

ANNEX 1
(AIR)

GLOBAL MONITORING PLAN
FOR PERSISTENT ORGANIC POLLUTANTS

UNDER THE STOCKHOLM CONVENTION ARTICLE 16 ON EFFECTIVENESS EVALUATION

FIRST REGIONAL MONITORING REPORT

WESTERN EUROPE AND OTHER STATES GROUP (WEOG) REGION

APRIL 16 2009

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A1. Air: Programme Summaries

The following compilation of programme summaries for international and national monitoring efforts for persistent organic pollutants (POPs) is the basis for Chapter 5 of the WEOG region report. The programme summaries were prepared according to a template provided by the regional organizational group (ROG). The summaries were submitted by program leads/managers and have not been edited by the ROG. For further information, please contact the program managers/leads or refer to the appropriate contact information provided in each summary.

A1.1 International Monitoring Programmes for POPs in Air

A1.1.1 AMAP-EMEP

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Persistent organic pollutants (POPs) in the Atmosphere

Evaluation based upon established POP monitoring of the European Monitoring and Evaluation Programme (EMEP) and the Arctic monitoring and Assessment programme (AMAP)

Key Message

The established international atmospheric monitoring initiatives under the umbrella of the European Monitoring and Evaluation programme (UNECE/CLRTAP-EMEP or just EMEP) and the Arctic Monitoring and Assessment Programme (AMAP) include the longest time series for POPs in atmospheric samples. This scientific information has been used as the basis for a first evaluation of temporal and spatial trends within the WEOG region. Specific emphasis has been laid upon potential regulatory effects after the inauguration of the Stockholm convention for the global regulation of POPs.

Background

After the identification of adverse effects on human and wildlife population caused through unintended long-term exposure to persistent organic pollutants (POPs), the regional monitoring programs EMEP and AMAP have included selected POPs into their list of target chemicals. Whereas EMEP mainly focus on atmospheric transport and deposition, AMAP includes also other environmental compartments like biota, the marine and terrestrial environment etc. into their monitoring portfolio. Since the European atmospheric Arctic monitoring data are reported

both to the AMAP and the EMEP databases, we, thus, report AMAP and EMEP as one fact sheet for the here-presented Efficacy assessment.

Atmospheric levels for the 12 priority POPs, namely aldrin, chlordane, dichlorodiphenyltrichloroethane (DDT), dieldrin, endrin, heptachlor, mirex, toxaphene, polychlorobiphenyls (PCBs), hexachlorobenzene, dioxins and furans, are evaluated for temporal and spatial trends in the EMEP and AMAP atmospheric monitoring databases.

The main objective of the EMEP program is to regularly provide Governments and subsidiary bodies under the LRTAP Convention with qualified scientific information to support the development and further evaluation of the international protocols on emission reductions negotiated within the Convention. The EMEP vision is to be the main science based and policy-driven instrument for international cooperation in atmospheric monitoring and modeling activities, emission inventories and projections, and integrated assessment to help solve transboundary air pollution problems in Europe. Initially, the EMEP program focused on evaluation of transboundary atmospheric transport of more “classical” air pollutants, such as acidifying substances, and about a hundred different monitoring stations exists across the EMEP region. Later, the scope has widened to include substances like POPs, but only a few of all EMEP stations are reporting data for POPs in air and/or deposition, see Figure 1 which displays a map of the EMEP POPs network for the latest year data has been reported (Aas and Breivik, 2007). The geographical scope of EMEP - or the area where monitoring is carried out – has also expanded in recent years to include new countries in the EECCA region (East Europe, Caucasus and Central Asia).

POPs including polycyclic aromatic hydrocarbons (PAHs) are only reported from 20 monitoring stations (14 European countries). Due to statistical restrictions, temporal trends are only assessed for stations that have reported more than 4 years of air concentration data. From the 20 UNECE-EMEP stations reporting atmospheric POPs, only 7 meet the needs of the here-performed trend assessment.

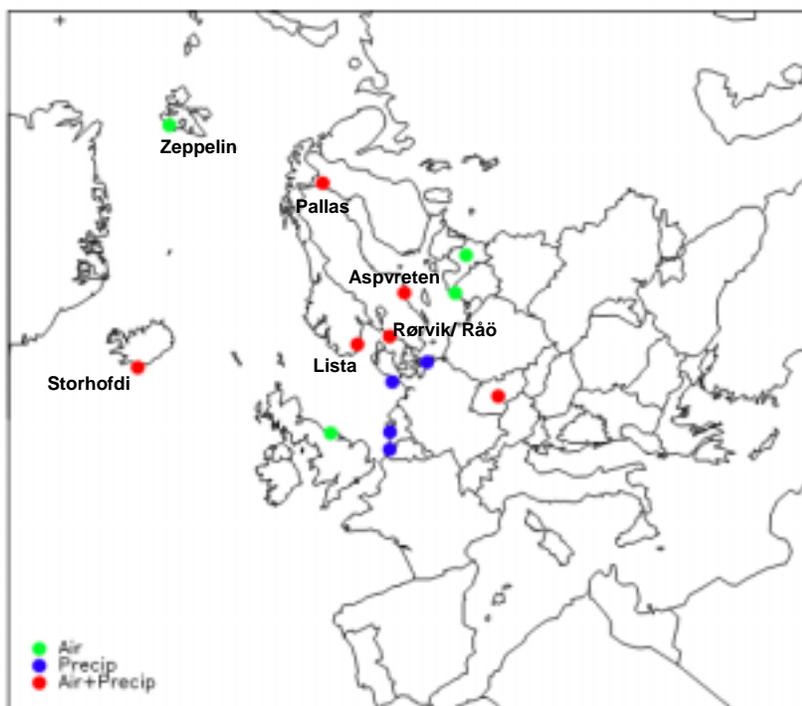


Figure 1: Monitoring network of POPs in EMEP, 2005 (Aas and Breivik, 2007). All Monitoring stations used for the assessment are marked. Alert as only non-EMEP station is not presented on the map.

Long-term air monitoring data for the AMAP station of Alert in the Canadian high Arctic are also reported here, in addition to the 7 EMEP established monitoring stations. The list of the AMAP and EMEP stations providing data for the here-presented evaluation is given in table 1. In addition to EMEP, the stations Storhofdi, Pallas and Zeppelin report their monitoring data also into the AMAP database. As part of AMAP, atmospheric measurements of POPs were conducted at Nuuk in Greenland (operated by Danish Environmental Protection Agency) in 2004-2005. Air concentration data from this station are also included in the current assessment.

In addition to the high-volume active air sampling monitoring network maintained by AMAP and EMEP, a global passive atmospheric monitoring network for POPs has been established (Global Atmospheric Passive Sampling Network = GAPS). GAPS will summarize their findings in a separate executive summary.

Table 1: Monitoring locations used for the here performed evaluation

Station name	Country	Location	Monitoring period	Priority POPs monitored
Alert	Canada	82 30 N, 62 20 W	1992 - 2005	Chlordanes, Mirex, Heptachlor, Heptachlor epoxide, Endrin, Dieldrin,

				dichlorodiphenyltrichloroethane-derivatives (DDT), mirex, PCB-congeners, Hexachlorobenzene (HCB)
Pallas/Särkijärvi	Finland	68 00 N 24 09 E	1995 - 2005	DDT, PCBs, HCB
Storhofdi	Island	63 24 N 20 17 W	1995 - 2005	DDT, PCBs, HCB
Zeppelin mountain	Svalbard/Norway	78 54 N 11 53 E	1993 - 2005	Chlordanes, DDTs, PCBs, HCB
Lista	Norway	58 6 N 6 34 E	1991 - 2003	HCB
Rörvik	Sweden	57 25 N 11 56 E	1994 - 2001	DDT, PCBs, HCB
Aspvreten	Sweden	58 48 N 17 23 E	1995 - 2005	DDT, PCBs, HCB
Råö	Sweden	57 23 N 11 54 E	2002 - 2005	DDT, PCBs, HCB
Nuuk	Greenland/Denmark	64 06 N 51 24 W	2004-2005	DDT, chlordanes, dieldrin, heptachlor epoxide

AMAP is an international organization established in 1991 to implement components of the Arctic Environmental Protection Strategy (AEPS). The primary function of AMAP is to advise the governments of the eight Arctic countries (Canada, Denmark/Greenland, Finland, Iceland, Norway, Russia, Sweden and the United States) on matters relating to threats to the Arctic region from pollution, and associated issues. AMAP is responsible for measuring the levels, and assessing the effects of anthropogenic pollutants in all compartments of the Arctic environment, including humans; documenting trends of pollution; documenting sources and pathways of pollutants; examining the impact of pollution on Arctic flora and fauna, especially those used by indigenous people; reporting on the state of the Arctic environment; and giving advice to Ministers on priority actions needed to improve the Arctic condition.

For EMEP, the POPs activities have three main pillars: (a) collection of emission data; (b) measurement of air and precipitation quality; and (c) modeling of atmospheric dispersion. Only the measurement activities related to POPs in air are discussed in the context of this report. The monitoring activities for POPs and other pollutants are coordinated by the Chemical Coordinating Centre of EMEP (EMEP-CCC). The main tasks of the EMEP-CCC include recommendation of methods to be employed in participating countries in their monitoring, quality assurance and training, data validation and reporting as well as data storage. The EMEP Chemical Coordinating Centre (EMEP-CCC) has been hosted by the Norwegian Institute for Air Research (NILU) since the beginning of the program in 1979. The data on POPs in air and precipitation from EMEP are publically available through a designated website where users may access and download the data (www.nilu.no/projects/ccc/emepdata.html). In addition, data reports are published each year (Berg et al 1996/1997/2000/2001/2002; Berg and Hjellbrekke, 1998; Aas and Hjellbrekke, 2003; Aas and Breivik 2004/2005/2006/2007).

Sampling

The standard recommended methods for sampling (and chemical analysis) for the EMEP measurement network are described in the on-line EMEP manual for sampling and analysis (www.nilu.no/projects/ccc/manual/index.html), and please refer to this manual for further details.

In brief, the methods and procedures are generally derived from the development and experience gained within EMEP as well as information provided by similar programs in North America, World Meteorological Organization, various research groups and various EMEP workshops (e.g. Lükeville, 1998).

As the purpose of EMEP is to provide Parties with information on concentrations of air pollutants in the context of long-range atmospheric transport, monitoring takes place at carefully selected background monitoring sites. A key goal is thus to obtain measurement data representative for the background air concentrations of a larger area. Detailed site criteria for EMEP stations have been developed and are described in the EMEP manual for sampling and analysis.

Within EMEP, it is furthermore recommended to use high-volume sampling (HVS) at all sites to determine concentrations of POPs in air. Although separate analysis of particle and gaseous concentrations are considered desirable, bulk concentrations are typically reported to minimize cost of analysis. Typically, a sampling duration of 24 to 48 hours are applied to balance the need for obtaining detectable amounts (i.e. sufficiently long sampling time) and to have the possibility to correlate the measurement results to air mass trajectories (i.e. sufficiently short sampling time). However, some stations use a longer sampling duration. The sampling frequency also varies from site to site and may typically be one sample per week or one sample per month.

A key advantage of the HVS approach in contrast to most passive air sampling (PAS) strategies is that it provides an actual quantitative measure of the air concentrations of POPs for a relatively short time-period. This information is essential in order to evaluate relevant features of operational models that are used within EMEP to calculate long-range atmospheric transport of POPs. Passive air sampling of POPs has so far not been recommended within EMEP, but is likely to be discussed and considered as a complementary sampling technique in future updates of EMEP monitoring strategies. In order to gain more experience with PAS, a campaign was coordinated by EMEP in 2006 in collaboration with the GAPS initiative and other research groups to evaluate potential limitations of the current EMEP POP measurement network (see Figure 1).

Sample analytical procedures

The recommended methods used for sample preparation and chemical analysis are described in the above-mentioned on-line EMEP manual for sampling and chemical analysis (www.nilu.no/projects/ccc/manual/index.html).

Data comparability

A key goal of the EMEP and the AMAP program is to obtain comparable data on concentrations of POPs and other pollutants in air and deposition as comparable measurements are essential to make regional assessments. An important tool to achieve this goal is the EMEP manual on sampling and analysis which has been developed with this in mind. Thus, participating laboratories are expected to follow the recommended guidelines for sampling and analysis as detailed in EMEP manual. This includes proper siting for representative measurements. Secondly, participating institutes or laboratories are encouraged to use the recommended field and laboratory methods described in the EMEP manual. However, participating institutes / laboratories may also use their own alternative methods, given that these can be shown to be equally reliable. At the national level, participants are expected to evaluate their data prior to submission and flag or deleted biased or erroneous data. The data should furthermore be

submitted to EMEP in a proper format along with necessary meta-data, such as information on methods used, detection limits, analytical precision and site information. Prior to being made available on the internet, further checks of data submissions are carried out at EMEP/CCC (e.g. checks for time trends etc.). In spite of this, it is still recognized that continuous efforts are needed to achieve comparable data and that comparison of data originating from different laboratories should be interpreted with caution (Manø and Schaug, 2003). Following recommendations of an expert meeting on POP measurements in air and precipitation (Lükewille, 1998), an analytical comparison of 20 different laboratories was arranged by EMEP/CCC in 2000 and 2001 (Manø and Schaug, 2003). This exercise included selected PCBs (28, 52, 101, 118, 138, 153 and 180), organochlorine pesticides (*p,p'*-DDT, *p,p'*-DDE, *trans*-chlordane, *cis*-chlordane, γ -hexachlorocyclohexanes (γ -HCH), α -HCH and HCB) as well as 19 individual polycyclic aromatic hydrocarbons (PAHs). A new analytical comparison is now being considered within EMEP, tentatively to be arranged in 2009.

Data storage.

A key goal of the EMEP and the AMAP atmospheric monitoring data is to collect and archive data on long-term temporal trends to evaluate the effectiveness of the protocols under the LRTAP Convention. The data from the EMEP stations are submitted using a specified template and stored at a database at EMEP/CCC as well as the AMAP database. This database contains POP measurement data as well as metadata dating back to 1991. The AMAP and EMEP database is hosted by the Norwegian Institute for Air Research (NILU), which is among the largest institutions within the organization of atmospheric ground-based measurements.

Results.

Only selected compound groups identified as the 12 priority POPs under the Stockholm convention are regularly monitored in the AMAP/EMEP atmospheric monitoring programs as summarized in table 1. Continuous monitoring data exists only for PCBs, HCB and DDT for most stations. Three of the stations (Alert, Zeppelin, Storhofdi) also report level on chlordanes (*trans*- and *cis* isomers of chlordane and nonachlor). Air concentrations of HCB and PCBs were not reported at Nuuk but those of *trans*- and *cis*-chlordane, heptachlor epoxide and dieldrin were included (Bossi et al., 2008). Alert also includes heptachlor, heptachlor epoxide, mirex, dieldrin and endrin in the monitoring program. No continuous monitoring data for Toxaphene[®] as well as polychlorinated dioxins and furans (PCDD/F) exists in the EMEP and AMAP atmospheric monitoring databases. Toxaphene[®] has been measured at Alert in 2005 but the concentrations were generally found to be below detection limits are, thus, not reported here.

PCBs is the most investigated group of organic pollutants. This is also true for the atmospheric environment. Concentration values for PCB are available from 7 of the 8 AMAP and EMEP stations included in this evaluation (table 2). **Hexachlorobenzene (HCB)** is known to be ubiquitously distributed (table 3). The concentration levels seems to be in the same order of magnitude for all stations including the high Arctic except for Storhofdi were considerably lower levels are reported (3-10 times lower). For all stations except for Alert and Nuuk, all air samples have been take as 48h composite samples (1 glass fiber filter and two Polyurethane plugs) representing 1000 – 1200m³ air. For those stations no breakthrough for HCB is reported. At Alert, however, each air sample was taken over a period of 7 days, i.e. ~168 h per sample per week, with one glass fiber filter and 2 polyurethane foam plugs (PUF). Analysis of the back

PUF has shown that breakthrough (with >33 % of the total amount of HCB trapped found in the back PUF) occurred in about 20-30 % of all samples each year. Therefore, the concentrations at this location may be underestimated. At Nuuk, samples were taken over a period of about 14 days twice a month. Significant breakthrough of HCB was detected in the back PUF in many samples collected at this location and thus the concentrations were not reported (Bossi et al., 2008).

DDT derivatives are reported differently from the stations, thus, data are difficult to compare (table 4). However, there seem to be pronounced south – north gradient, with highest values in the middle latitude and lower concentrations in the North.

Chlordanes are reported from 3 stations (table 5). However, Storhovdi only reports values for *trans*-chlordane and *cis*-nonachlor. Thus, the comparability is restricted. However, the levels reported seem to be in the same order of magnitude for all 3 stations. This is consistent with the finding of Su et al. (2008) which reported seasonally and spatially uniform concentrations of chlordane-related compounds among 6 AMAP Arctic stations in 2000-2003.

Table 2: Annual average PCB concentrations from 7 AMAP and EMEP stations. Concentrations are given in [pg/m³]. Number of congeners contributing to the sum is given in brackets. n.a. = not available

Please note: Råö, Rørvik, Aspreveten and Pallas reported 7 standard PCB congeners only (numbers in parenthesis). Storhofdi, Zeppelin, and Alert PCB data are based upon the sum of 10 congeners (PCB 28, 31, 52, 101, 105, 118, 138, 153, 156, 180).

Note that for Alert, the laboratory reports PCB 28 as coeluting with PCB 31 and PCB 138 as coeluting with PCB 163 starting from 2002. Therefore, the concentrations shown here for 2002 and thereafter include PCB 163.

