be determined. The Magnehelic gauge indicates the pressure differential (in inches of water) across a venturi throat in the flow line. This reading relates to gas flow rate. To enable continuous reading of this pressure differential, a pressure transducer was fitted across the venturi throat in parallel with the Magnehelic gauge. The voltage from this transducer (0-1 VDC) was recorded on a data logger.

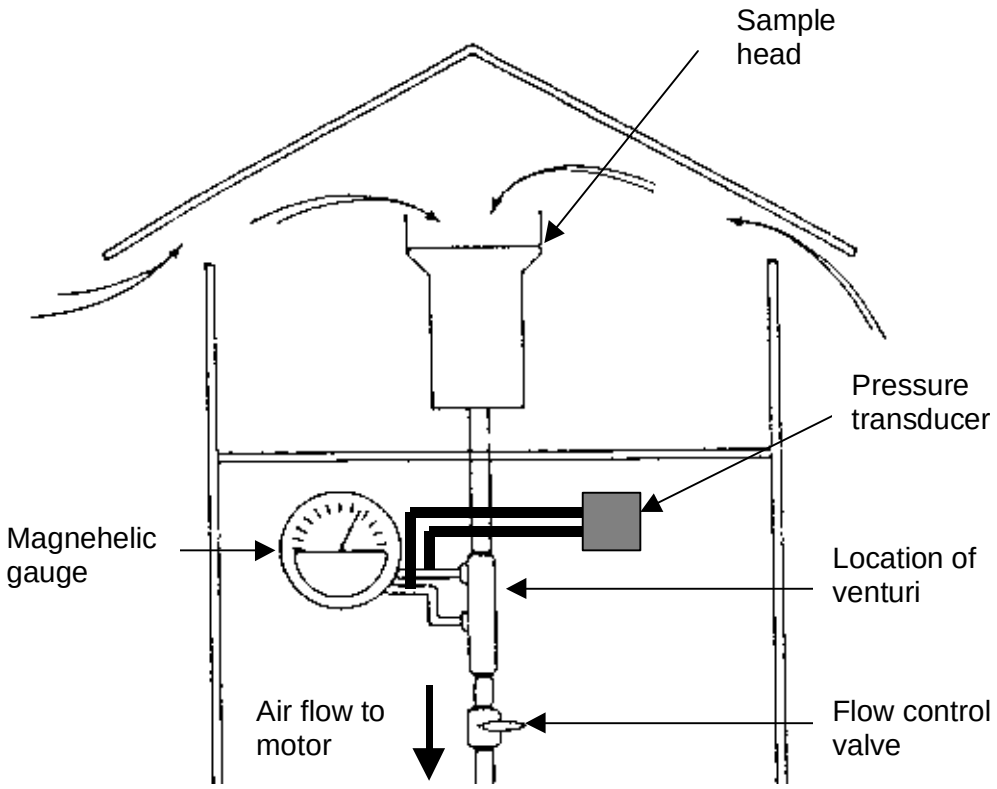

Figure 14: Diagram of PS-1 high volume air sampler

C2. Instrument calibration

C2.1 Calibration of air flow against Magnehelic gauge

The Magnehelic gauge gives a reading of the pressure differential which develops across the venturi as the air flows through the system. It was necessary to calibrate this for flow rates of between 100 and 200 litres/minute at approximately 27°C. Since the motor operates at a constant speed, the calibration needed to be carried out at the motor speed which was used in the field.

In the field, variation of air flow can occur due to three separate effects:

a) variations in the speed of the motor—such variations were expected to take the form of a slow drift as mechanical wear occurred
b) variations in air density due to normal fluctuations in atmospheric temperature and pressure
c) restrictions of the air flow due to the build up of particles on the sampling head filter paper.

To ensure that the motor speed remained effectively constant, a simple brass restrictor was made for each instrument. This restrictor could be fitted in the flow path in place of the sampling head. The restrictor had a constant bore and so served as a constant, if uncalibrated, flow controller. With the restrictor in place, the Magnehelic reading was set at 40 inches of water by adjusting the speed of the motor. This restrictor was left with each instrument and could be put in the flow path as needed to check that the flow was maintaining a constant value. Periodic checking indicated that the flow rate was quite stable and that motor wear was thus not an issue. Flow variations due to effects b) and c) above were allowed for by measurement of the air flow during the sampling period for each sample.

Calibration of the flow rate thus meant that the motor speed was carefully adjusted so the Magnehelic reading was 40 inches of water with the restrictor in place. This restrictor was then replaced by a standard orifice for which the pressure differential could be accurately and independently measured. This standard orifice also incorporated a flow control valve which could be used to alter the flow rate and thereby effectively mimic the effect of the build up of particles on the sampling head filter paper. Calibration consisted of taking a paired series of Magnehelic readings and standard orifice pressure differential readings over the range of air flows anticipated. The standard orifice pressure differential readings were immediately convertible to an air flow and thus a paired series of air flow and Magnehelic readings was obtained.

The flow rate through the venturi was given by the equation:

Flow rate = Constant * √(Magnehelic reading)

The air flow and Magnehelic readings were graphed and the value of the constant obtained.

This was repeated for each instrument. The values of these constants were entered into the database.

C2.2 Calibration of the Magnehelic readings and the pressure transducer/ data logger combinations

The Magnehelic gauge can only be read when there is a human operator present. Since extended unattended operation was to occur, it was necessary to have regular values of these gauge readings so that air flow variations could be accommodated within air volume determinations. To achieve this, a pressure transducer was connected across the pressure tubes which connected the Magnehelic gauge to the instrument. A voltage, proportional to the Magnehelic reading, was thus produced.