Year/Location	Råö (7)	Rørvik (7)	Aspreveten (7)	Storhofdi (10)	Pallas (7)	Zeppelin (10)	Alert (10)
1998	n.a.	14,16	7,79	19	6,21	34	4,2
1999	n.a.	12,31	0,00	17	7,53	23	5,8
2000	n.a.	13,52	13,11	5,7	6,40	14	2,8
2001	n.a.	8,88	6,87	8,7	5,37	9,9	2,2
2002	16,30	n.a.	5,85	6,7	6,16	7,6	1,1
2003	12,17	n.a.	12,65	5,1	5,12	6,3	3,9
2004	9,90	n.a.	6,67	11	5,47	5,7	2,3
2005	8,91	n.a.	4,55	7,0	5,12	7,5	4,9
2006	n.a.	n.a.	n.a.	n.a.	n.a.	9,0	n.a.

Table 3: Annual average HCB concentrations from 4 AMAP and EMEP stations. Concentrations are given in [pg/m³]. n.a. = not available

Year/location	Lista	Storhofdi	Zeppelin	Alert
1998	92,64	14	82,03	70
1999	82,96	6,0	87,72	69
2000	54,46	5,8	55,66	57
2001	50,92	6,8	54,72	69
2002	57,32	3,7	57,12	29
2003	58,61	4,3	53,94	49
2004	n.a.	2,8	65,04	29
2005	n.a.	2,0	67,38	52
2006	n.a.	n.a.	71,79	n.a.

Table 4: Annual average Sum DDT concentrations from 6 AMAP and EMEP stations. Concentrations are given in [pg/m³]

n.a. = not available

Please note: Aspvreten only reports values for p,p'-DDE. Therefore the data are not listed. Råö, Rørvik and Pallas reports only the p,p'-derivatives for DDT, DDE and DDD whereas Storhofdi reports all isomers except o,p'-DDD. Thus, the comparison of sum values is limited.

Year/location	Råö	Rørvik	Storhofdi	Pallas	Zeppelin	Alert	Nuuk
1998	n.a.	2,65	2,96	0,86	1,90	1,26	
1999	n.a.	4,60	0,16	4,41	2,04	0,95	
2000	n.a.	5,56	0,57	1,21	1,14	0,96	
2001	n.a.	n.a.	0,75	0,00	1,36	0,58	
2002	3,99	n.a.	0,54	0,63	1,41	1,05	
2003	4,08	n.a.	1,05	0,86	1,43	0,93	
2004	3,26	n.a.	0,74	0,78	1,04	1,6	0,97
2005	3,79	n.a.	0,55	0,94	1,01	0,99	
2006	n.a.	n.a.	n.a.	n.a.	1,66	n.a.	

Table 5: Annual average Sum Chlordanes (Sum *trans*-/ *cis*- chlordane and nonachlor) concentrations from 3 AMAP and EMEP stations. Nuuk reports *trans*- and *cis*-chlordane only; therefore the sum given here is of these 2 isomers. Concentrations are given in [pg/m³]. n.a. = not available. Please note: Storhofdi reported only *trans*-chlordane and *cis*-nonachlor.

Year/Location	Zeppelin	Storhofdi	Alert	Nuuk
1998	1,37	0,43	1,81	
1999	1,72	0,81	1,29	
2000	1,39	1,08	1,11	
2001	1,82	0,95	0,95	
2002	1,75	0,43	1,18	
2003	1,60	0,63	1,20	
2004	1,55	0,48	2,13	0,86
2005	1,47	0,16	1,28	
2006	1,39	n.a.	n.a.	

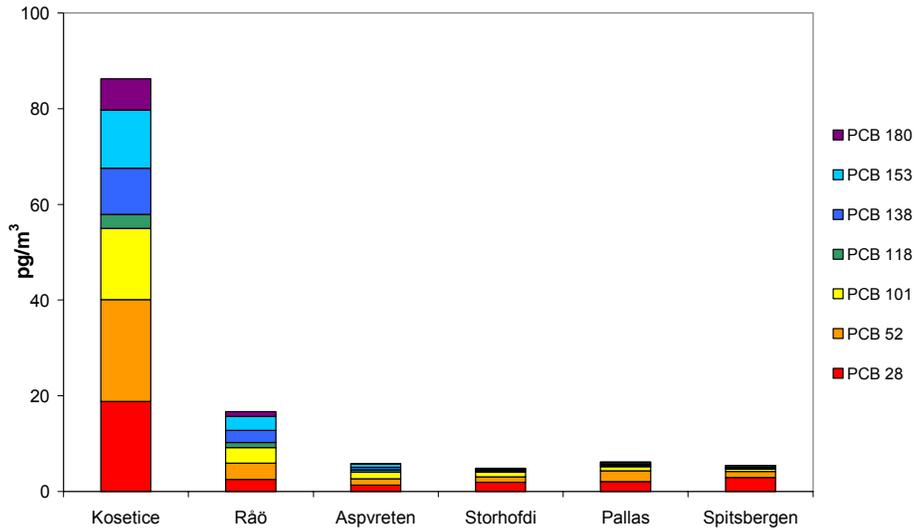
Levels for endrin, aldrin, mirex and heptachlor were only reported from Alert (Canada). The reported levels are usually below detection or very close to detection, except for occasional high concentration episodes. Therefore, these data were not used for further assessment.

Discussion

Sources and transport

Atmospheric transport is considered the most important source for contamination in the Polar Regions including the Arctic. Depending on the location and the meteorological conditions, many rapid long-range transport events (LRT) are identified annually transporting polluted air masses within a few days into the central Arctic region.

Annual average concentration for the AMAP & EMEP stations reporting POPs in 2004. It should be noted that for Alert, PCB 28 was reported as coeluting with PCB 31 and PCB 138 as coeluting with PCB 163. Concentrations and percentages shown in this figure are, thus, presented as the sum of the coeluting congeners. However, local and seasonal conditions like ambient temperature, open or ice covered ocean surface and distance to potential sources are contributing to the general levels of POPs in the atmosphere of remote areas like the Arctic.



Percentage distribution of selected PCBs in AMAP and EMEP Atmospheric POP distribution from 7 stations in 2002

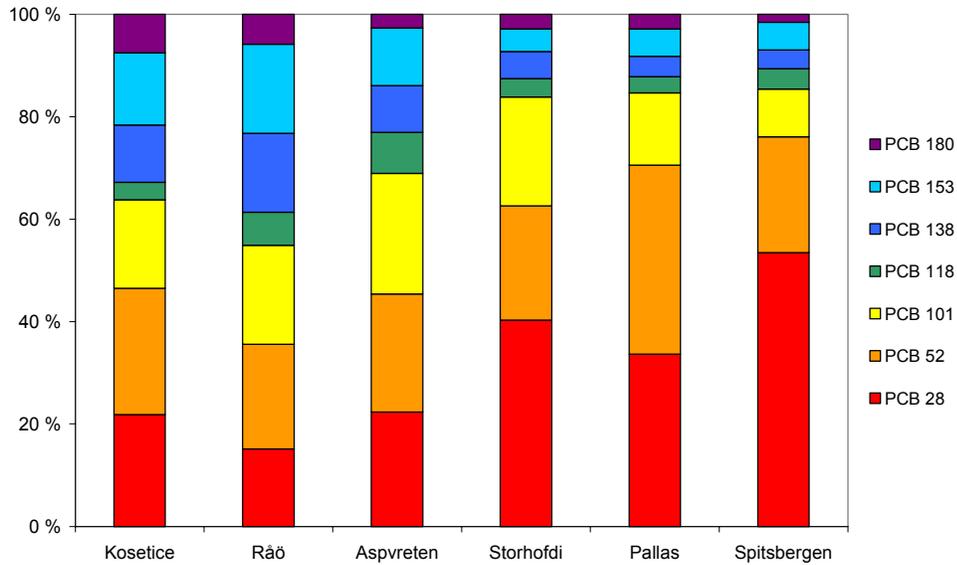


Figure 2: Annual average concentrations [pg/m^3] and percentage PCB congener distribution in 7 AMAP and EMEP POP monitoring sites for 2002

Latitudinal pattern comparison and spatial distribution

The seven AMAP/EMEP stations selected for the here performed comparison are located on a direct latitudinal transect ranging from 57 °N - 82 °N which allows us to investigate latitudinal patterns in concentrations and relative PCB patterns. For PCBs within this South - North transect the overall concentration levels are significantly decreasing due to obvious dilution and transformation effects as well as the distance to potential emission sources. The percentage contribution of the isomeric PCB group is characterized through their degree of chlorination (represented by characteristic single congeners). The PCB patterns changes significantly from predominant tetra- and penta-chlorinated PCBs in central European station towards dominating tri- and tetra-chlorinated PCBs in the Far North (figure 2). This is caused by a shift in phase partitioning whereby heavier PCBs are increasingly sorbed to atmospheric particles at decreasing temperatures, which again contributes to a relative depletion of heavier congeners due to atmospheric deposition and thus an increased prevalence of lighter PCBs in the northernmost samples. Concentration gradients along a south – north gradient, from middle latitudes up-to the far North are also evident for all other POPs reported including DDTs and chlordanes but not for HCB. For HCB a more or less equal concentration levels were found for all station except for Storhovdi, where considerable lower levels were determined.

Temporal trends

For evaluation of long-term temporal trend, a statistical trend analysis was performed using the Digital Filtration (DF) Technique, which is a sophisticated statistical time series tool used in the modeling of environmental data sets to provide long term trend information and forecast scenarios. This model has been described previously in more detail (Hung et al., 2005). DF has been applied on the data from Storhofdi, Pallas, Zeppelin (Spitsbergen) and Alert (Canada). Note that a laboratory change has occurred at Alert in 2002, resulting in a disruption of the temporal trends. An extensive interlaboratory comparison has been performed to eliminate the discrepancies between the two laboratories in order to maintain the long-term trends as more data become available in the future. Therefore, for the current report, trends have only been reported up to the end of 2001.

Hexachlorobenzene

For hexachlorobenzene (HCB) generally a downward trend can be expected. However, during the past 4 years the levels for the Zeppelin station (Spitsbergen) are increasing continuously (figure 3). This increasing concentration levels may be due to increased evaporation of previously deposited HCB from open surfaces along the western coast of Spitsbergen (Svalbard, Norway) which has been ice-free also during the past 4 winter seasons. This signal can be interpreted as a possible influence of local climate change on POP distribution in the Arctic environment.

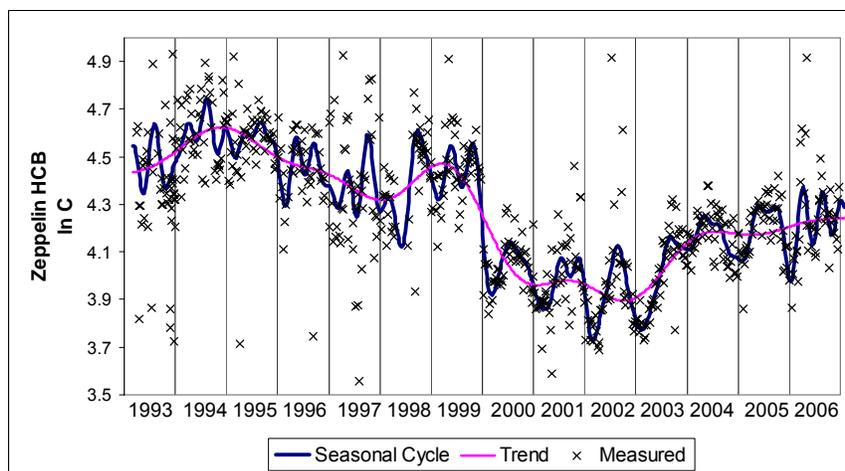


Figure 3: DF analysis of HCB levels in Zeppelin air [pg/m^3] from 1993 – 2006. Measured data, seasonal cycles and trend line is presented.

Please note: The concentration axis is given in logarithmic scale (ln).

Polychlorinated biphenyls

Due to the above mentioned reasons a slight increase of Sum PCB levels is reported for Zeppelin air as well (figure 4.)

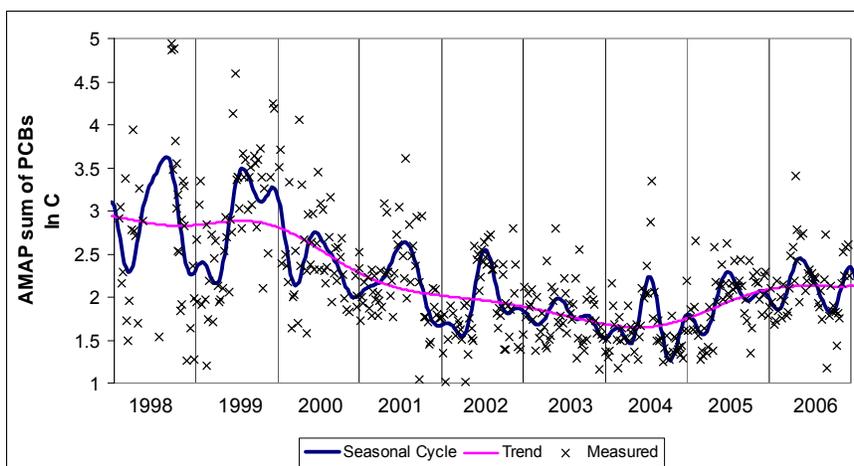


Figure 4: DF analysis of PCB levels in Zeppelin air [pg/m^3] from 1993 – 2006. Measured data, seasonal cycles and trend line is presented.

Please note: The concentration axis is given in logarithmic scale (ln).

The same phenomena were not found for Alert (Canada) obviously due to the minor influence of evaporation from ocean surfaces on the overall PCB levels in Alert Air (figure 5). However, for Alert the trend analysis was only derived up to 2001. Downward trends for PCBs were also

observed upto 2001 in Zeppelin. It is, thus, interesting to follow up and investigate whether an up-ward trend could also be established for Alert for the years 2004 to 2007.

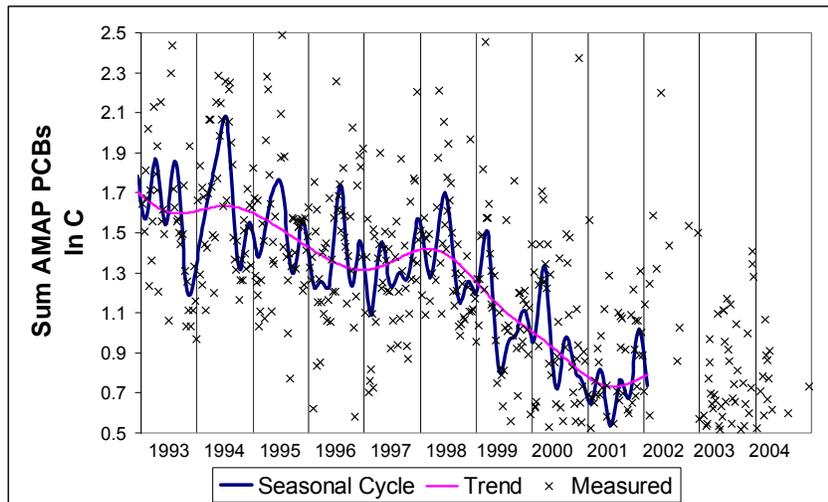


Figure 5: DF analysis of PCB levels in Alert air [pg/m^3] from 1993 – 2001. Air concentrations reported after 2001 are shown without the derivation of the trend and seasonal cycle. Measured data, seasonal cycles and trend line is presented (legend: see figure above). **Please note:** The concentration axis is given in logarithmic scale (ln).

For Storhovdi, an opposite pattern has been identified for the sum of 7 PCBs. A continuous increase of annual PCB concentrations occurred until 2004. From 2004 until 2005 PCB levels were decreasing (Figure 6).

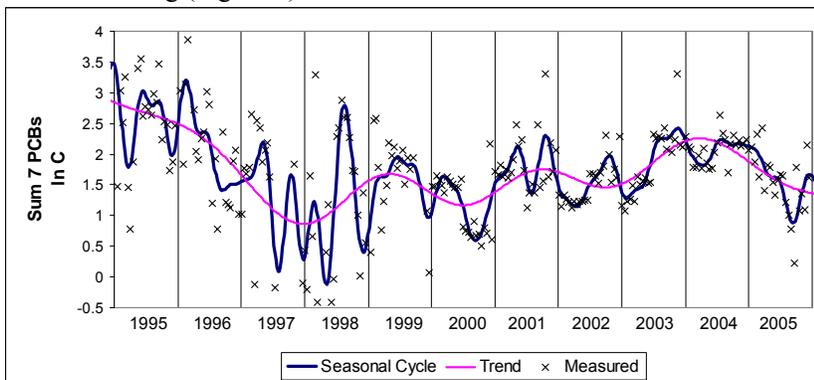


Figure 6: DF analysis of PCB levels in Storhovdi (Iceland) air [pg/m^3] from 1995 – 2005. Measured data, seasonal cycles and trend line is presented. **Please note:** The concentration axis is given in logarithmic scale (ln).

For Pallas, a slightly continuous decreasing trend has been identified for the sum of 7 PCBs in the period 1993 – 2005.

Dichlorodiphenyltrichloroethane (DDT)-derivatives

Due to the difference in reporting from the various stations, the sum distribution is difficult to compare. However, for the sum of 6 DDT-derivatives (*o,p'*-/*p,p'*-DDT, DDE, DDD) in Zeppelin air, slightly increasing trend occurred during the past 2 years: 2005 – 2006, mainly caused by a hike in concentration in winter of 2006 (figure 7).