A Hydromace TRS data logger was chosen to record these voltages. Signal output from the pressure transducer was connected to a head amplifier which converted the signal (0 to 1 V DC) into a frequency count between 0 and 4096. The data logger recorded this frequency count. Calibration could thus consist of 2 steps:

- calibration of the Magnehelic reading against pressure transducer voltage
- calibration of input voltage against frequency count for the head amplifier.

Since previous experience had shown these data loggers to be quite reliable, it was not anticipated that there would need to be any change of data logger or head amplifier for the entire sampling period and thus it was decided to calibrate each setup as a single unit—i.e. Magnehelic reading against frequency count.

To calibrate the instruments in this mode, the brass restrictor (see C2.1 above) was placed in the instrument. The motor speed was varied so that a series of Magnehelic readings and frequency counts, read from the LCD screen of the data logger, was obtained. The Magnehelic readings varied over the range from approximately 70 to 5 inches of water. Graphing of this data indicated that there was a slight curvature in the plot, especially at low values of the Magnehelic readings, so a cubic equation was fitted in each case. The values of the equation coefficients were entered into the database.

C3. Field air flow measurement and data handling

The Hydromace TRS data logger has its own internal registers which keep track of the month, day of the month and time (to the nearest minute). When it records a value it also records the time of day of that reading. At midnight, it also records the

new day and month number. It requires that the operator keep an external record of the year.

In the field, the data logger was programmed to record the pressure transducer voltage (as a count) every hour. A data logger record for one day thus consisted of a midnight (day and month) mark followed by 24 time and voltage count pairs.

Each time a new sample canister and filter paper was put into a sampler, the memory pack of the data logger was exchanged also. Each memory pack was individually numbered. A manual record of the site and the start and finish dates and times for each memory pack was kept. These details were manually entered into the database.

When exchanging canisters, filter papers and data logger memory packs, the air flow was stopped by turning off the motor. A manual record of the Magnehelic gauge readings immediately prior to motor turn off and immediately after motor turn on was also taken.

Each high volume air sampler incorporated a motor run-time meter. The meter reading was recorded whenever the motor was turned off (generally when canisters etc were being exchanged). This served as a check on the operation time of the instrument as calculated from start and finish dates and times and thus also served as an internal check on the accuracy of data entry to the database.

At the office, the contents of the data logger memory pack were downloaded into a computer. Spreadsheet software was used to calculate time and date of each voltage count record, along with the memory pack ID number. These records were also stored in the database.

Appendix D—Sample handling

Since the anticipated concentrations of dioxins were so low, particular precautions had to be taken during sample handling to prevent contamination and to otherwise ensure sample integrity.

Sampling canisters consisted of a glass cylinder, 130 mm long x 57 mm wide, which was open at both ends and which had a stainless steel wire mesh perpendicular to the axis and about 10 mm from one end. This mesh provided a support for the polyurethane foam and XAD resin which served as the absorbent material for the dioxins. These canisters were impregnated with ^{13}C labelled dioxin congeners which were internal standards for the GC/MS analysis (see Appendix E for details). The canisters were supplied in bulk lots of 20 to 50 canisters. Canisters were individually sealed with laboratory sealing film and individually wrapped in bubble wrap plastic to prevent breakage. The bubble wrap and sealing film were only removed immediately before the canister was put into the sampling head (see Figure 15 on page 36). Exposed canisters had fresh sealing film applied and were bubble wrapped immediately after being removed from the sampling head. The sealing film helped prevent loss of standards and collected dioxins as well as preventing contamination from other volatile organic compounds.

With three sampling sites and 24- or 12-day sampling durations, approximately eight canisters were used, on average, per month. The batches of canisters as supplied thus lasted for two to six months. To prevent loss of internal standards prior to use and loss of absorbed dioxins after collection, both unused and exposed canisters (still film sealed and wrapped) were stored in a freezer. Canisters were transported to and from the field in polystyrene containers in the presence of ‘freezer bricks’, again to minimise losses of dioxins and standards by volatilisation. Exposed canisters were

retained in the freezer until air freighted to the New Zealand laboratory in batches of about 8–12 canisters, i.e. about 4–6 weeks sampling effort. It was not possible to keep canisters under cooled conditions during transport to the laboratory. Delivery times to the laboratory were generally 24 to 36 hours. Advice from the laboratory was that such a period without cooling would have no effect on the results. Indeed, this advice was that much longer periods without cooling were permissible, however, samples were kept cool or frozen wherever possible since such freezing or cooling was relatively easy to arrange and it was felt to be a wise precaution.

The polyurethane foam and XAD resin used in the sampling canisters are extremely efficient at absorbing a wide range of volatile organic compounds and so exposure of the canisters to such compounds was kept to a minimum. As mentioned above, laboratory sealing film was used at all times to prevent vapours coming into contact with the absorbent materials when the canister was not actually in the sampler. Since humans can be a significant source of such volatile compounds (natural body oils, perfumes from deodorants, some soaps, shampoos, etc) field staff were instructed to avoid use of these materials when servicing samplers. In addition, when handling the sampling heads, silicone rubber gloves were always worn.

Figure 15 on page 36 shows an exploded view of the sampling head. When handling this head in the field, it was necessary to disassemble the head as indicated in Figure 15. The disassembled pieces were placed on a 50 cm square sheet of stainless steel which had been rinsed in nanograde acetone followed by nanograde hexane immediately prior to use. This rinsing removed any traces of organic matter which might have been adhering to the sheet and which could have contaminated the sampling head. The exposed filter paper was removed using forceps which had also been rinsed in the above solvents. This paper was replaced in the aluminium foil wrap it had been supplied in by the laboratory and which had been retained since that filter paper had been installed on the previous visit. When the exposed canister was removed from the sampling head, it was immediately sealed at both ends with laboratory sealing film. Prior to installing the new canister, all parts of the sampling head were rinsed in the above solvents. The sealing film was removed from the new canister which was then rapidly installed in the sampling head which in turn was rapidly re-assembled. The new filter paper was taken from its supplied foil wrap and using only washed forceps, was placed into position on the supporting mesh. The filter holding ring was then locked in position. The aluminium foil wrap was carefully re-folded and put aside ready to receive the filter once it had been used.

Both the canisters and the filter papers had unique identifying numbers allocated to them. When exchanging canisters and filters in the field, careful note of identifying numbers and times and dates of installation/removal were made for later entry in the database (see Appendix F). The identifying number on the canister was written on a label affixed to it, whereas for the filter, the identifying number was written on the foil wrap. It was thus crucial that the foil wrap be retained to re-wrap the exposed filter in each case.

A spare sampling head was available which permitted an assessment of the effectiveness of these handling procedures. Over the first few months of the overall sampling program, the spare head, with a new canister and filter in each case, was left in the sampler housing next to the operational head. This was retrieved when the site was next visited to exchange canisters and filters. This ‘handling blank’ was handled and analysed identically to exposed filters except that it was not exposed to the pumped air flow. In all, six ‘handling blanks’ were prepared, two at each of the sites. In five of the six ‘handling blanks’, all dioxin congeners or congener groups were reported to be below the laboratory detection limit. The use of ‘handling blanks’ was discontinued once it became apparent that contamination was not occurring.

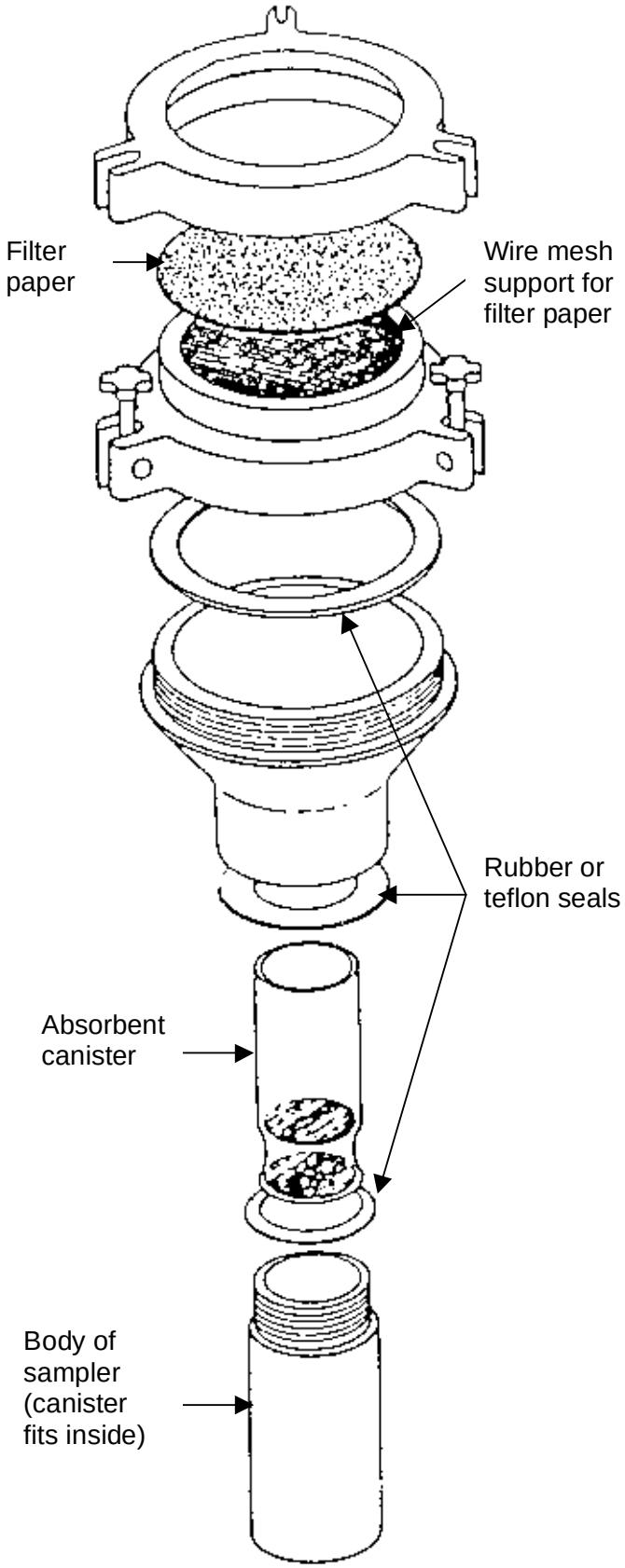

Figure 15: Exploded view of the high volume air sampler head

Appendix E—Analytical methods

E1. Collection media preparation

All absorbent cartridges and filters were prepared by the laboratory which conducted the analyses viz ESR/AgriQuality, of Wellington New Zealand.

PUF, XAD-2 resin and GF/C filters were precleaned prior to use. PUF discs as supplied (General Metal Works) were subjected to Soxhlet extraction for 20 hours with toluene (twice) then dried under vacuum. Resin (Supelco) was washed on a glass sinter funnel (16–20 times) with hot distilled water, then subjected to Soxhlet extraction for 20 hours with methanol, 20 hours with dichloromethane (DCM) and a further 20 hours with fresh DCM. The resin was dried in a fluid bed apparatus using oxygen-free nitrogen, passed first through a bed of activated charcoal.