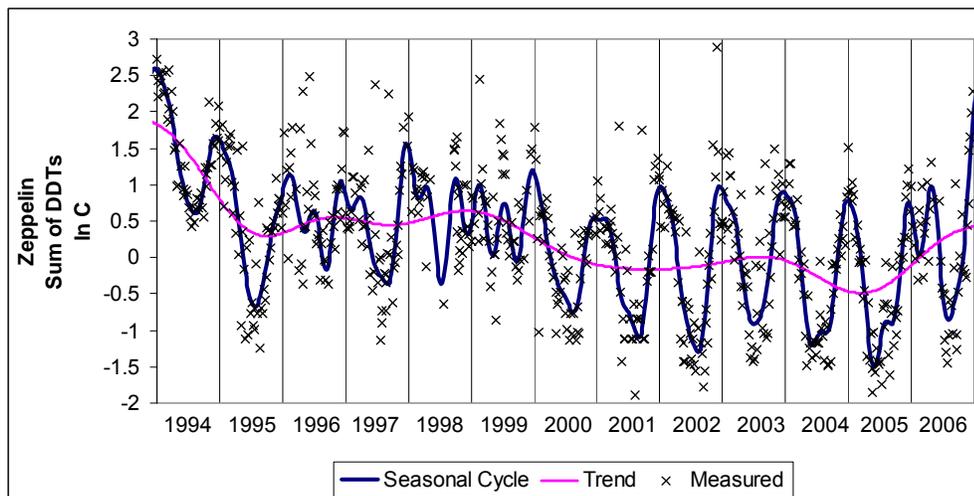


Figure 7: DF analysis of SUM concentration of 6 DDTs Zeppelin air [pg/m^3] from 1994 – 2006. Measured data, seasonal cycles and trend line is presented.

Please note: The concentration axis is given in logarithmic scale (ln).

In Alert, the sum of 6 DDT derivatives shows a downward trend in the period 1993 -2001, similar to that found for Zeppelin. The trends for Alert are presented in figure 8. After 2002, the air concentration of DDT seems to have increased. However, this observation could partially be the result of interlaboratory discrepancies. This could be confirmed when more data become available in the future.

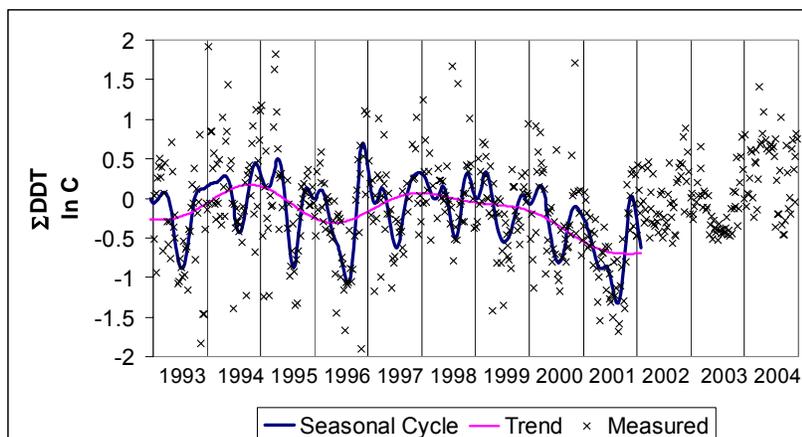


Figure 8: DF analysis of SUM concentration of 6 DDTs Alert air [pg/m^3] from 1993 – 2001. Air concentrations reported after 2001 are shown without the derivation of the trend and seasonal cycle.

Please note: The concentration axis is given in logarithmic scale (ln).

For the sum of *p,p'*-DDT related isomers, reported in Pallas and Storhofdi air, no consistent trend was confirmed through DF statistical analysis.

Chlordanes (*trans*-/ *cis*- chlordane and nonachlor)

Chlordanes (*trans*-/ *cis*- chlordane and nonachlor) temporal trends have been investigated for Zeppelin and Alert air.

For Zeppelin air, a continuous downward trend could be established for the period 1993 – 2006 (figure 9).

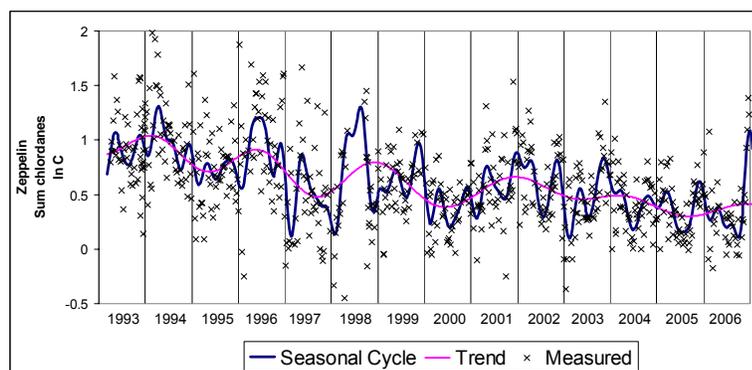


Figure 9: DF analysis of SUM concentration of chlordanes (*trans*-/ *cis*- chlordane and nonachlor) in Zeppelin air [pg/m^3] from 1993 – 2006. Measured data, seasonal cycles and trend line is presented.

Please note: The concentration axis is given in logarithmic scale (ln).

Also for Alert, a continuous downward trend for atmospheric chlordanes concentrations were found (figure 10).

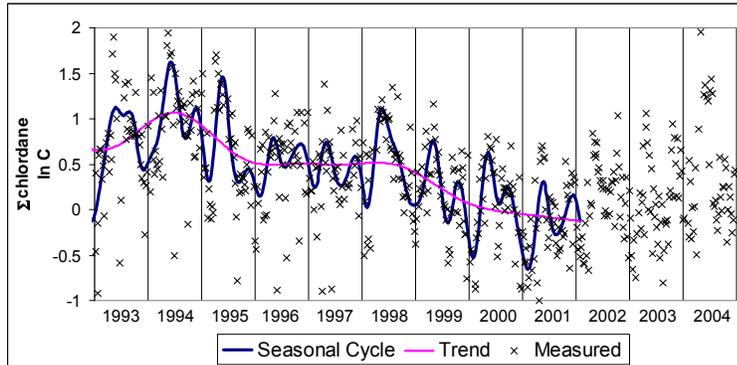


Figure 10: DF analysis of SUM concentration of chlordanes (*trans-/ cis-* chlordanes and nonachlor) Alert air [pg/m³] from 1993 – 2001. Measured data, seasonal cycles and trend line is presented (legend: see figures above). Air concentrations reported after 2001 are shown without the derivation of the trend and seasonal cycle.

Thus, a continuous reduction in atmospheric contamination for chlordanes can also be expected in the future.

Final conclusions

The levels of POPs in the atmosphere reflect a combination of local, regional and global factors. Local meteorology and location contributes to deposition regime and potential influence of local sources (secondary and primary sources). The distance to potential sources (waste handling sites, industry, urban diffusive sources) is also reflected in atmospheric POP levels. For remote, pristine monitoring sites, like Alert and Zeppelin, atmospheric long-rang transport is considered the major POP contamination source. However, on their way to the North, air masses interact with ocean and soil surfaces and may, thus, change the composition and the levels of their POP burden underway.

Due to the close vicinity to the marine environment, POP levels in Zeppelin air (Svalbard, Norway) seem to reflect climate change features along the West coast of Svalbard. Due to short-term changes in the ocean current regime along the Fram-Strait, Deep Atlantic waters were continuously up-welling onto the surface causing increased surface water temperatures during the winter season. Consequently, the West coast of Spitsbergen has been ice free since 2004 leading to increased evaporation of POPs including (PCB and HCB). This process seems to be reflected in the Zeppelin atmospheric POP data.

These local differences lead to different conclusions, for mid-latitude monitoring stations like Rørvik and Aspvreten, a continuous decrease of POPs can be reported. However, for the Arctic Zeppelin station, increasing trends for PCB, HCB and DDT were found. These increased levels, however, may possibly be associated to regional changes in the climate regime.

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A1.1.2 GAPS - Global Atmospheric Passive Sampling (GAPS) Network: Executive Summary for Western Europe and Others Group (WEOG)

Key message

The first year results (January–December 2005) from the Global Atmospheric Passive Sampling (GAPS) Network provide baselines of air concentrations for persistent organic pollutants (POPs) at 24 sampling sites in the Western Europe and Others Group (WEOG) region. These data will be useful for assessing temporal and spatial trends and regional and global transport of POPs in air.

Background

The GAPS Network is a key program for producing comparable global-scale data for POPs. This program was initiated in December 2004 as a two-year pilot study before evolving into a network, and consists of more than 60 sites on seven continents. Its objectives are to i) demonstrate the feasibility of passive air samplers (PAS) for POPs; ii) determine spatial and temporal trends for POPs in air; and iii) contribute useful data for assessing regional and global long-range atmospheric transport of POPs. PAS are advantageous because of their low cost, simple construction and electricity-free operation. Deployment of PAS worldwide over several years will allow for temporal trends to be established and thus, the effectiveness of POPs control measures to be evaluated.

The GAPS Network has been active at 38 sites in the WEOG region since 2005 – see Figures 1 through 5 and Table 1.

Figure 1. Sampling sites in North America and sampling years

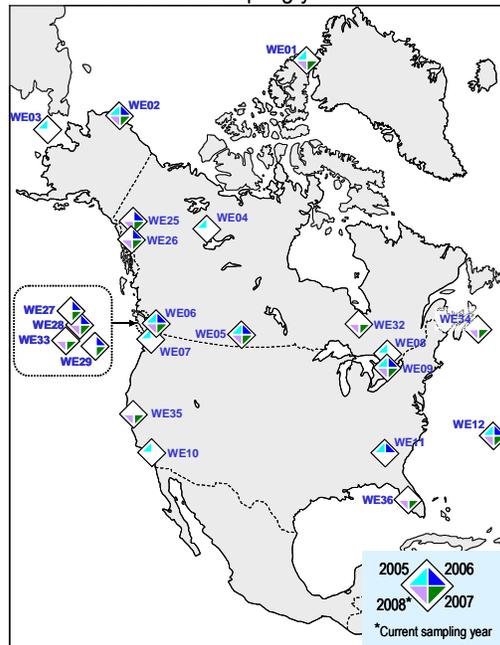


Figure 2. Sampling sites in Europe and Svalbard (see insert) and sampling years

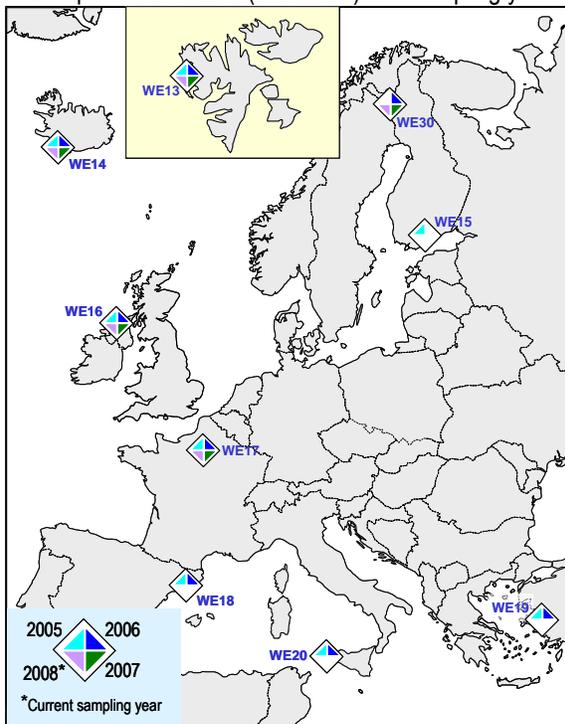


Figure 3. Sampling site in the Canary Islands (Spain) and sampling years

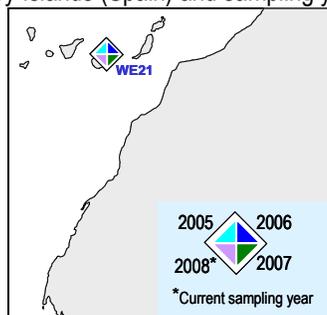


Figure 4. Sampling sites in Australia (top), New Zealand (bottom left) and Antarctica and sampling years

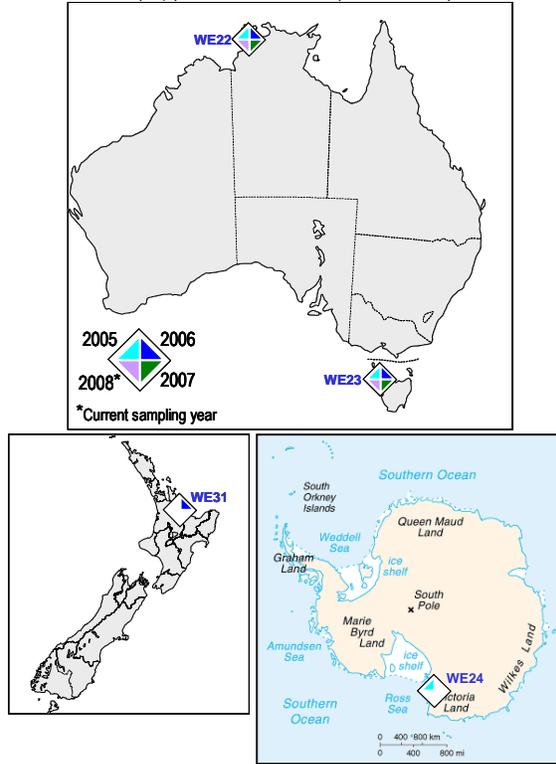


Figure 5. Sampling sites in the Pacific Ocean and sampling years

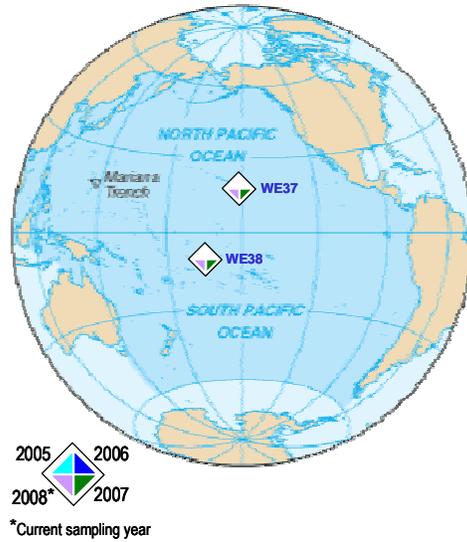


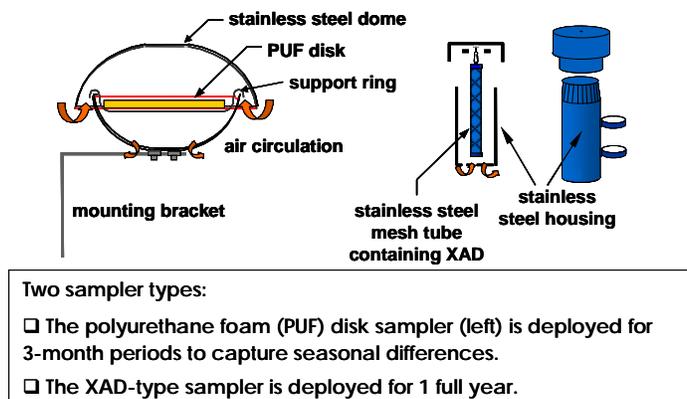
Table 1. Information on sampling locations in the WEOG region (PO = polar; BA = background; RU = rural; AG = agricultural and UR = urban)

Site ID	Location	Country	Site Type	Latitude	Longitude	Elevation (m a.s.l.)
WE01	Alert, NU	Canada	PO	82°27'N	63°30'W	
WE02	Barrow, Alaska	USA	PO	71°19'N	156°36'W	11
WE03	St. Lawrence Island, Bering Strait, Alaska	USA	PO	63°42'N	170°29'W	
WE04	Snare Rapids, NWT	Canada	BA	63°31'N	116°00'W	240
WE05	Bratt's Lake, SK	Canada	AG	50°12'N	104°43'W	595
WE06	Whistler, BC	Canada	BA	50°04'N	122°57'W	2180
WE07	Vancouver, BC	Canada	UR	49°13'N	123°07'W	
WE08	Dorset, ON	Canada	BA	45°13'N	78°56'W	320
WE09	Downsview, ON	Canada	UR	43°47'N	79°28'W	204
WE10	Simi Valley, CA	USA	RU	34°16'N	118°46'W	
WE11	Athens, GA	USA	AG	33°22'N	83°29'W	
WE12	Tudor Hill	Bermuda	BA	32°22' N	64°39'W	32
WE13	Ny-Alesund	Norway	PO	78°54'N	11°53' E	475
WE14	Storhofdi	Iceland	BA	63°24'N	20°17'W	118
WE15	Hollola	Finland	RU	61°03'N	25°40'E	
WE16	Malin Head	Ireland	BA	55°22'N	07°20'W	20
WE17	Paris	France	UR	48°52'N	02°22'E	35-40
WE18	Barcelona	Spain	UR	41°23'N	02°11'E	
WE19	Izmir	Turkey	UR	38°25'N	27°08'E	
WE20	Isola Marettimo	Italy	BA	37°58'N	12°04'E	22
WE21	Telde, Las Palmas	Canary Islands, Spain	BA	27°59'N	15°22'W	
WE22	Darwin	Australia	BA	12°22'S	130°52'E	
WE23	Cape Grim	Australia	BA	40°41'S	144°41'E	94
WE24	Mario Zucchelli Station, Antarctica	Italy	PO	74°42'S	164°07'E	15
WE25	Little Fox Lake, YK	Canada	PO	61°21'N	135°38'W	1128
WE26	Dyea, AK	USA	BA	59°31'N	135°21'W	
WE27	Cortes Island, BC	Canada	BA	50°00'N	124°57'W	
WE28	Lasqueti Island, BC	Canada	BA	49°29'N	124°21'W	
WE29	Saturna Island, BC	Canada	BA	48°47'N	123°02'W	
WE30	Pallas	Finland	BA	68°00'N	24°14'E	340
WE31	North Island	New Zealand	BA	37°49'S	176°11'E	
WE32	Fraserdale, ON	Canada	BA	49°53'N	81°34' W	210
WE33	Ucluelet, BC	Canada	BA	48°56'N	125°31'W	
WE34	Sable Island, NS	Canada	BA	43°34'N	60°07'W	4
WE35	Point Reyes, CA	USA	BA	38°03'N	122°48'W	36
WE36	Tampa, FL	USA	BA	27°58' N	82°28'W	
WE37	Hilo, HI	USA	BA	19°32'N	155°35'W	3397
WE38	Tula, AS	USA	BA	14°14'S	170°34'W	42

Sampling

Two types of PAS are used (Figure 6). The PUF-disk sampler is deployed for three-month periods to capture seasonal differences and the XAD sampler is exposed for a full year.