The PUF and XAD-2 resin were packed into a cleaned glass sample cartridge as: bottom PUF, layer of XAD-2 resin, top PUF. The packed cartridge was spiked with a range of isotopically labelled PCDD, PCDF standards, (Wellington Laboratories-Ontario, Canada) prior to the collection of the sample. The nominal amounts of each surrogate standard added are given in Table 5. The sample cartridge was labelled with a unique identification number. The cartridge was sealed at each end with laboratory sealing film and then wrapped in bubble-wrap plastic for transportation to the NSW EPA. Upon receipt by the EPA, canisters were stored, as packed, in a freezer until required in the field.

GF/C filters (1.2 µm mesh) were precleaned by Soxhlet extraction with toluene for 20 hours and dried. Each filter was weighed, wrapped in hexane-rinsed aluminium foil and given a unique identification number prior to shipment to the NSW EPA.

Table 5: Nominal amounts of isotopically labelled surrogate standards added to each PUF/XAD-2 cartridge pre-sampling

$^{13}C_{12}$ PCDD congener	ng added	$^{13}C_{12}$ PCDF congener	ng added
2,3,7,8-TCDD	0.5	2,3,7,8-TCDF	0.5
1,2,3,7,8-PeCDD	0.5	1,2,3,7,8-PeCDF	0.5
1,2,3,4,7,8-HxCDD	0.5	2,3,4,7,8-PeCDF	0.5
1,2,3,6,7,8-HxCDD	0.5	1,2,3,4,7,8-HxCDF	0.5
1,2,3,4,6,7,8-HpCDD	0.5	1,2,3,6,7,8-HxCDF	0.5
OCDD	1	2,3,4,6,7,8-HxCDF	0.5
		1,2,3,7,8,9-HxCDF	0.5
		1,2,3,4,6,7,8-HpCDF	0.5
		1,2,3,4,7,8,9-HpCDF	0.5

E2. Sample preparation

Following sample collection and receipt at the laboratory, samples were stored at 4 °C pending analysis. Each ambient air sample consisted of a single sample cartridge holding the PUF/XAD-2 adsorbent and a single filter. Each filter was dried to constant weight in a desiccator, weighed and the particulate content determined gravimetrically (see Figure 16 on page 38).

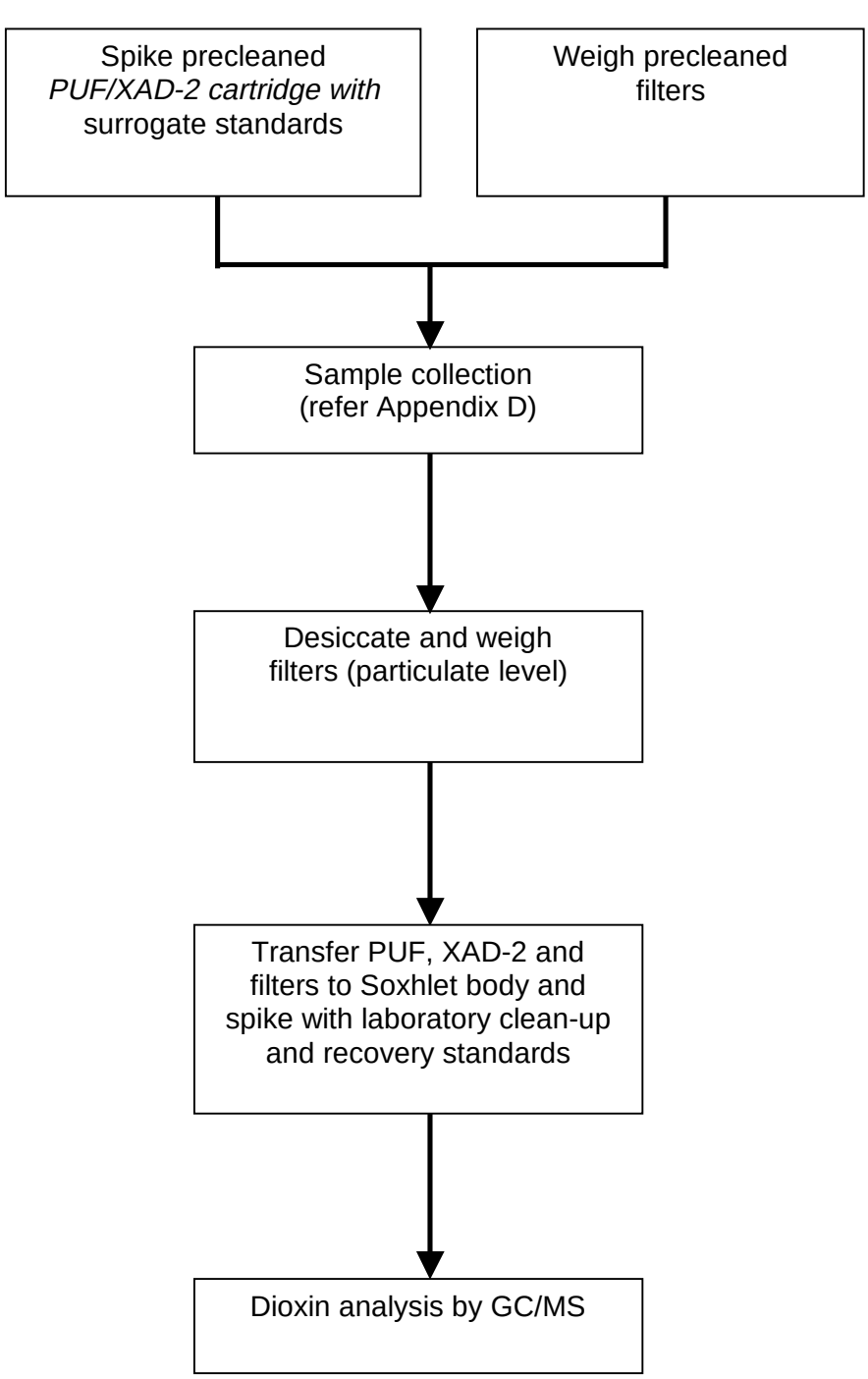

Figure 16: Sample collection and analysis scheme

E3. Sample extraction

PUF is an extremely efficient absorbent for a broad range of chlorinated organic compounds including chlorinated pesticides, chlorophenols, polychlorinated biphenyls and dioxins. The sample extraction and purification steps were only conducted for dioxins.

The PUF and XAD-2 adsorbents were removed from the glass cartridge and, along with the filters, were loaded into a Soxhlet body and spiked with an isotopically labelled extraction and clean-up recovery standard. The extraction and clean-up recovery standard added was 0.4 ng of $^{37}Cl_4$ 2,3,7,8-TCDD. The sample was Soxhlet extracted for 16 hours with ethanol/toluene (68:32).

The ethanol/toluene extracts were reduced using rotary evaporation. The ethanol/toluene extract was solvent-exchanged to hexane dried (anhydrous Na_2SO_4), and made up to volume with hexane.

The extract was then partitioned with concentrated sulphuric acid, washed with water, dried (anhydrous Na_2SO_4) and reduced by rotary evaporation. The extract was further purified by column chromatography as follows:

- acid and base modified silica gel (eluent: hexane)
- alumina (neutral) (eluent: hexane, 1:20 diethyl ether/hexane, diethyl ether)
- Carbopack C (18% dispersed on Celite 545) (eluent: hexane, 1:1 DCM/cyclohexane, 15:4:1 DCM/methanol/toluene, toluene)

Following purification, a volume of $^{13}C_{12}$ labelled laboratory recovery spike (1,2,3,4-TCDD and 1,2,3,7,8,9-HxCDD) in tetradecane was added and the extract was reduced by rotary evaporation, blown down gently under a stream of nitrogen, and transferred to a vial for PCDD and PCDF analysis using capillary gas chromatography-high resolution mass spectrometry (GC/MS).

Extracts were analysed by GC/MS on an HP5890 Series II Plus GC interfaced to a Micromass Autospec Ultima high resolution mass spectrometer. All extracts were run on an Ultra2 or ZB-5 capillary column. If a peak was detected at the correct retention times for 2,3,7,8-TCDF, 2,3,7,8-TCDD, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF or 1,2,3,7,8,9-HxCDD, the extract was re-analysed on a SP2331 capillary column for full congener-specific quantification. Chromatographic conditions are given below (in Table 6), and the mass spectral ions monitored are detailed in Table 7.

Table 6: Chromatographic conditions

Column	25 m Ultra2 or ZB-5	60 m SP2331
Carrier gas head pressure	150 kPa	200 kPa
Injector temperature	260 ^{0}C	270 ^{0}C
Injection	2 µl splitless	2 µl splitless
Temperature program	Initial temp 210 ^{0}C (hold 4 min), 3 ^{0}C min -1 to 275 ^{0}C (11 min).	Initial temp 210 ^{0}C (hold 3.3 min), 3 ^{0}C min -1 to 255 ^{0}C (40 min).

Table 7: Ions monitored for dioxins

Congener group	^{12}C Quantification ion (m/z)	^{12}C Confirmation ion (m/z)	^{13}C Quantification ion (m/z)	^{13}C Confirmation ion (m/z)
TCDF	305.8987	303.9016	317.9389	315.9419
TCDD	321.8936	319.8965	333.9339	331.9368
PeCDF	339.8597	337.8626	351.9000	349.9029
PeCDD	355.8546	353.8575	367.8949	365.8978
HxCDF	373.8207	375.8178	385.8610	387.8580
HxCDD	389.8156	391.8127	401.8559	403.8530
HpCDF	407.7818	409.7788	419.8220	421.8191
HpCDD	423.7767	425.7737	435.8169	437.8140
OCDF	443.7398	441.7428		
OCDD	459.7347	457.7377	471.7750	469.7780

E4. Analyte identification and quantification criteria

For positive identification and quantification the following criteria must be met:

- the retention time of the analyte must be within one second of the retention time of the corresponding $^{13}C_{12}$ surrogate standard
- the ion ratio obtained for the analyte must be ±10% of the theoretical ion ratio
- the signal to noise ratio must be greater than 3:1
- levels of dioxin congeners in a sample must be greater than five times any level found in the corresponding laboratory blank analysed (three times the level in the blank for OCDD)
- surrogate standard recoveries must be in the range 25–150%.

E5. Quantification

Quantification was by the isotope dilution technique using the surrogate standards listed in Table 5. Relative response factors (RRFs) were calculated for each targeted analyte from a series of calibration standards analysed under the same conditions as the samples. Non 2,3,7,8-substituted dioxin congeners were quantified using the RRF of the first eluting surrogate standard in each mass spectral group. Targeting of all analytes was performed by the MS software (OPUS). Text files created by OPUS were electronically transferred to a customised spreadsheet for further data reduction and preparation of the final analytical report.

E6. Limits of detection

If no peak was distinguishable above the background noise at the retention time for a targeted analyte, the area was recorded as being less than the limit of detection. The limit of detection was calculated by multiplying by three the area of the section of baseline noise at the retention time of the analyte. If a peak was present at the correct retention time for the targeted analyte but failed to meet all analyte identification and quantification criteria, the area of that analyte was recorded and the calculated concentration was reported as a limit of detection.