Figure 6. Schematic diagrams of passive air samplers



The PUF-disk sampler is described in Shoeib and Harner (2002) and Pozo *et al.* (2006) and the XAD sampler is described in Wania *et al.* (2003). Both types of PAS are installed outdoors far away from potential sources of contamination to the site (e.g., exhaust vents, electronics, sources of combustion or human activity). They are mounted approximately two meters above the ground in an open area with unobstructed airflow.

Sample analytical procedures

PUF Disk PAS

Details for the extraction and analysis of the PUF-disk samples and field blanks are given in Pozo *et al.* (2006). The following QA/QC procedures were employed for the PUF-disk sampler:

- Field blanks – A PUF disk field blank was collected once a year from each site to assess possible contamination caused by shipping, handling and storage.
- Method blanks – A solvent blank was extracted with every set of eight samples to assess possible contamination during laboratory analysis (i.e., from sample preparation to instrumental analysis). Also, during preparation of PUF disks for deployment, one sample from each batch was extracted and checked for purity.
- Instrument blanks – A solvent blank was analyzed with every set of twelve field samples to assess for any instrument contamination.
- Surrogate spikes – Prior to extraction, PUF-disk samples were spiked with a method recovery standard consisting of ^{13}C -PCB-105, d_6 - α -HCH, and d_8 - p,p' -DDT to confirm analytical integrity.
- Matrix spikes – Analytical (method) recoveries were determined by spiking clean PUF disks with known quantities of the target chemicals and treating them as samples to assess matrix effects on extraction efficiencies.

- Field collocated samples – Duplicate samples were collected at several sites in the GAPS Network to assess overall precision of both sampling and laboratory methods.
- Mirex was added as an internal standard to correct for volume differences in sample extracts.

All samples and field blanks were quantified for target compounds including organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs). OCPs, PCBs, and PBDEs were analyzed on a Hewlett-Packard 6890 gas chromatograph-5973 mass spectrometer (GC-MS) using electron impact (EI) for PCBs and negative chemical ionization (NCI) for OCPs and PBDEs in the selected ion monitoring mode.

XAD PAS

Cleaning of XAD-2 resin, and packing of XAD PAS samples were carried out as described previously by Wania *et al.* (2003). Cleaning, preparation and extraction of PAS were done in a clean lab.

The XAD-2 resin was Soxhlet extracted with dichloromethane for 20 hours. Prior to extraction, the resin was spiked with standards consisting d_6 - α -HCH, $^{13}C_{10}$ -HEPX, $^{13}C_{10}$ -TN, $^{13}C_{12}$ -dieldrin, d_8 - p,p' -DDT and $^{13}C_{12}$ -PCB-32, $^{13}C_{12}$ -PCB-77, $^{13}C_{12}$ -PCB-118 and $^{13}C_{12}$ -PCB-126 to test for the loss of the compounds during the extraction and clean-up procedures. The extracts were volume reduced using a rotary evaporator and concentrated to around 1 ml using a gentle stream of nitrogen. The extracts from first year samples were cleaned using alumina columns, but not those from the second year. After reducing samples to 3 ml using a rotary evaporator, the extracts from second year samples were passed through sodium sulfate (baked at 450 °C overnight) columns to remove any water present in sample. The extracts from the first year air samples were cleaned on a column with 1 g of 6% deactivated alumina (baked at 450 °C overnight) and 0.5 cm of sodium sulfate. The samples were eluted with 20 ml of DCM: PE (5:95; v/v). The extracts were concentrated to 1 ml using a stream of nitrogen and then the extracts were solvent-exchanged to isooctane. The final volume of the extracts was 1 ml, and 100 ng of mirex was added to the sample as an internal standard for correcting volume differences in the sample.

The sample and blank (field and laboratory) extracts were analyzed for Stockholm Convention POPs as well as pesticides not classified under Stockholm Convention POPs using an Agilent 6890 gas chromatograph (GC) coupled to a 5973 mass selective detector (MSD) with a negative chemical ionization source for organochlorine pesticides (OCPs) in selected ion mode. The analyzed non-Stockholm Convention pesticides in air samples are: α -HCH, γ -HCH, α -endosulfan, β -endosulfan, endosulfan sulfate, dacthal, chlorothalonil, pendimethalin and trifluralin.

Quality assurance and control measures were used to monitor all analytical procedures. Field blanks were collected to determine the levels of contaminants introduced by handling, shipping and storage and one laboratory blank was analyzed for every set of sample extractions to determine the levels of contaminants introduced during extraction and clean-up. The laboratory blanks and field blanks were processed in the same way as the samples. Air samples were not spiked with surrogates for the pesticides that are not classified under the Stockholm Convention POPs, such as chlorothalonil, dacthal, metribuzin, pendimethalin, and trifluralin. To test for the loss of these compounds during the extraction and clean-up procedure, six samples of 20 g of XAD-2 were spiked with the pesticides, then extracted and cleaned in the same way as the samples.

Data comparability

All PUF-disk samples are prepared and analyzed in the same laboratory (Hazardous Air Pollutants (HAPs), Environment Canada in Toronto) to ensure that the data can be compared spatially and temporally. The

HAPs laboratory participates in international intercalibration studies for POPs and performs well in these exercises.

Data storage

Sample extracts are capped tightly in GC vials and stored in a freezer at a temperature of about -20°C. Air concentration results and relevant sample information (e.g. sample ID, site ID, location name, sample duration, meteorological conditions etc.) are recorded in Excel spreadsheets.

Results

PUF-disk PAS were deployed at 24 WEOG sites in 2005. Table 2 shows the exposure times (days), average temperatures (°C) and effective sampling rates (m³/day) for each of the four sampling periods at each site. Generally, the PUF-disk sampling occurs as follows: January–March (Period 1); April–June (Period 2); July–September (Period 3); and October–December (Period 4). The air concentrations (pg/m³) at each of the four sampling periods are presented in Tables 3 through 6 for selected target chemicals, several of which are POPs listed under Annex A of the Stockholm Convention on POPs. Results are reported for: *cis*-chlordane (CC), *trans*-chlordane (TC) and *trans*-nonachlor (TN); *p,p'*-dichlorodiphenyltrichloroethane (DDT) and *p,p'*-dichlorodiphenyldichloroethylene (DDE); dieldrin; heptachlor (HEPT) and heptachlor epoxide (HEPX); polychlorinated biphenyls (PCBs); α -hexachlorocyclohexane (α -HCH); γ -HCH; endosulfan I (Endo I), endosulfan II (Endo II) and endosulfan sulfate (EndoSO₄).

XAD-based PAS were deployed at 18 sites in the WEOG region in 2005 and 15 sites in 2006. By sampling air for one year, XAD resin-based PAS provide annually averaged concentrations of organic pollutants. Table 7 reports the sampling lengths and the sequestered amounts of selected OCPs in ng/PAS. Results are reported for pesticides that are classified under the Stockholm Convention: CC, TC, TN, DDT, DDE, dieldrin, HEPT, and HEPX (acronyms defined in previous paragraph) and for pesticides that are not classified under Stockholm Convention, including α - and γ -HCH, Endo I and II, EndoSO₄, chlorothalonil (CT), dacthal (DT), and trifluralin (TF).

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Table 2. Exposure times, average temperatures and effective sampling rates during deployment periods for PUF-disk sampling in 2005

2005	Period 1			Period 2			Period 3			Period 4		
Site ID	Exposure Time (Days)	Average Temp (°C)	R# (m ³ /day)	Exposure Time (Days)	Average Temp (°C)	R# (m ³ /day)	Exposure Time (Days)	Average Temp (°C)	R# (m ³ /day)	Exposure Time (Days)	Average Temp (°C)	R# (m ³ /day)
WE01	163	-27	3.9	275	-14	3.8	**	**	**	**	**	**
WE02	91	-3	24.4	86	-11	7.7	92	-3	5	116	-19	4.8
WE03	**	**	**	**	**	**	296	-10	8.3	296	-10	8.3
WE04	**	**	**	**	**	**	**	**	**	93	-5	9
WE05	120	-13	2.6	183	9	5.4	183	9	5.4	95	0	3.9
WE06	105	-2	3.9	129	-2	8.7	**	**	**	99	-2	3.8*
WE07	**	**	**	**	**	**	92	16	3.8*	91	9	3.8*
WE08	139	-3	3.9	92	5	5.2	97	10	6	91	-9	3.8*
WE09	91	-3	3.9	98	10	3.4	91	21	4	100	-6	6.2
WE10	162	18	3.9	162	16	2.2	91	19	3.4	91	17	3.8*
WE11	82	8	2.7	105	19	2.1	193	19	1.7	193	19	1.7
WE12	97	17	4	92	20	4.1	84	26	4	97	21	3.3
WE13	78	-9	3.9	94	-5	6.5	92	2	3.8*	57	-5	8.2
WE14	107	1	3.9	94	6	7.4	94	9	7	110	2	6.9
WE15	**	**	**	98	-4	1.7	128	-2	3.8*	128	-2	3.8*
WE16	88	8	6.5	106	10	5.8	119	15	3	100	8	3.1
WE17	**	**	**	92	13	2.1	91	18	2.9	91	8	2.2
WE18	77	10	14	110	17	4.4	92	22	2	103	12	2.7
WE19	89	8	3.2	89	16	4.8	95	25	3.9	90	15	3.6
WE20	92	11	9.2	92	17	6.2	91	24	3	91	24	5.3
WE21	84	5	14	96	20	4.5	147	22	3	42	9	8.2
WE22	94	29	3.4	92	28	3.7	92	10	3	91	21	5.7
WE23	91	13	8	91	13	3.2	101	25	3.6	82	13	6.1
WE24	74	-4	3.9	**	**	**	**	**	**	**	**	**

R = effective sampling rate

* Mean sampling rate calculated based on 4 sampling periods.

** Sample not available

Table 3. Air concentrations (pg/m³) of OCPs, PCBs and PBDEs for Period 1 in 2005 using PUF-disk samplers

2005 – Period 1															
Site ID	α HCH	γ HCH	HEPT	HEPX	TC	CC	TN	Endo I	Endo II	EndoSO ₄	Dieldrin	ppDDE	ppDDT	PCBs [#]	PBDEs ^{##}
WE01	48	9	0.6	1.9	0.7	1.7	1.3	60	1.8	0.8	55	BDL	BDL	55	2
WE02	34	5	BDL	2.5	0.4	0.7	0.5	22	0.9	BDL	2	BDL	BDL	30	5
WE03	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
WE04	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
WE05	21	10	BDL	BDL	0.8	0.7	0.6	62	BDL	BDL	BDL	BDL	BDL	45	BDL
WE06	11	4	BDL	BDL	0.8	1.3	0.9	129	BDL	BDL	BDL	BDL	BDL	6	14
WE07	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
WE08	1.3	0.6	BDL	BDL	0.2	2.1	BDL	7	BDL	BDL	BDL	BDL	BDL	23	5
WE09	9	5	BDL	BDL	1.7	2.5	1.9	34	BDL	BDL	BDL	BDL	BDL	196	10
WE10	9	10	BDL	26	16	18	13	21	2	BDL	37	232	BDL	102	19
WE11	102	17	BDL	13	0.5	2.8	1.6	107	BDL	BDL	BDL	BDL	BDL	24	24
WE12	18	7	BDL	8.7	2.1	3.8	2.9	73	4.1	BDL	BDL	BDL	BDL	137	5
WE13	21	7	0.7	40	1.4	2.5	1.5	37	BDL	BDL	11	6	BDL	58	5.3
WE14	23	21	BDL	13	3.4	8.2	6.9	107	BDL	BDL	26	9	BDL	90	NA
WE15	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
WE16	6	6	BDL	BDL	0.3	1.6	1.2	29	BDL	BDL	BDL	6	36.3	29	4.1
WE17	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
WE18	4	20	BDL	7	2.8	1.4	0.7	57	13	1	12	11	BDL	68	4.7
WE19	20	9	BDL	5	BDL	0.7	0.5	126	24	1.1	BDL	51	BDL	644	NA
WE20	2	2	BDL	BDL	0.7	0.8	0.6	21	BDL	BDL	4	58	BDL	28	3.5
WE21	0.8	20	BDL	5	1.1	0.9	0.9	1758	673	10	189	192	BDL	6	1.4
WE22	BDL	BDL	BDL	BDL	9.4	4.6	2.9	17	BDL	BDL	BDL	BDL	BDL	13	BDL
WE23	BDL	BDL	BDL	BDL	BDL	BDL	BDL	27	BDL	BDL	BDL	BDL	BDL	7	BDL
WE24	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
MDL	0.1	0.3	0.1	0.1	0.1	0.4	0.2	0.7	0.8	0.5	0.14	0.1	0.5	0.12	3.7

Sum of 48 PCB congeners

Sum of PBDE-47, 99, 100

NA = PUF disk not deployed during the period/sample not available

MDL = method detection limit (pg/m³); BDL = below detection limit

Table 4. Air concentrations (pg/m³) of OCPs, PCBs and PBDEs for Period 2 in 2005 using PUF-disk samplers

2005 – Period 2															
Site ID	αHCH	γHCH	HEPT	HEPX	TC	CC	TN	Endo I	Endo II	EndoSO ₄	Dieldrin	ppDDE	ppDDT	PCBs [#]	PBDEs ^{##}
WE01	32	5	BDL	5	0.4	1.6	1.5	24	BDL	BDL	0.2	BDL	--	NA	NA
WE02	28.2	5.5	BDL	BDL	0.6	1.3	1.8	19	0.3	BDL	13	15	--	39	BDL
WE03	NA	NA	NA	NA	NA	NA									
WE04	NA	NA	NA	NA	NA	NA									
WE05	4.4	14.3	BDL	BDL	0.7	0.6	1.2	13	1.4	BDL	3.6	0.8	--	23	BDL
WE06	6.4	2.1	BDL	BDL	0.3	0.6	0.4	60	0.2	BDL	1.8	1	--	6	BDL
WE07	NA	NA	NA	--	NA	NA									
WE08	2.5	2.8	BDL	BDL	0.6	1	0.9	19.8	0.2	BDL	10	2.4	--	28	BDL
WE09	7	15.2	2	BDL	6.9	8.4	7.3	168.4	8.7	0.35	52.5	53.8	--	149	BDL
WE10	12	14	BDL	46	27.3	29.5	23	35	3.9	BDL	62.5	404	--	102	6.63
WE11	24	23	BDL	BDL	BDL	11.9	9.6	71.2	10.8	2.1	9.3	8.6	--	48	BDL
WE12	2.1	2.2	BDL	BDL	1.2	1.4	1.3	6	0.6	BDL	BDL	BDL	--	80	BDL
WE13	12.2	3.7	0.3	20.4	0.7	1.2	0.8	18.9	0.1	0.1	5.7	3.2	--	3.5	NA
WE14	18	15	BDL	8	2	5	4	67	0	0	16	5	--	6	1.7
WE15	53	25	BDL	BDL	BDL	4.5	2.8	73	6	1.4	BDL	BDL	--	122	BDL
WE16	9	12	BDL	26.8	0.6	1.6	1.1	30.7	1	0.1	21.2	3.1	--	16	BDL
WE17	25	404	8	BDL	7	6	7	4421	98	1	147	29	--	2401	3.7
WE18	5	40	BDL	587	8.2	3.4	2.5	1188	550	BDL	BDL	66	--	33	BDL
WE19	18	13	BDL	18	0.7	1.1	0.8	494	46	45	BDL	46	--	174	0.02
WE20	7	15	1.8	BDL	0.9	1.2	1	407	6	BDL	18	11	--	23	BDL
WE21	0.6	3	BDL	BDL	0.5	0.6	0.3	73.9	6.9	0.2	21.1	17.4	--	52	BDL
WE22	BDL	3.1	21.4	BDL	18	6.1	5.1	47	4	BDL	282	BDL	--	21	BDL
WE23	0.4	0.6	1.1	BDL	0.9	0.7	0.5	203	15	1.9	23.5	8.2	--	6	BDL
WE24	NA	NA	NA	NA	NA	NA									
MDL	0.1	0.3	0.1	0.1	0.1	0.4	0.2	0.7	0.8	0.5	0.14	0.1	0.5	0.12	3.7

[#] Sum of 48 PCB congeners

^{##} Sum of PBDE-47, 99, 100

NA = PUF disk not deployed during the period/sample not available

MDL = method detection limit (pg/m³); BDL = below detection limit

Table 5. Air concentrations (pg/m³) of OCPs, PCBs and PBDEs for Period 3 in 2005 using PUF-disk samplers

2005 – Period 3															
Site ID	αHCH	γHCH	HEPT	HEPX	TC	CC	TN	Endo I	Endo II	EndoSO ₄	Dieldrin	ppDDE	ppDDT	PCBs [#]	PBDEs ^{##}
WE01	NA	NA	NA	--	NA	NA									
WE02	53	6	BDL	BDL	0.2	1	1	11	0.3	0.2	7	BDL	--	16	BDL
WE03	30.3	3	BDL	0	1	0.6	0.4	6.6	0.2	BDL	BDL	BDL	--	8	1.23
WE04	NA	NA	NA	--	NA	NA									
WE05	13	9	BDL	BDL	1	2	3	28	4	0.8	BDL	BDL	--	23	3.8
WE06	NA	NA	NA	--	NA	NA									
WE07	40	5	BDL	7	0.5	1	1	17	3	0.3	BDL	12	--	18	0.76
WE08	9	6	BDL	BDL	2	3	4	77	0	0	BDL	BDL	--	117	BDL
WE09	17	25	BDL	BDL	9	9	12	457	113	9	71	112	--	300	BDL
WE10	13	16	BDL	53	31	34	26	40	4	BDL	72	464	--	161	BDL
WE11	16	22	BDL	BDL	83	13	9	56	11	3	BDL	BDL	--	48	BDL
WE12	2	1	BDL	6	2	3	0.2	13	0.9	0.3	BDL	BDL	--	702	BDL
WE13	21	6	1	36	1	2	1	33	0.2	0.1	10	6	--	27	BDL
WE14	9	6	BDL	BDL	0.2	1	1	5	0.3	BDL	3	BDL	--	11	BDL
WE15	9	6	BDL	BDL	0.2	1	0	8	1	BDL	BDL	BDL	--	25	BDL
WE16	14	19	BDL	46	1	3	2	52	2	0.2	36	5	--	37	BDL
WE17	60	650	12	BDL	9	3	10	2593	1101	64	198	62	--	4052	1.53
WE18	29	89	BDL	16	BDL	11	6	683	118	BDL	41	52	--	128	BDL
WE19	30	18	BDL	19.5	1	2	1	1352	464	7	BDL	60	--	287	BDL
WE20	13	7	BDL	BDL	BDL	2	47	2	39	BDL	78	BDL	--	39	BDL
WE21	3	17	BDL	BDL	1	4	1	451	103	BDL	29	58	--	174	BDL
WE22	BDL	BDL	BDL	BDL	6.3	1.8	2	5.7	1.5	0.4	25	BDL	--	13	BDL
WE23	BDL	BDL	BDL	BDL	9	3	3	8	2.1	0.7	37	BDL	--	17	BDL
WE24	NA	NA	NA	NA	NA	NA									
MDL	0.1	0.3	0.1	0.1	0.1	0.4	0.2	0.7	0.8	0.5	0.14	0.1	0.5	0.12	3.7

[#] Sum of 48 PCB congeners

^{##} Sum of PBDE-47, 99, 100

NA = PUF disk not deployed during the period/sample not available

MDL = method detection limit (pg/m³); BDL = below detection limit

Table 6. Air concentrations (pg/m³) of OCPs, PCBs and PBDEs for Period 4 in 2005 using PUF-disk samplers

2005 – Period 4															
Site ID	αHCH	γHCH	HEPT	HEPX	TC	CC	TN	Endo I	Endo II	EndoSO ₄	Dieldrin	ppDDE	ppDDT	PCBs [#]	PBDEs ^{##}
WE01	NA	NA	NA	--	NA	NA									
WE02	77	9	BDL	5.4	0.8	2.7	1.7	55	BDL	0.2	14	BDL	--	45	BDL
WE03	30.3	3	BDL	BDL	1	0.6	0.4	6.6	0.2	BDL	BDL	BDL	--	8	1.23
WE04	30	16	BDL	BDL	4	BDL	1	262	45	6	BDL	BDL	--	11	BDL
WE05	34.5	18.4	BDL	33	1.7	2.6	2	56.8	BDL	0.3	33	BDL	--	54	BDL
WE06	14.2	2.6	BDL	3.1	0.5	1.1	0.2	32.7	1.6	0.3	2.1	2.1	--	20	0.32
WE07	31.4	5.5	BDL	5	0.7	1.8	1.3	26.5	BDL	0.4	BDL	BDL	--	21	4.45
WE08	10.4	2.7	1.2	13.1	1.9	2.3	2	22.8	2.6	0.3	16	6	--	55	0.59
WE09	8.4	3.7	2.4	13.2	2.9	3.3	2.6	40.7	11.6	1	21	20	--	83	BDL
WE10	9	10	BDL	24	15	16	12	20	2	BDL	35	214	--	38	BDL
WE11	16	22	BDL	0	83	13	9	56	11	3	BDL	BDL	--	48	BDL
WE12	7	8	BDL	BDL	3	4	4	13	BDL	BDL	BDL	BDL	--	492	BDL
WE13	8	3	BDL	BDL	1	1	1	13	BDL	BDL	6	BDL	--	2	15
WE14	33	19	BDL	BDL	1	3	2	12	BDL	BDL	6	BDL	--	40	BDL
WE15	9	6	BDL	BDL	0	1	0	8	1	BDL	BDL	BDL	--	25	BDL
WE16	13	18	BDL	50	1	3	2	54	2	0	38	6	--	74	BDL
WE17	45	492	15	508	10	8	13	363	75	7	245	44	--	2837	BDL
WE18	NA	NA	NA	--	259	BDL									
WE19	38	58	BDL	17	1	3	1	338	85	4	19	104	--	594	BDL
WE20	11	5	BDL	BDL	BDL	1	28	1	25	BDL	47	BDL	--	34	BDL
WE21	BDL	41	BDL	6	2	2	1	975	300	4	263	251	--	207	BDL
WE22	BDL	BDL	BDL	BDL	6	2	2	6	1	0.5	24.8	BDL	--	24	BDL
WE23	BDL	50	22	2	BDL	BDL	--	27	BDL						
WE24	NA	NA	NA	NA	NA	NA									
MDL	0.1	0.3	0.1	0.1	0.1	0.4	0.2	0.7	0.8	0.5	0.14	0.1	0.5	0.12	3.7

Sum of 48 PCB congeners

Sum of PBDE-47, 99, 100

NA = PUF disk not deployed during the period/sample not available

MDL = method detection limit (pg/m³); BDL = below detection limit

Table 7. Length of sampling in days and amounts of selected organochlorine pesticides sequestered in XAD-based PAS in ng/PAS for 2005

Year 1 – 2005																	
Site ID	Days	α -HCH	γ -HCH	HEPT	HEPX	TC	CC	TN	Endo I	Endo II	EndoSO ₄	Dieldrin	ppDDE	ppDDT	TF	CT	DT
WE02	399	14	1.7	ND	0.2	0.2	0.4	0.4	2.5	ND	ND	ND	ND	ND	BMDL	0.2	BMDL
WE03	365	7.6	0.9	ND	ND	0.1	0.2	0.2	0.1	ND	ND	ND	ND	ND	BMDL	ND	ND
WE05	371	8.6	7.0	ND	2.8	0.6	0.5	0.6	5.2	ND	ND	ND	ND	ND	17	66	0.6
WE09	393	7.0	4.5	0.5	1.8	2.0	2.1	2.0	43	4.3	0.5	4.4	7.1	ND	6.8	78	8.4
WE11	359	6.2	8.4	2.3	2.5	4.8	3.1	1.6	12	2.1	0.7	1.7	ND	ND	1.9	22	2.3
WE12	386	3.4	1.3	ND	0.6	1.3	1.2	1.1	3.5	0.1	ND	6.7	ND	ND	0.2	2.3	0.5
WE13	371	6.2	1.1	ND	0.3	0.2	0.3	0.4	2.7	ND	ND	ND	ND	ND	ND	0.2	0.1
WE14	405	9.6	2.0	ND	0.5	0.3	0.6	0.5	3.2	ND	0.1	ND	ND	ND	BMDL	3.2	0.2
WE15	365	5.7	2.6	ND	0.1	0.2	0.3	0.3	2.8	0.1	ND	ND	ND	ND	2.9	2.0	0.2
WE16	414	7.6	4.1	ND	0.6	0.3	0.5	0.4	3.9	0.1	0.1	1.5	ND	ND	17.5	4.0	0.8
WE17	365	17	118	7.4	1.7	1.9	1.7	1.9	213	25	1.9	7.2	2.9	1.7	188	168	3.1
WE18	365	8.1	19	ND	4.0	3.3	1.4	0.8	138	34	3.8	3.9	8.0	ND	1.8	24	5.9
WE19	365	18	8.7	ND	0.7	0.3	0.3	0.4	27	3.0	0.4	ND	7.5	ND	8.2	6.1	0.3
WE20	365	8.6	8.2	ND	1.6	0.5	0.7	0.6	56	8.0	1.6	1.5	5.7	8.8	0.5	15	3.0
WE21	369	4.9	23	0.9	0.6	0.9	0.8	0.6	60	1.3	0.2	4.2	23	2.6	0.5	3.4	0.1
WE22	370	0.5	1.1	4.0	1.9	6.1	1.5	3.3	3.5	0.1	ND	7.6	ND	ND	BMDL	0.9	0.1
WE23	366	0.4	0.2	ND	ND	0.2	0.2	0.1	9.0	0.2	0.1	ND	ND	ND	9.6	1.0	0.8
WE24	365	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
MDL		0.1	0.1	0.2	0.1	0.04	0.06	0.09	0.09	0.03	0.02	0.5	0.3	0.3	0.08	0.1	0.04

BMDL = below method of detection limit

ND = not detected

MDL = method detection limit (ng/PAS)

Table 8. Length of sampling in days and amounts of selected organochlorine pesticides sequestered in XAD-based PAS in ng/PAS for 2006

Year 2 – 2006																	
Site ID	Days	α -HCH	γ -HCH	HEPT	HEPX	TC	CC	TN	Endo I	Endo II	EndoSO ₄	Dieldrin	ppDDE	ppDDT	TF	CT	DT
WE02	365	5.3	0.8	ND	ND	ND	0.1	0.2	1.8	ND	ND	ND	ND	ND	ND	BMDL	BMDL
WE05	359	5.1	3.4	ND	2.2	0.3	0.2	0.3	6.2	0.5	0.2	ND	ND	ND	6.5	232	2.3
WE06	315	5.0	0.9	ND	ND	ND	0.2	0.1	8.3	0.8	0.3	ND	ND	ND	ND	9.4	0.7
WE09	350	2.5	1.5	ND	1.1	0.8	0.7	0.8	23	4.5	0.5	ND	ND	ND	7.0	135	4.5
WE12	327	1.1	0.5	ND	ND	ND	0.5	0.6	3.2	BMDL	0.1	9.4	ND	ND	0.2	5.9	0.2
WE14	361	6.8	1.4	ND	ND	0.2	0.3	0.3	3.2	BMDL	0.1	ND	ND	ND	ND	12	0.4
WE16	363	4.1	3.3	ND	0.7	0.2	0.3	0.2	4.2	0.3	0.1	ND	ND	ND	13	49	1.2
WE17	344	8.3	72	1.3	10	0.9	0.7	1.1	166	49	3.8	9.0	ND	ND	247	466	3.8
WE19	372	10	4.7	ND	ND	0.1	0.2	0.2	42	20	2.1	ND	ND	ND	16	28	0.6
WE21	370	14	5.9	ND	0.8	0.4	0.3	0.2	70	14	1.7	15	ND	ND	ND	47	0.6
WE22	348	BMDL	0.3	3.2	ND	3.0	0.8	0.9	2.9	0.3	0.1	9.4	ND	ND	BMDL	5.1	2.1
WE23	295	BMDL	ND	ND	1.4	0.1	ND	ND	4.8	0.4	0.2	ND	ND	ND	1.9	4.2	0.9
WE26	377	2.0	0.2	ND	ND	ND	ND	ND	BMDL	ND	ND	ND	ND	ND	BMDL	BMDL	BMDL
WE29	397	5.1	0.7	ND	ND	0.2	0.2	0.2	4.8	1.1	0.2	ND	ND	ND	1.0	12	0.5
WE30	365	2.9	1.0	ND	ND	0.1	ND	0.1	2.8	BMDL	0.1	ND	ND	ND	ND	18	0.2
MDL		0.2	0.2	0.4	0.4	0.03	0.07	0.04	0.5	0.05	0.03	0.9	-	-	0.05	1.2	0.2

BMDL = below method of detection limit

ND = not detected

MDL = method detection limit (ng/PAS)

Table 9. Length of sampling in days and amounts of selected organochlorine pesticides sequestered in XAD-based PAS in pg/m³ for 2005

Year 1 – 2005																		
Site ID	Days	α -HCH	γ -HCH	HEPT	HEPX	TC	CC	TN	Endo I	Endo II	EndoSO ₄	Dieldrin	ppDDE	ppDDT	TF	CT	DT	
WE02	399	34	4.3	ND	0.5	0.5	1.0	1.0	6.3	ND	ND	ND	ND	ND	BMDL	0.5	BMDL	
WE03	365	21	19	ND	ND	0.3	0.5	0.5	0.3	ND	ND	ND	ND	ND	BMDL	ND	ND	
WE05	371	23	12	ND	7.5	1.6	1.3	1.6	14	ND	ND	ND	ND	ND	45	178	1.6	
WE09	393	18	23	1.3	4.6	5.1	5.3	5.1	109	11	1.3	11	18	ND	17	199	21	
WE11	359	17	3.4	6.4	7.0	13	8.6	4.5	32	5.8	1.9	4.7	ND	ND	5.3	62	6.4	
WE12	386	8.8	3.0	ND	1.6	3.4	3.1	2.8	9.1	0.3	ND	17	ND	ND	0.5	6.0	1.3	
WE13	371	17	4.9	ND	0.8	0.5	0.8	1.1	7.3	ND	ND	ND	ND	ND	ND	0.5	0.3	
WE14	405	24	7.1	ND	1.2	0.7	1.5	1.2	7.9	ND	0.2	ND	ND	ND	BMDL	7.9	0.5	
WE15	365	16	9.9	ND	0.3	0.5	0.8	0.8	7.7	0.3	ND	ND	ND	ND	7.9	5.5	0.5	
WE16	414	18	323	ND	1.4	0.7	1.2	1.0	9.4	0.2	0.2	3.6	ND	ND	42	9.7	1.9	
WE17	365	45	52	20	4.7	5.2	4.7	5.2	584	69	5.2	20	7.9	4.7	515	460	8.5	
WE18	365	22	23	ND	11	9.0	3.8	2.2	378	93	10	11	22	ND	4.9	65	16	
WE19	365	49	24	ND	1.9	0.8	0.8	1.1	73	8.2	1.1	ND	21	ND	23	17	0.8	
WE20	365	24	62	ND	4.4	1.4	1.9	1.6	153	22	4.4	4.1	16	24	1.4	41	8.2	
WE21	369	13	23	2.4	1.6	2.4	2.2	1.6	163	3.5	0.5	11	63	7.0	1.4	9.2	0.3	
WE22	370	1.4	3.0	11	5.1	16.5	4.1	8.9	9.5	0.3	ND	21	ND	ND	BMDL	2.4	0.3	
WE23	366	1.1	0.5	ND	ND	0.5	0.5	0.3	25	0.5	0.3	ND	ND	ND	26	2.7	2.2	
WE24	365	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	
MDL		0.4	0.3	0.6	0.3	0.1	0.2	0.3	0.3	0.08	0.05	1.2	0.9	0.9	0.2	0.4	0.1	

BMDL = below method of detection limit

ND = not detected

MDL = method of detection limit (pg/m³)

Table 10. Length of sampling in days and amounts of selected organochlorine pesticides sequestered in XAD-based PAS in pg/m³ for 2006

Year 2 – 2006																	
Site ID	Days	α-HCH	γ-HCH	HEPT	HEPX	TC	CC	TN	Endo I	Endo II	EndoSO ₄	Dieldrin	ppDDE	ppDDT	TF	CT	DT
WE02	365	15	2.2	ND	ND	ND	0.3	0.5	4.9	ND	ND	ND	ND	ND	ND	BMDL	BMDL
WE05	359	14	9.5	ND	6.1	0.8	0.6	0.8	17	1.4	0.6	ND	ND	ND	18	646	6.4
WE06	315	16	2.9	ND	ND	ND	0.6	0.3	26	2.5	1.0	ND	ND	ND	ND	30	2.2
WE09	350	7.1	4.3	ND	3.1	2.3	2.0	2.3	67	13	1.4	ND	ND	ND	22	386	13
WE12	327	3.4	1.5	ND	ND	ND	1.5	1.8	9.8	BMDL	0.3	29	ND	ND	0.6	18	0.6
WE14	361	19	3.9	ND	ND	0.6	0.8	0.8	8.9	BMDL	0.3	ND	ND	ND	ND	33	1.1
WE16	363	11	9.1	ND	1.9	0.6	0.8	0.6	12	0.8	0.3	ND	ND	ND	37	135	3.3
WE17	344	24	209	3.9	30	2.6	2.0	3.2	482	143	11	26	ND	ND	718	1355	11
WE19	372	27	13	ND	ND	0.3	0.5	0.5	113	54	5.6	ND	ND	ND	42	75	1.6
WE21	370	38	16	ND	2.2	1.1	0.8	0.5	189	39	4.6	39	ND	ND	ND	128	1.6
WE22	348	BMDL	0.9	9.2	ND	8.6	2.3	2.6	8.3	0.9	0.3	27	ND	ND	BMDL	15	6.0
WE23	295	BMDL	ND	ND	4.7	0.3	ND	ND	16	1.4	0.7	ND	ND	ND	6.4	14	3.1
WE26	377	5.3	0.5	ND	ND	ND	ND	ND	BMDL	ND	ND	ND	ND	ND	BMDL	BMDL	BMDL
WE29	397	13	1.8	ND	ND	0.5	0.5	0.5	12	2.8	0.5	ND	ND	ND	2.5	31	1.3
WE30	365	7.9	2.7	ND	ND	0.3	ND	0.3	7.7	BMDL	0.3	ND	ND	ND	ND	49	0.5
MDL		0.5	0.5	1.1	1.1	0.08	0.2	0.1	1.4	0.1	0.08	2.5	-	-	0.1	3.3	0.5

BMDL = below method of detection limit

ND = not detected

MDL = method of detection limit (pg/m³)

A1.1.3 Executive Summary of the Integrated Atmospheric Deposition Network (IADN)

Key Message

IADN is a joint Canada-United States monitoring and research program called for in the Great Lakes Water Quality Agreement (GLWQA). It was established in 1990 to monitor trends of nonpoint priority toxic pollutant sources in the Great Lakes basin.