E7. Surrogate standard recoveries

The recovery of each isotopically labelled surrogate standard (Table 5) and extraction and clean-up recovery standard, was calculated from the ratio of the area of the surrogate standard in the sample (normalised to its laboratory recovery spike) to the area of the surrogate standard in the calibration standards (normalised to its laboratory recovery spike).

E8. Quality control

- The batch size was typically 8–10 samples.
- A laboratory blank was analysed with each batch of samples.
- The GC/MS resolution, performance and sensitivity were established for each MS run.
- The recoveries of all isotopically labelled surrogate standards were calculated and reported.

Confidence levels for each congener are presented in Table 8.

Table 8: Confidence levels

Congener	Precision ± 2SD	Congener	Precision ± 2SD
2,3,7,8-TCDD	14%	2,3,7,8-TCDF	14%
1,2,3,7,8-PeCDD	5%	1,2,3,7,8-PeCDF	25%
1,2,3,4,7,8-HxCDD	27%	2,3,4,7,8-PeCDF	20%
1,2,3,6,7,8-HxCDD	12%	1,2,3,4,7,8-HxCDF	9%
1,2,3,7,8,9-HxCDD	12%	1,2,3,6,7,8-HxCDF	14%
1,2,3,4,6,7,8-HpCDD	10%	1,2,3,7,8,9-HxCDF	14%
OCDD	11%	2,3,4,6,7,8-HxCDF	10%
		1,2,3,4,6,7,8-HpCDF	6%
		1,2,3,4,7,8,9-HpCDF	10%
		OCDF	24%

E9. Data reporting

The data for each air sample is for the total sample (i.e. combined gaseous plus particulate phases). Data are corrected for recovery of $^{13}C_{12}$ surrogate standards. Laboratory data for detected analytes are reported to two or three significant figures and non-detected analytes are reported to one significant figure. Concentrations presented in this report are rounded to two significant figures.

Appendix F—Database design and operation

F1. Input data sources and forms

Data for entering into the database came from four separate sources:

a) manual records—these include all details relating to samples, data logger memory pack usage and visual observations of Magnehelic gauge readings

b) spreadsheet records of sample chemical analyses as provided by the laboratory (ESR, Wellington, New Zealand)
c) data logger records of digital counts relating to high volume air sampler pressure transducer voltages (see Appendix C).
d) calibration data—these include the calibration data for air flow and data logger/pressure transducer response (see Appendix C); these data also include basic information which should only need to be entered very infrequently such as instrument locations and data logger locations.

F2. Manual records

Manual records consisted of:

- samples (date and time of deployment and retrieval, site ID, canister and filter paper ID, motor run-time meter readings)
- data logger memory pack usage (site ID, dates and times of deployment and retrieval, memory pack ID number)
- visual observations of Magnehelic gauge readings.

Each of these types of records has its own table in the database. Data were entered into these tables on each occasion when a field visit was completed.

F3. Chemical analysis records

Results of chemical analyses were provided by ESR in the form of Excel spreadsheets. After some minor re-arrangement, the results could be directly imported into the relevant database table using a simple database query.

F4. Data logger records

As indicated in Appendix C, the data logger records consisted of a sequence of 24 pairs of time and count readings with each group of 24 readings headed by a new date reading. The time and date values were in an internal data logger format which required some pre-processing before they could be stored in the database. This pre-processing was accomplished in a spreadsheet template from which the data could be directly introduced into the relevant database table using a simple database query.

F5. Calibration data

These data were manually entered into the database tables. The nature of these data was that they were expected not to alter frequently, if at all, during the conduct of the sample collection and thus data entry was only expected to occur a few times over that period. Data in this category included details of instrument locations, installation and retrieval information regarding data loggers, instrument air flow calibration data and data logger/pressure transducer calibration data.

F6. Overall database operation

The overall database structure showing individual tables, the data stored within those tables and the relationships between the tables is shown in Figure 17.

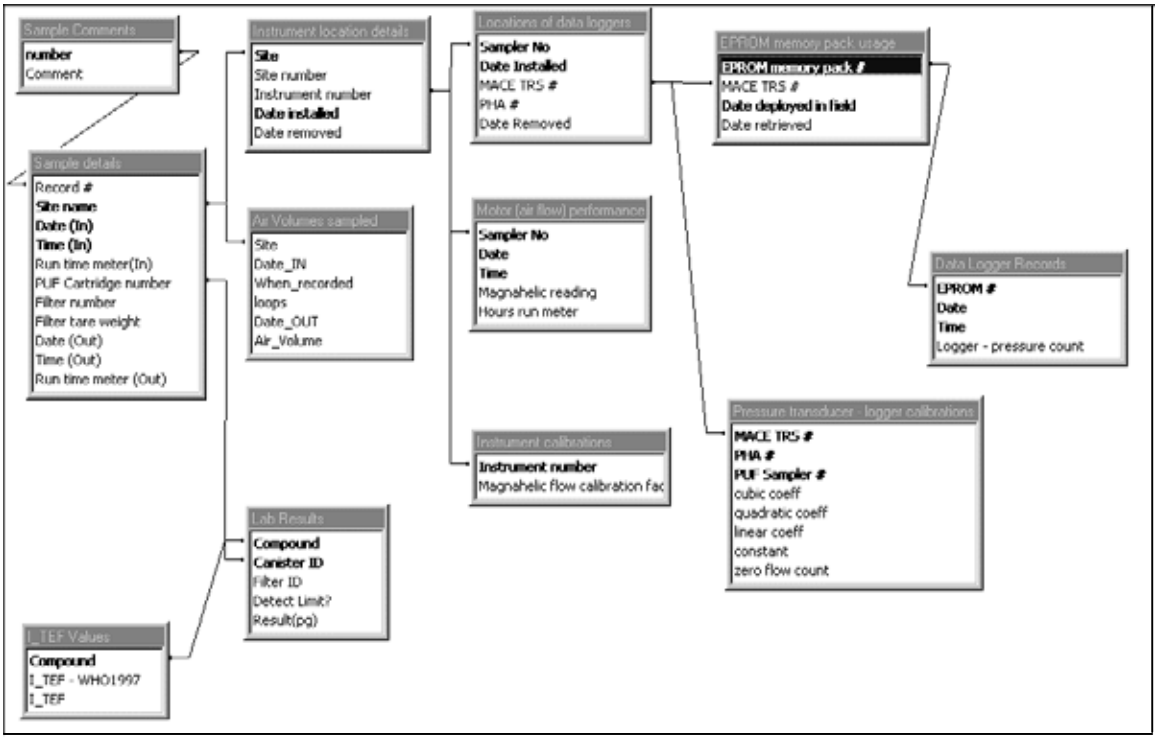

Figure 17: Database structure

Figure 18 outlines the logic flow in the calculation of the air concentrations. The text boxes at the top of the page, each with a bold text heading, represent different data input streams as outlined in sections F1 to F5 above. The text in italics in these boxes indicates the relevant data content in each stream. The flow of the arrows and lines indicates the way in which these individual data streams are joined and the nature of the intermediate data which are created. The calculation starts at the top right hand corner and works down. The process is as follows:

- the data logger count is converted to a Magnehelic gauge reading by the application of the data logger/pressure transducer calibration equation
- these calculated data are combined with the manual Magnehelic gauge readings to produce an intermediate file of date, time and gauge readings
- the instrument flow calibration factor is then used to convert these gauge readings to air flow rates, with their corresponding dates and times
- for each sample, these date, time and air flow readings are integrated to produce the total air volume which was sampled
- the chemical analysis data consist of the mass of each congener contained within the sample canister and its associated filter paper. These masses are converted to concentrations by dividing by the total sampled air volume
- the toxic equivalents were derived by multiplying the congener concentrations by their appropriate I-TEF
- the details relating to the individual samples are then used to ensure that the final reported air concentrations relate to a sample from a specific site and for a specific sampling period.

All these calculations were carried out in the database and each process was checked manually on a small data subset using spreadsheets.