IADN maintains a master monitoring station on the shoreline of each of the five Great Lakes along with several additional satellite stations and provides long-term data on regionally representative concentrations of toxic substances in gas, particle and precipitation samples. The target list of pollutants studied by IADN has undergone some modifications since its inception, but the network has continued to focus consistently on toxic semi-volatile organic compounds (SVOCs), including polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), and trace elements. A priority goal for IADN has been the study of the temporal behaviour exhibited by the target toxic organics. With many years of data now available from most IADN stations for these species, this information has aided scientific understanding of the sources, fate, time trends, and distribution of these pollutants, many of which are also common to the list of Persistent Organic Pollutants (POPs) identified by the Stockholm Convention. In consequence, IADN represents a pertinent source of long-term monitoring data relevant to the atmospheric concentrations of these chemicals.

Background

Objectives of IADN: The objectives of IADN are to acquire quality-assured air and precipitation concentration measurements; determine atmospheric loadings and trends of toxic substances to the Great Lakes; and determine the sources of continuing inputs of these pollutants.

Geographic boundaries: The current configuration of IADN is shown in Figure 1. Master stations located on Lakes Erie (Sturgeon Point, STP), Michigan (Sleeping Bear Dunes, SBD) and Superior (Eagle Harbour, EGH) are operated by the U.S. (Indiana University, IU), while Canada (Environment Canada, EC) operates the master stations on Lakes Huron (Burnt Island, BNT) and Ontario (Point Petre, PPT). On the U.S. side, two satellite urban stations are in operation in Chicago and Cleveland. Both air and precipitation samples are collected at these sites. On the Canadian side, air samples are collected at Egbert (EGB) while precipitation samples are collected at the other seven stations: Sibley, Turkey Lakes, Grand Bend, St. Clair, Pt. Pelee, Rock Point, and Burlington.

In addition, a research buoy (ECO-1) operated by EC in the western end of Lake Ontario has been under development as an IADN satellite site since 1999. This over-water platform, although only available for 4-6 months of each year due to weather limitations, has provided atmospheric measurements in the urban plume of Toronto/Hamilton and potentially allows for simultaneous air-water monitoring, which is important for improving the calculations of air-water exchange for the target analytes. Improved assessments of atmospheric inputs from urban areas and concurrent air-water measurements are ongoing priorities of IADN. Such spatial gradients will be explored further via the use of temporary stations or passive samplers. Additional urban stations or short-term urban sampling will be pursued within resource limitations.

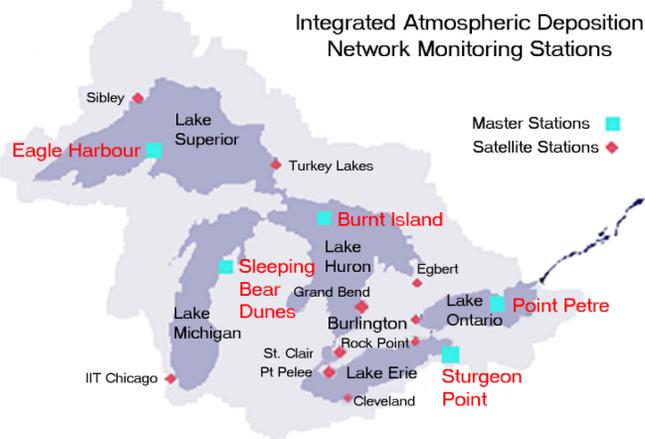


Figure 1. IADN master and satellite sampling stations

Sampling

Sampling frequency: IADN collects gas- and particle-phase air samples for 24 hours every 12 days at all master and some satellite sites using high-volume air samplers. Precipitation samples are taken during every rain or snow event and composited every 28 days in the U.S. and every 14 days in Canada using samplers that open only during a rain or snow event. Meteorological data such as air, temperature, wind speed and direction are also collected at most sites and averaged on an hourly basis.

Ambient air sampling

Full details of the air sampling protocols used by IADN for regular operations are given in the Standard Operating Procedure (SOP) manuals of the respective agencies (Environment Canada, 2002; Basu and Bays, 2005). For the target SVOCs, at the U.S. sites, 24-hour air samples were collected by modified Anderson high-volume air samplers (General Metal Works, model GS 2310) every 12 days. Particles were retained on quartz fiber filters (Whatman QM-A), and the gas-phase organic compounds were retained on 40 g of XAD-2 resin (20-60 mesh). This allows for a $>800 \text{ m}^3$ sample volume. Prior to May 4, 1992, polyurethane foam (PUF) was used to collect gas-phase samples. At the two Canadian sites, General Metal Works PS-1 high-volume samplers were used to collect air samples. The sampling head held a 10.2 cm diameter glass fiber filter (GFF, Gelman A/E Microfiber) for particle collection followed by a 7.5 cm high \times 6.2 cm diameter PUF plug (LevIT Safety) for gas-phase absorption. In this case, sample volumes are kept below 400 m^3 to minimize breakthrough of volatile species during warm summer months. Sampling events occurred every 6 days through April 1994 and every 12 days since that time.

Sample analytical procedures

Target analyte list: OCPs measured regularly by IADN of relevance to the focus of this summary are aldrin, α - and γ -chlordane, p,p' - and o,p' -DDT, p,p' - and o,p' -DDD, p,p' -DDE, dieldrin, endrin, hexachlorobenzene (HCB), and *trans*-nonachlor. Toxaphene has also been determined in a series of special study samples collected at Point Petre. Other OCPs determined include α - and β -endosulfan, endosulfan sulfate, α -, β -, and γ -hexachlorocyclohexane (HCH), heptachlor epoxide, and methoxychlor. PCB congeners determined and potentially included in the "total PCB" summation are: 4+10, 5+ 8, 6, 7+9,

12+13, 15+17, 16+32, 18,19, 22, 26, 28, 31, 33+53, 37+42, 41+64+71, 44, 45, 47+48, 49, 52, 56+60+84+92, 70+76, 74, 77+110, 83, 85, 87+81,89, 91, 95+66, 97, 99,100, 101, 105+132+153, 114+131, 118, 119, 123+149, 126, 128+167,135+144,138+163, 156+171+202, 169, 170+190, 172, 174, 180, 194+205, 199, 201, 206, and 207. Each congener in this list either contributes more than 1% to the total PCB mass for at least one site within the network or is regarded to be toxicologically important (PCB 77, 105, 126, 128, 138, 156, 169 and 170).

Sample processing and instrumental analysis: The methodologies employed for processing and subsequent instrumental analysis are different for the air samples collected at the U.S. and Canadian sites. Details of these analyses can be found in the SOPs of the relevant laboratories (IU SOP 2007; EC air toxics, 2006) or the agency-specific Quality Assurance Project Plans (QAPjPs). A useful summary of the methodologies has been provided by Cortes et al. (1998) and Sun et al. (2005) have also discussed the differences in the procedures. Table 1 provides a brief description and comparison of the U.S. and Canadian methods.

Table 1. Comparison of methods for determination of OCPs and PCBs in U.S. and Canadian air samples

	U.S. SAMPLES	<i>CANADIAN SAMPLES</i>
Sampler Media	QFF + XAD-2	GFF + PUF
Sample Extraction	XAD-2 Soxhlet (24 hours) with 1:1 hexane: acetone GFF same as for XAD-2	PUF Soxhlet (24 hours) with hexane GFF not analyzed routinely for OCPs or PCBs
Cleanup/Fractionation	Silica gel (3.5% w/w water-deactivated) column chromatography: Fraction 1: hexane elution of PCBs, HCB, p,p'-DDE, o,p'-DDT; Fraction 2: 50% hexane / 50% DCM elution of other target OCPs.	Florisil (~3% water-deactivated) column chromatography: Fraction 1: hexane elution of PCBs, HCB, heptachlor, aldrin, p,p'-DDE, o,p'-DDT, t-nonachlor (partial), p,p'-DDT (partial); Fraction 2: 15% DCM / 85% hexane elution of HCHs, o,p'-DDD, p,p'-DDD, chlordanes, t-nonachlor (partial), p,p'-DDT (partial) + coplanar PCBs; Fraction 3: DCM elution of polar OCPs (dieldrin, endosulfans, methoxychlor, endrin, heptachlor epoxide).
Instrumental Measurement	GC-ECD (HP5890): heated splitless/split injector, 60-m DB-5 capillary column	GC-ECD (HP5890 Series II): dual heated splitless/split injectors, dual capillary columns (60-m DB-5 and 30-m DB-17)
Instrument Calibration	Internal standardization	External standardization

Data comparability

IADN quality assurance (QA) studies: All IADN operations are subject to the requirements detailed in the Quality Assurance Program Plan (QAPP; EC and USEPA, 2001) and in related agency QAPjPs. The measurement activities involved can essentially be considered as “state-of-the-art” at the background levels expected, with the various agencies already pursuing customised methodologies developed as part of ongoing research efforts. Retaining this diversity of approaches was regarded as beneficial for the network, offering the possibility of important information on comparability and allowing the method development to continue.

In accordance with the QAPP, a considerable effort has been expended from the early days of IADN on QA studies to ensure data comparability between the U.S. and Canadian

measurements in both air and precipitation and these have been fully documented (Fowlie, 2001); a summary of recent activities has been provided by Wu et al. (in prep). These include: analysis of common reference standard (CRS) mixtures; interlaboratory comparisons involving exchange of atmospheric samples (raw and processed); conduct of a long-term co-location sampling study; as well as additional special QA-investigations.

CRS mixtures for PCBs and OCPs were distributed in 2001 to determine the level of analytical agreement between the two laboratories. For the OCP CRS, all laboratories are within 90-95% of the standard amount. There is more variation in the results for the PCB CRS, the agreement was between 65 and 140% of the standard value, which was considered acceptable.

A split-sample interlaboratory comparison was also conducted in 2001 to evaluate possible systematic biases between the participating laboratories from the extraction, fractionation, and analytical procedures (Fowlie, 2002). U.S. laboratory values were 20-60% higher than Canadian laboratory values for PCB congeners 18, 37+42, 45, 49, 52, 95, 101, 132+105+153, 123+149, and 180, congeners selected to represent tri- to hepta-chlorinated homologues. A comparison of the OCPs in vapor phase samples also showed the IU laboratory results were higher than the EC's Organics Analysis Laboratory (OAL) results. The mean OAL/IU ratio for the 16 individual OCP was 0.92 ± 0.05 , which indicates acceptable overall performance.

An important requirement of the QAPP was the regular collocation of samplers operated by the participants at the Point Petre master station to provide an ongoing measure of comparability; such a study has been in operation since 1998 (air samples are collected simultaneously every 24 days) and is intended to identify differences in measurements accrued over the entire sampling, extraction and analysis process, especially analyte sample collection efficiencies. This co-location experiment gave PCB concentrations that sometimes differed by up to a factor of 2.5 between the two laboratories during the summertime. In order to quantify the sources of these differences, an intensive inter-laboratory study was conducted in 2003, in which 8 samples were collected under winter and summer conditions. For these samples, four co-located samplers were used, and media (PUF and XAD) were exchanged between the two laboratories to investigate variables such as analytical methodology, sampling media, and sampler. A separate breakthrough study was also conducted in the summer of 2004 using two PUF plugs in series; this latter special study revealed appreciable breakthrough of some of the mono- and di-chlorinated PCB congeners but showed that for tri-chlorinated congeners (e.g. PCB 18) the potential errors resulting from the use of a single PUF plug were acceptable. For congeners with four or more chlorines, breakthrough on PUF was found to be essentially insignificant. The 2003 study suggested that PCB 18 in the U.S. data may have been over-reported by a factor of 2.2; the source of this discrepancy has not yet been determined. For the vapor phase OCP samples, concentrations of 10 of the 13 samples had significant differences with higher values reported by the IU laboratory (ratios < 1.00). The average ratio over all compounds for the vapor phase samples was 0.90 ± 0.08 . The overall contributions to the OCP concentration differences observed between laboratories were: analytical method and calibration, $\pm 5\%$; chemical interferences, $\pm 35\%$; and sampling differences, $\pm 10\%$.

Data management: All air and precipitation chemical data and all meteorological data measured by IADN go through a quality control process via the Research Data Management and Quality Control System™ (Sukloff et al., 1995). Data is available online via the Canadian National Atmospheric Chemistry (NAtChem) Database (<http://www.msc-smc.ec.gc.ca/natchem/>).

The implementation and use of RDMQ™ ensures that all the data entering the IADN loading calculation is treated in a consistent manner. RDMQ™ allows the large amounts of

data acquired through IADN to be quality controlled in a timely, efficient manner. Each year of data from each site undergoes several evaluation steps before being accepted as valid.

Data storage.

Data: IADN operates a centralized database maintained by a network-wide data manager. The laboratories operated by EC-OAL, EC-Burlington, and US EPA-IU submit data to the database manager at EC where it is archived and undergoes processing according to the QA/QC procedures. The finalized data are then submitted to the National Air Chemistry Database (NAtChem/Toxics) at EC. Data is sequestered for a period of 2 years after submission to NAtChem to allow the preparation of publications by the Steering Committee and then will become public. This data policy is aligned with that of other networks such as the Northern Contaminants Program (NCP), CAPMoN (Canadian Air and Precipitation Monitoring Network), and CAMNet. Summary data and IADN publications are accessible via the IADN website.

Samples: At Point Petre, replicate air samples for SVOCs have been collected routinely since 1990; these samples have been stored in an unprocessed state in freezers and many are still available for retrospective examination and analysis if needed. In addition, processed sample extracts are routinely stored by the participating laboratories following analysis.

Results

PCBs: Means & Spatial Trends

Table 2 provides a summary of mean atmospheric gas-phase concentrations of “Suite PCBs” measured at the IADN sites from 1990-2003. Gas-phase concentrations of total-PCBs in samples collected in Chicago from 1996 are significantly higher ($1.4 \pm 0.1 \text{ ng/m}^3$) than those observed at the nearest Lake Michigan master station (Sleeping Bear Dunes; $0.1 \pm 0.08 \text{ ng/m}^3$), implicating such large urban areas as sources of PCBs to the Great Lakes. The levels at sites near Lakes Michigan, Erie, and Ontario are relatively higher than those measured at sites near Lakes Superior and Huron, with the maxima being observed at the site near Lake Erie, most likely due to nearby urban activity. However, this relatively higher concentration is still 6-10 times lower than that previously reported at the Chicago site.

Table 2. Average total PCB^a concentrations, half-lives, Clausius-Clapeyron slopes, and phase-transition energies at the seven IADN sites.

	$C_{\text{avg}} \pm$ std err (pg/m^3)	Half-life, $t_{1/2}$ ^b (year)	Slope ^c	ΔH ^d (kJ/mol)	N ^e	r^2 ^f
Brule River	86 ± 6.9	-10 ± 2.8	-5300 ± 280	43 ± 2.3	187	0.67
Eagle Harbor	86 ± 5.4	26 ± 9.5	-5200 ± 270	42 ± 2.2	361	0.51
Sleeping Bear	110 ± 6.5	7.7 ± 0.8	-5600 ± 270	46 ± 2.2	332	0.60
Sturgeon Point	230 ± 11	20 ± 4.3	-6200 ± 220	51 ± 1.7	355	0.70
Burnt Island	60 ± 2.1	NS	-1500 ± 220	12 ± 1.8	345	0.12
Point Petre	80 ± 2.6	7.1 ± 0.4	-4100 ± 190	34 ± 1.5	392	0.64
Chicago	1300 ± 74	8.0 ± 1.1	-5400 ± 230	44 ± 1.9	219	0.74

- Congeners included in the total PCB summation are: 15+17, 16+32, 18,19, 22, 26, 28, 31, 33+53, 37+42, 41+64+71, 45, 47+48, 49, 52, 56+60+84+92, 70+76, 74, 77+110, 83, 85, 87+81,89, 91, 95+66, 97, 99,100, 101, 105+132+153, 114+131, 118, 119, 123+149, 126, 128+167,135+144,138+163, 156+171+202, 169, 170+190, 172, 174, 180, 194+205, 199, 201, 206, and 207.
- The results of half-life, slope, and phase-transition energies are listed as mean \pm standard error. Normal font numbers are significant for $0.01 < p < 0.05$; italic font numbers are significant for $0.001 < p < 0.01$, bold font numbers are significant at level of $p < 0.001$. NS means the result is not significant at $p < 0.05$ level. A negative half-life is actually a doubling time.
- The slope value is from the linear regression of the natural logarithm of the partial pressure (P) vs. the reciprocal of T (see equation 2).
- ΔH is the characteristic phase-transition energy.
- N is the number of samples collected up to 2003 and used in the regressions. r^2 is the Pearson's multi-regression coefficient between $\ln(P)$, $1/T$, and time.