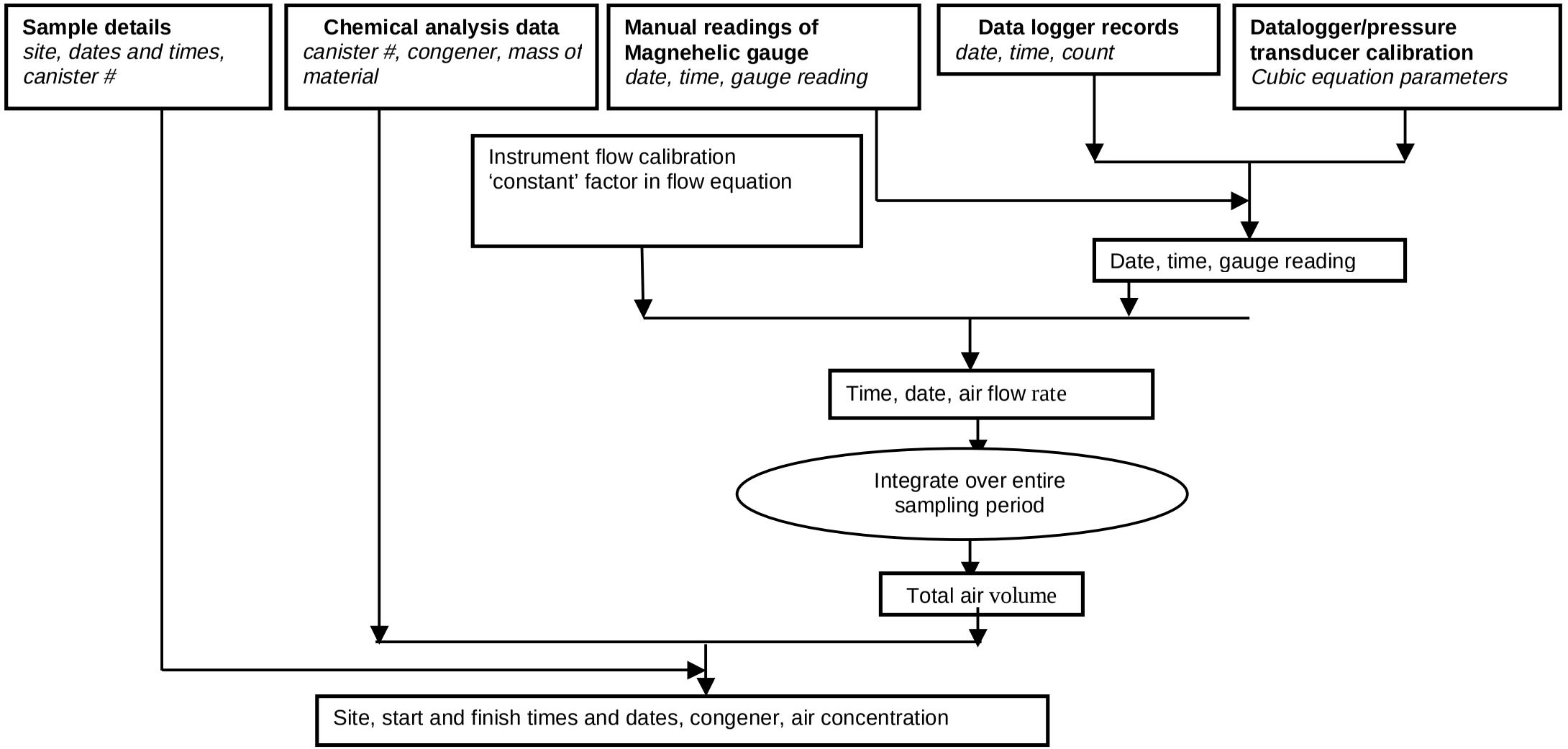

Figure 18: Database calculation logic flow

Appendix G—Number and percentage of samples below the detection limit

Congener	Siding Spring	Warrawong	Westmead
	n=15	n=33	n=34
2,3,7,8-TCDD	14 (93%)	17 (52%)	19 (56%)
1,2,3,7,8-PeCDD	14 (93%)	16 (48%)	13 (38%)
1,2,3,4,7,8-HxCDD	14 (93%)	20 (61%)	14 (41%)
1,2,3,6,7,8-HxCDD	13 (87%)	16 (48%)	12 (35%)
1,2,3,7,8,9-HxCDD	13 (87%)	16 (48%)	13 (38%)
1,2,3,4,6,7,8-HpCDD	11 (73%)	6 (18%)	3 (9%)
OCDD	11 (73%)	9 (27%)	3 (9%)
2,3,7,8-TCDF	7 (47%)	0 (0%)	2 (6%)
1,2,3,7,8-PeCDF	14 (93%)	0 (0%)	4 (12%)
2,3,4,7,8-PeCDF	14 (93%)	0 (0%)	3 (9%)
1,2,3,4,7,8-HxCDF	13 (87%)	0 (0%)	3 (9%)
1,2,3,6,7,8-HxCDF	13 (87%)	0 (0%)	3 (9%)
1,2,3,7,8,9-HxCDF	14 (93%)	25 (76%)	24 (71%)
2,3,4,6,7,8-HxCDF	13 (87%)	0 (0%)	3 (9%)
1,2,3,4,6,7,8-HpCDF	12 (80%)	2 (6%)	3 (9%)
1,2,3,4,7,8,9-HpCDF	14 (93%)	11 (33%)	13 (38%)
OCDF	12 (80%)	5 (15%)	3 (9%)
Total 2,3,7,8-congeners (17)	216 of 255 (85%)	143 of 561 (25%)	138 of 578 (24%)

Notes: if equal to 0 then the congener was detected in every sample at that site
n = number of samples.

Appendix H—2,3,7,8-congener concentrations and I-TEQS

Siding Spring			Warrawong			Westmead		
Middle sample date	Total 2,3,7,8-congener concentration fg m^{-3}	TEQ fg m^{-3}	Middle sample date	Total 2,3,7,8-congener concentration fg m^{-3}	TEQ fg m^{-3}	Middle sample date	Total 2,3,7,8-congener concentration fg m^{-3}	TEQ fg m^{-3}
9 Dec 98	28	0.6	2 Dec 98	200	16	2 Dec 98	290	7.7
			24 Dec 98	73	6.0	14 Dec 98	570	18
30 Dec 98	28	1.1	5 Jan 99	170	7.6	24 Dec 98	150	3.3
			18 Jan 99	120	7.6	5 Jan 99	160	2.7
28 Apr 99	12	0.7	27 Apr 99	130	8.4	22 Apr 99	380	7.9
			10 May 99	250	13	4 May 99	780	20
22 May 99	12	0.3	24 May 99	260	15	17 May 99	1100	31
			8 Jun 99	170	13	29 May 99	1100	39
16 Jun 99	6.0	0.4	22 Jun 99	170	13	10 Jun 99	890	32
			3 Jul 99	320	20	22 Jun 99	860	35
11 Jul 99	3.1	0.2	13 Jul 99	190	15	3 Jul 99	1500	53
			25 Jul 99	320	16	15 Jul 99	700	23
5 Aug 99	13	0.5	5 Aug 99	55	7.6	28 Jul 99	830	32
			17 Aug 99	260	13	9 Aug 99	850	24
29 Aug 99	43	0.4	28 Aug 99	250	11	20 Aug 99	680	23
			10 Sep 99	190	17	31 Aug 99	290	8.1
21 Sep 99	33	0.7	22 Sep 99	150	11	11 Sep 99	450	17
			2 Oct 99	99	5.0	23 Sep 99	410	13
17 Oct 99	9	0.4	14 Oct 99	130	8.8	5 Oct 99	430	12
			27 Oct 99	140	5.8	16 Oct 99	230	5.5
			7 Nov 99	81	4.1	28 Oct 99	260	4.7
11 Nov 99	26	2.4	18 Nov 99	110	6.8	9 Nov 99	320	6.9
			1 Dec 99	72	5.3	21 Nov 99	180	4.4
			14 Dec 99	120	10	2 Dec 99	230	2.7
21 Dec 99	9.7	0.3	28 Dec 99	57	3.8	16 Dec 99	150	2.3
			10 Jan 00	130	7.9	31 Dec 99	83	3.7
17 Jan 00	10	0.4	23 Jan 00	71	4.1	13 Jan 00	110	2.3
			3 Feb 00	300	14	25 Jan 00	120	2.3
10 Feb 00	11	0.5	16 Feb 00	40	3.0	7 Feb 00	290	4.0
			27 Feb 00	230	16	18 Feb 00	110	3.8
7 Mar 00	14	0.4	9 Mar 00	120	3.7	29 Feb 00	240	3.1
			21 Mar 00	110	4.9	12 Mar 00	820	7.5
			2 Apr 00	230	17	23 Mar 00	170	4.8
						4 Apr 00	500	15