Temporal Trend Analysis

From data obtained in the early years of IADN, Hillery et al. [1997] described the behaviour of gas-phase PCBs at the U.S. master stations, showing that the observed concentrations are clearly linked to fluctuations in the ambient temperature. Observed gas-phase concentrations are cyclic and increase in the warmer summer months. Thermodynamically, the gas-phase behaviour of SVOCs can be described by the Clausius-Clapeyron equation:

$$\ln(P) = \left(\frac{-\Delta H_{vap}}{R} \right) \left(\frac{1}{T} \right) + const \quad (1)$$

where P is the partial pressure in atmospheres, T is the temperature in $^{\circ}\text{K}$, ΔH_{vap} is the heat of vaporization in J mol^{-1} , and R is the gas constant. Figure 2 shows such plots (CC plots) of the natural logarithm of the partial pressure for total PCBs (based on the summation of the partial pressures of individual congeners) versus the reciprocal of the average atmospheric temperature for the appropriate 24 hour sampling period for three U.S. sites, covering the period from inception of sampling at each site to November 1995.

Clearly, PCB partial pressures increase with temperature. A regression applied to these data gives a linear relationship. ΔH_{vap} , calculated from the slopes of the regression lines, are 37 kJ mol^{-1} at Eagle Harbor, 37 kJ mol^{-1} at Sleeping Bear Dunes, and 38 kJ mol^{-1} at Sturgeon Point. Because such atmospheric temperature variations affect the gas phase PCB concentrations, it is necessary to remove these variations before a temporal trend can be determined. The temperature correction procedure was reported by Cortes et al. (1998). Briefly, the gas phase concentrations of each PCB congener were first converted to a partial pressure (P) using the ideal gas law. These partial pressures were then corrected to a reference temperature of 288 K by application of equation (1) in a modified form as follows:

$$P_{288} = P \exp \left[\frac{\Delta H}{R} \left(\frac{1}{T} - \frac{1}{288} \right) \right] \quad (2)$$

where \exp is the exponential function, where P is the partial pressure in atmospheres, T is the temperature in $^{\circ}\text{K}$, ΔH is heat of vaporization (in J mol^{-1}) determined from the regression as previously described and R is the gas constant.

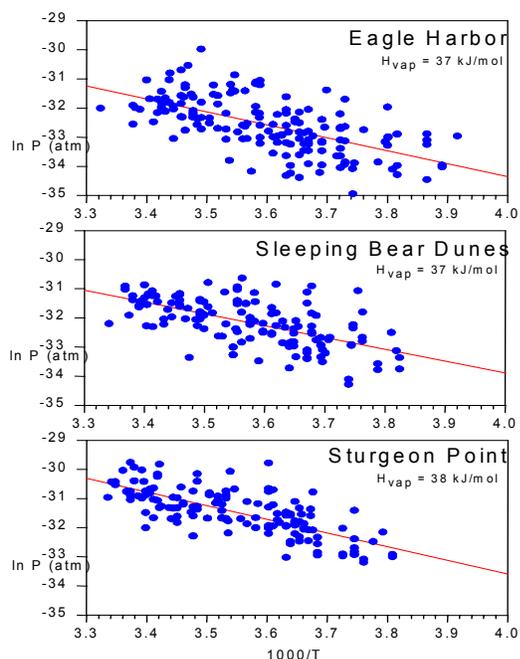


Figure 2. CC plots for gas-phase PCBs at IADN master stations

The values of $\ln P_{288}$ were then regressed vs. time (t , in Julian days relative to January 1, 1990) using equation 3 to determine the rate of exponential increase ($a > 0$) or decrease ($a < 0$) of these partial pressures. If this rate was statistically significant ($p < 0.05$), these rates were then converted to half-lives ($t_{1/2}$, in years) by dividing the values of a into the $\ln(2)/365$ for each compound at each site.

$$\ln P_{288} = at + b \quad (3)$$

Table 2 lists the values of ΔH and the calculated half-lives of total PCB from the a values in equation 3. Figure 3 shows the significant long-term trend of total PCB gas-phase concentrations at the six regionally representative IADN sites. The total PCB concentrations at Brule River showed a significant increasing trend over time. Given that the data for the Brule River site covered only 6 years, we do not consider these trends reliable; thus, PCB trends at this site will not be discussed further. For all remaining IADN sites, average PCB half-lives were 7-8 years.

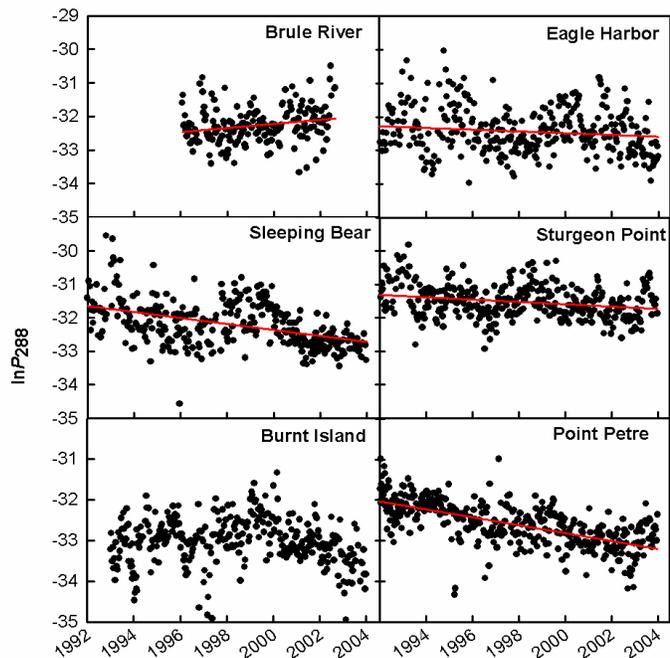


Figure 3. Long-term trend of temperature corrected total PCB partial pressures in the gas-phase at the six regionally representative IADN sites. Red lines indicate statistically significant ($p < 0.05$) regressions of the data. A significant long-term increasing trend is observed at Brule River. Significant decreasing trends are observed at Eagle Harbor, Sleeping Bear Dunes, Sturgeon Point, and Point Petre.

OCs: Means & Spatial Trends

The average concentrations of the OCPs in the gas- and particle-phases as measured by IADN are listed in Tables 3 and 4, respectively (Sun et al, 2005).

Generally, pesticide concentrations in the particle-phase are much lower (usually less than 10%) than those in the gas-phase. The preferred partitioning of OCPs toward the gas-phase is consistent with what would be expected from their relatively high vapor pressures.

The spatial trend of the gas-phase concentrations of all the OCPs show higher values in or closer to urban areas. For example, for chlordanes (presented as the sum of α - and γ -chlordane and *trans*-nonachlor concentrations) the order is: Chicago > Sturgeon Point > Sleeping Bear Dunes > Point Petre > Brule River \approx Eagle Harbor \approx Burnt Island. Chlordane's most common use in the U.S. was for termite control near homes, suggesting that urban areas could be emission sources. Although most abundant in the south and southeastern United States, subterranean termites are found in every state except Alaska, with moderate to heavy structural infestations in Chicago. It has been suggested that volatilization of chlordane from soil in the southern United States was the predominant source of chlordane to the Great lakes. Thus, both historical local applications used to control termites and the influence of long-range transport from areas of high chlordane use could contribute to the relatively high chlordane concentrations at Chicago.

Temporal Trend Analysis

Cortes et al. (1998) have described the gas-phase behaviour of a number of OCPs (e.g., p,p'-DDT, p,p'-DDD, p,p'-DDE, α - and γ -HCH, HCB, cis- and trans-chlordane, trans-nonachlor and dieldrin) observed at the U.S. master stations and Point Petre in the initial years

of IADN. In a similar fashion to the behaviour noted previously for PCBs, a very strong relationship was observed between the atmospheric concentrations and the ambient temperature. It is worthy to note that the effect of temperature on the gas-phase OCP concentrations is so strong that it is necessary (as was the case for PCBs) to remove these variations before a temporal trend can be determined. The procedures described earlier for PCBs have been applied by Sun et al. (2006) in an analogous fashion. Figure 4 shows the temporal trends of gas-phase OCP concentrations at the seven IADN sites. Table 3 lists the corresponding values of ΔH and the calculated half-lives of the OCPs.

Table 3. Average concentrations and fit parameters for pesticides in the gas-phase at IADN sampling stations.

OC Pesticide	Average conc. (pg/m ³)	Half-life (years)	ΔH (kJ/mol)	No. of detects	r^2
α -Chlordane-BR	3.2 ± 0.18	8.8 ± 2.5	33 ± 2.6	182	0.50
α -Chlordane-EH	3.3 ± 0.16	13 ± 2.6	40 ± 2.1	309	0.55
α -Chlordane-SBD	6.5 ± 0.37	11 ± 1.7	48 ± 2.3	323	0.60
α -Chlordane-STP	11 ± 0.56	10 ± 1.3	57 ± 1.8	331	0.76
α -Chlordane-I IT	39 ± 2.8	11 ± 2.7	59 ± 2.4	215	0.74
α -Chlordane-BNT	2.4 ± 0.14	16 ± 3.4	51 ± 1.8	313	0.73
α -Chlordane-PPT	3.9 ± 0.20	9.3 ± 1.0	60 ± 2.0	388	0.72
γ -Chlordane-BR	2.4 ± 0.17	NS	27 ± 4.1	171	0.22
γ -Chlordane-EH	2.9 ± 0.24	6.5 ± 0.9	42 ± 3.3	301	0.41
γ -Chlordane-SBD	6.1 ± 0.39	6.1 ± 0.8	53 ± 3.4	312	0.49
γ -Chlordane-STP	10 ± 0.51	7.4 ± 0.8	57 ± 2.5	323	0.65
γ -Chlordane-IIT	46 ± 3.8	6.7 ± 1.2	55 ± 2.8	215	0.66
γ -Chlordane-BNT	1.9 ± 0.12	11 ± 1.9	46 ± 2.1	313	0.61
γ -Chlordane-PPT	3.6 ± 0.18	8.6 ± 1.0	52 ± 2.4	384	0.58
Dieldrin-BR	8.0 ± 0.81	9.6 ± 4.7	73 ± 4.0	174	0.67
Dieldrin-EH	10 ± 0.78	4.9 ± 0.5	84 ± 3.5	341	0.66
Dieldrin-SBD	24 ± 2.1	5.3 ± 0.7	92 ± 3.8	336	0.65
Dieldrin-STP	26 ± 1.9	5.7 ± 0.6	85 ± 3.2	340	0.69
Dieldrin-IIT	110 ± 11	6.1 ± 1.2	68 ± 3.5	215	0.65
Dieldrin-BNT	9.2 ± 0.59	8.9 ± 1.4	61 ± 2.4	309	0.69
Dieldrin-PPT	13 ± 0.86	8.1 ± 0.9	72 ± 2.5	382	0.70
Hexachlorobenzene-BR	66 ± 1.4	9.5 ± 2.8	11 ± 2.4	190	0.14
Hexachlorobenzene-EH	68 ± 1.4	18 ± 2.7	10 ± 1.4	357	0.2
Hexachlorobenzene-SBD	74 ± 1.6	12 ± 1.0	13 ± 1.2	339	0.42
Hexachlorobenzene-STP	77 ± 1.5	15 ± 1.4	16 ± 1.0	349	0.52
Hexachlorobenzene-I IT	90 ± 3.0	8.3 ± 0.9	20 ± 1.3	216	0.60
Hexachlorobenzene-BNT	29 ± 0.52	32 ± 7.2	NS	316	0.20
Hexachlorobenzene-PPT	32 ± 0.63	30 ± 5.6	NS	387	0.46
<i>p,p'</i> -DDT-BR	1.6 ± 0.18	NS	25 ± 6.2	135	0.11
<i>p,p'</i> -DDT-EH	2.7 ± 0.20	16 ± 5.8	41 ± 3.9	280	0.31
<i>p,p'</i> -DDT-SBD	4.9 ± 0.45	11 ± 3.1	60 ± 4.0	295	0.45
<i>p,p'</i> -DDT-STP	9.0 ± 0.61	9.1 ± 1.8	68 ± 3.5	336	0.54
<i>p,p'</i> -DDT-IIT	23 ± 1.9	14 ± 6.1	66 ± 3.3	211	0.66
<i>p,p'</i> -DDT-BNT	0.68 ± 0.04	5.2 ± 0.6	42 ± 2.7	300	0.51
<i>p,p'</i> -DDT-PPT	2.8 ± 0.19	5.4 ± 0.5	25 ± 6.2	385	0.66
<i>p,p'</i> -DDD-BR	1.4 ± 0.13	NS	NS	117	N/A
<i>p,p'</i> -DDD-EH	1.2 ± 0.09	14 ± 5.2	9.7 ± 4.6	217	0.06
<i>p,p'</i> -DDD-SBD	1.8 ± 0.17	9.2 ± 2.7	18 ± 5.0	231	0.10
<i>p,p'</i> -DDD-STP	3.5 ± 0.36	5.0 ± 0.8	NS	259	0.13
<i>p,p'</i> -DDD-IIT	4.2 ± 0.46	5.8 ± 2.1	NS	144	0.05
<i>p,p'</i> -DDD-BNT	0.17 ± 0.01	5.1 ± 0.6	27 ± 3.0	200	0.42
<i>p,p'</i> -DDD-PPT	0.43 ± 0.02	6.0 ± 0.6	0.3 ± 0.01	290	0.52
<i>p,p'</i> -DDE-BR	1.2 ± 0.10	7.9 ± 2.5	53 ± 3.3	180	0.59
<i>p,p'</i> -DDE-EH	1.9 ± 0.12	6.0 ± 0.5	49 ± 2.4	353	0.60
<i>p,p'</i> -DDE-SBD	8.1 ± 0.51	5.9 ± 0.5	72 ± 2.3	339	0.76
<i>p,p'</i> -DDE-STP	17 ± 0.92	7.0 ± 0.6	76 ± 2.0	353	0.81
<i>p,p'</i> -DDE-IIT	29 ± 1.9	6.3 ± 0.8	60 ± 2.1	216	0.80
<i>p,p'</i> -DDE-BNT	2.2 ± 0.11	6.5 ± 0.7	38 ± 2.1	313	0.57
<i>p,p'</i> -DDE-PPT	11 ± 0.69	6.3 ± 0.5	53 ± 3.3	386	0.72
<i>o,p'</i> -DDT-BR	0.53 ± 0.09	NS	71 ± 7.8	51	0.64
<i>o,p'</i> -DDT-EH	0.47 ± 0.05	NS	54 ± 4.8	81	0.62
<i>o,p'</i> -DDT-SBD	1.2 ± 0.13	-6.3 ± 2.1*	73 ± 4.5	113	0.71
<i>o,p'</i> -DDT-STP	2.1 ± 0.20	-3.0 ± 0.8*	71 ± 5.3	110	0.64
<i>o,p'</i> -DDT-IIT	7.2 ± 0.63	NS	60 ± 3.6	132	0.68
<i>o,p'</i> -DDT-BNT	0.98 ± 0.06	7.6 ± 1.4	40 ± 3.0	298	0.41
<i>o,p'</i> -DDT-PPT	2.9 ± 0.18	19 ± 4.7	NS	383	0.34
<i>o,p'</i> -DDD-BR	3.7 ± 0.58	LD	LD	71	N/A
<i>o,p'</i> -DDD-EH	2.4 ± 0.30	1.8 ± 0.3	12 ± 4.6	99	0.29
<i>o,p'</i> -DDD-SBD	2.6 ± 0.21	3.3 ± 0.7	NS	111	0.17
<i>o,p'</i> -DDD-STP	5.4 ± 0.61	3.3 ± 0.9	12 ± 5.2	87	0.18
<i>o,p'</i> -DDD-IIT	8.8 ± 1.4	LD	LD	23	N/A
<i>o,p'</i> -DDD-BNT	0.31 ± 0.03	8.8 ± 2.1	32 ± 3.3	178	0.37
<i>o,p'</i> -DDD-PPT	0.76 ± 0.05	4.5 ± 0.3	46 ± 3.2	250	0.55

Table 3. continued.

OC Pesticide	Average conc. (pg/m ³)	Half-life (years)	ΔH (kJ/mol)	No. of detects	r ²
Aldrin-BR	0.17 ± 0.02	NS	NS	51	N/A
Aldrin-EH	0.07 ± 0.01	2.4 ± 0.3	<i>13 ± 3.7</i>	68	0.50
Aldrin-SBD	0.08 ± 0.01	<i>3.7 ± 1.0</i>	25 ± 4.6	78	0.32
Aldrin-STP	0.14 ± 0.03	LD	LD	48	N/A
Aldrin-IIT	16 ± 2.2	NS	<i>34 ± 9.1</i>	135	0.11
Aldrin-BNT	0.91 ± 0.06	11 ± 5.2	40 ± 3.9	189	0.39
Aldrin-PPT	0.97 ± 0.06	NS	24 ± 5.0	191	0.14
Endrin-BR	3.4 ± 0.30	LD	LD	66	N/A
Endrin-EH	3.0 ± 0.33	NS	NS	112	N/A
Endrin-SBD	3.6 ± 0.32	NS	NS	96	N/A
Endrin-STP	4.6 ± 0.33	NS	NS	96	N/A
Endrin-IIT	9.4 ± 1.2	<i>-2.4 ± 0.9*</i>	<i>18 ± 6.2</i>	90	0.15
Endrin-BNT	0.78 ± 0.07	5.7 ± 1.0	38 ± 3.8	195	0.42
Endrin-PPT	1.3 ± 0.12	4.0 ± 0.3	41 ± 4.0	256	0.44

BR-Brule River, EH-Eagle Harbour, SBD-Sleeping Bear Dunes, STP-Sturgeon Point, IIT-Chicago, Illinois, BNT-Burnt Island, PPT-Point Petre. Normal font numbers are significant for 0.01 < p < 0.05; italic font numbers are significant for 0.001 < p < 0.01, bold font numbers are significant at level of p < 0.001. "NS" means "not significant" because p > 0.05. A negative half-life is actually a doubling time.

Table 4. Average concentrations and fit parameters for pesticides in the particle-phase at 5 IADN Sites.

OC Pesticide	Average conc. (pg/m ³)	Half-life (years), (ln2)/365b ₁	Peak-to- valley ratio, e ^{2b₂}	Maximum date (± days)	No. of detects	r ²
α-Chlordane-BR	0.61 ± 0.05	10 ± 5.1	2.3 ± 1.2	Jan 19 ± 11	163	0.17
α-Chlordane-EGH	0.4 ± 0.03	6.6 ± 1.5	2.2 ± 1.1	Jan 26 ± 10	172	0.25
α-Chlordane-SBD	0.61 ± 0.06	9.2 ± 3.2	2.9 ± 1.2	Jan 25 ± 8	187	0.26
α-Chlordane-STP	1.5 ± 0.11	7.7 ± 2.7	<i>1.8 ± 1.2</i>	Jan 15 ± 17	203	0.10
α-Chlordane-IIT	9.3 ± 0.9	4.7 ± 1.1	<i>2.0 ± 1.2</i>	Dec 14 ± 17	158	0.16
γ-Chlordane_BR	0.36 ± 0.03	7.3 ± 2.2	2.4 ± 1.2	NS	153	0.27
γ-Chlordane_EGH	0.28 ± 0.02	<i>8.4 ± 2.6</i>	2.4 ± 1.2	Feb 7 ± 9	175	0.23
γ-Chlordane_SBD	0.42 ± 0.02	7.0 ± 1.6	3.0 ± 1.1	Feb 14 ± 7	183	0.34
γ-Chlordane_STP	0.60 ± 0.03	<i>8.5 ± 2.4</i>	3.3 ± 1.1	Feb 15 ± 6	201	0.33
γ-Chlordane_IIT	3.4 ± 0.17	<i>11 ± 3.0</i>	3.4 ± 1.1	Jan 28 ± 5	201	0.46
Dieldrin-BR	2.2 ± 0.16	9.5 ± 4.7	2.0 ± 1.2	Mar 1 ± 15	171	0.12
Dieldrin-EGH	2.7 ± 0.19	3.9 ± 0.5	2.8 ± 1.1	Feb 18 ± 7	200	0.37
Dieldrin-SBD	4.1 ± 0.28	4.3 ± 0.67	4.3 ± 1.1	Feb 17 ± 5	201	0.44
Dieldrin-STP	4.1 ± 0.24	4.0 ± 0.53	3.2 ± 1.1	Feb 9 ± 6	210	0.43
Dieldrin-IIT	22 ± 1.3	6.2 ± 1.2	3.6 ± 1.1	Feb 8 ± 6	201	0.37
Hexachlorobenzene-BR	N/A	N/A	N/A	N/A	N/A	N/A
Hexachlorobenzene-EGH	N/A	N/A	N/A	N/A	N/A	N/A
Hexachlorobenzene-SBD	N/A	N/A	N/A	N/A	N/A	N/A
Hexachlorobenzene-STP	N/A	N/A	N/A	N/A	N/A	N/A
Hexachlorobenzene-IIT	N/A	N/A	N/A	N/A	N/A	N/A
p,p'-DDT-BR	0.95 ± 0.18	NS	NS	NS	50	NS
p,p'-DDT-EGH	0.41 ± 0.04	NS	1.8 ± 1.2	Jan 28 ± 22	90	0.19
p,p'-DDT-SBD	0.69 ± 0.11	NS	NS	NS	101	N/A
p,p'-DDT-STP	1.0 ± 0.09	NS	<i>4.9 ± 1.8</i>	NS	130	0.06
p,p'-DDT-IIT	7.6 ± 0.44	NS	<i>1.8 ± 1.2</i>	Jan 25 ± 15	188	0.09
p,p'-DDD-BR	0.57 ± 0.06	NS	4.6 ± 1.3	Aug 31 ± 56	106	0.23
p,p'-DDD-EGH	0.43 ± 0.09	LD	N/A	N/A	27	N/A
p,p'-DDD-SBD	0.40 ± 0.03	NS	4.1 ± 1.2	Sep 3 ± 49	107	0.28
p,p'-DDD-STP	0.60 ± 0.05	NS	4.4 ± 1.8	Sep 14 ± 41	128	0.26
p,p'-DDD-IIT	1.4 ± 0.13	3.8 ± 0.8	<i>2.1 ± 1.2</i>	NS	158	0.18
p,p'-DDE-BR	N/A	N/A	N/A	N/A	N/A	N/A
p,p'-DDE-EGH	N/A	N/A	N/A	N/A	N/A	N/A
p,p'-DDE-SBD	N/A	N/A	N/A	N/A	N/A	N/A
p,p'-DDE-STP	N/A	N/A	N/A	N/A	N/A	N/A
p,p'-DDE-IIT	N/A	N/A	N/A	N/A	N/A	N/A

Table 4. continued.

OC Pesticide	Average conc. (pg/m ³)	Half-life (years), (ln2)/365b ₁	Peak-to-valley ratio, e ^{2b₂}	Maximum date (± days)	No. of detects	r ²
<i>o,p'</i> -DDD-BR	1.6 ± 0.24	NS	NS	NS	61	N/A
<i>o,p'</i> -DDD-EGH	0.76 ± 0.12	NS	3.8 ± 1.5	Jan 22 ± 16	59	0.18
<i>o,p'</i> -DDD-SBD	2.6 ± 0.21	3.3 ± 0.7	NS	111	0.17	
<i>o,p'</i> -DDD-STP	0.99 ± 0.11	NS	NS	91	91	0.21
<i>o,p'</i> -DDD-IIT	3.1 ± 0.20	NS	2.0 ± 1.2	NS	121	0.09
Aldrin-BR	N/A	N/A	N/A	N/A	N/A	N/A
Aldrin-EGH	N/A	N/A	N/A	N/A	N/A	N/A
Aldrin-SBD	N/A	N/A	N/A	N/A	N/A	N/A
Aldrin-STP	N/A	N/A	N/A	N/A	N/A	N/A
Aldrin-IIT	N/A	N/A	N/A	N/A	N/A	N/A
Endrin-BR	0.30 ± 0.04	LD	N/A	N/A	43	N/A
Endrin-EGH	0.26 ± 0.02	LD	N/A	N/A	48	N/A
Endrin-SBD	0.46 ± 0.04	NS	NS	NS	63	N/A
Endrin-STP	0.69 ± 0.08	NS	NS	NS	53	NS
Endrin-IIT	1.0 ± 0.10	NS	NS	NS	86	NS

*A negative half-life indicates that the concentrations are increasing and the listed value is the doubling time.

For pesticide concentrations (C) in the particle-phase, equation 4 was used to represent the temporal behaviour:

$$\ln C = b_0 + b_1 t + b_2 \sin\left(\frac{t}{b_3} + b_4\right) \quad (4)$$

where t is the time in Julian Days relative to January 1 1990, b_0 is the intercept (unitless), b_1 is a first-order rate constant (in days⁻¹) describing the rate of exponential decrease or increase over time, b_2 is the periodic amplitude (unitless), b_3 is the length of the period (in days), and b_4 is the periodic offset (in days).

To establish the dates of maximum pesticide concentrations, the ratio between the highest pesticide concentration and the lowest concentration can be calculated from the fitted b_2 parameter (equation 4) by taking its anti-logarithm (e^{2b_2} , the factor of 2 in the exponent is needed to calculate the peak-to-valley amplitude). The sine wave would have a maximum at day 91 in a year. Therefore, the dates of the maximum of pesticide concentrations were calculated by first converting the fitted b_4 values from radians to days (multiplying by 365/2π) and then subtracting these values from 91. Table 4 shows results of the fit using equation 4 with b_3 set to 365 days. The results are listed as mean ± standard error.

Figure 5 shows the temporal trends of particle-phase OCP concentrations at the five U.S. IADN sites. The black curves are the fitting lines using the sinusoidal model with the period length (b_3) set to one year (equation 4); the red lines indicate long-term significant decreasing trends ($b_1 < 0$) or increasing trends ($b_1 > 0$).

For restricted pesticides, such as chlordane, the concentrations in the particle-phase peak in the winter (in January or February); these enter the atmosphere from re-volatilization from lake and terrestrial surfaces, and their concentrations in the atmospheric particle-phase tend to increase during the winter due to enhanced partitioning from the gas-phase to the particle-phase. This is different to the behaviour typically seen for current-use pesticides, such as endosulfan, where maxima occur in the summer, a time which corresponds well to their agricultural use.

Most of the OCP concentrations showed significant decreases over time either in the gas- or particle-phase. Although different half-lives between the gas- and particle-phase were observed for some OCPs, most of the half-lives ranged from 4 to 9 years. For example, similar half-lives were observed in both the gas- and particle-phases for dieldrin at all five U.S. sites. Significant increasing trends were observed for some restricted pesticides. For

example, in the gas-phase, the *o,p'*-DDT concentration increased at Sleeping Bear Dunes and Sturgeon Point, and endrin increased at Chicago. However, for these cases, only data from 1999 to 2003 were available.

Chlordane concentrations in the gas-phase declined at all seven sites. Overall, α -chlordane concentrations in the gas-phase had half-lives greater than 10 years and slightly less than 10 years in the particle-phase. Gas-phase γ -chlordane concentrations decreased with half-lives of ~7 years at most sites except Burnt Island.

Technical DDT consists of *p,p'*-DDT (65-80%), *o,p'*-DDT (15-21%), *p,p'*-DDD (<4%) and small amounts of other compounds. *p,p'*-DDT can dehydrochlorinate in the environment to form *p,p'*-DDE. IADN measures the gas-phase concentrations of several DDT-related compounds, including *p,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE, *o,p'*-DDT, and *o,p'*-DDD in the gas-phase, but in the particle-phase, *p,p'*-DDE and *o,p'*-DDT are not measured.

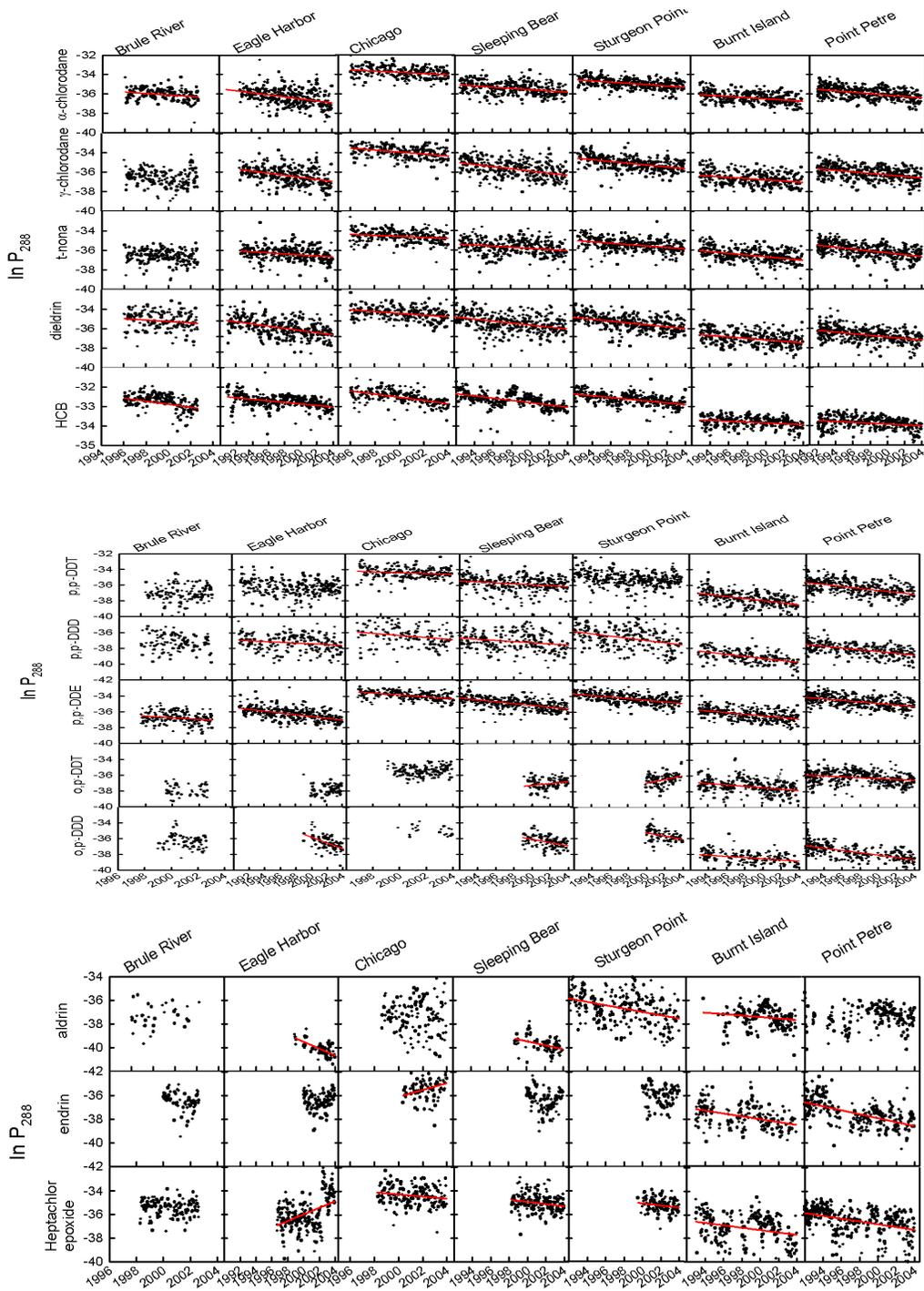


Figure 4. Temporal trends of gas-phase OCP concentrations at seven IADN sites. The red lines indicate long-term significant decreasing or increasing trends. Detailed information on the fitted parameters is in Table 3.

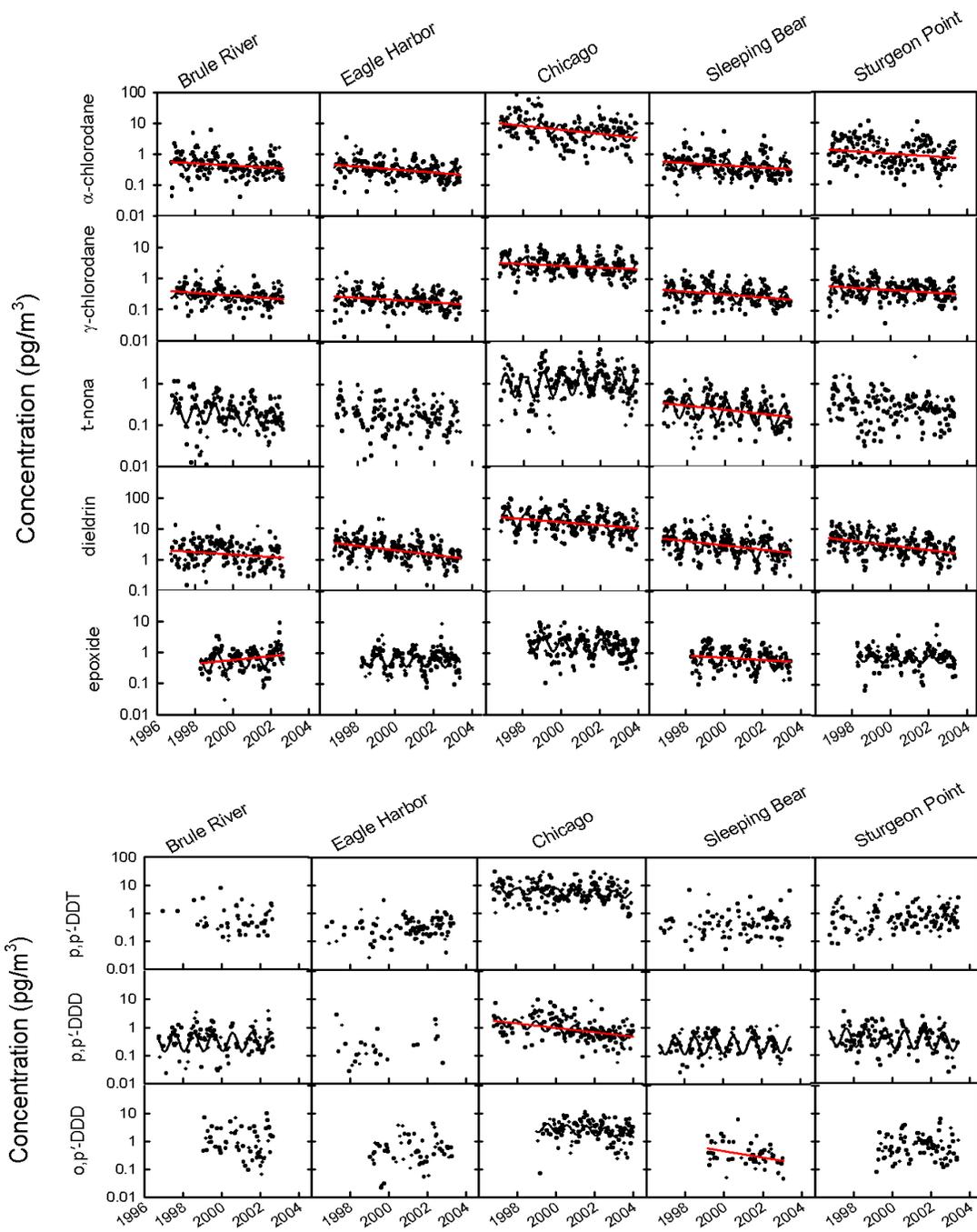


Figure 5. Temporal trends of particle-phase OCP concentrations at five U.S. IADN sites. The black curve is the fitted line using the sinusoidal model with a period length (b_3) set to one year. The red lines indicate long-term significant decreasing or increasing trends.

As shown in Figures 4 and 5, no long-term trends were observed for DDT-related compounds in the particle-phase with two exceptions: *p,p'*-DDD concentrations decreased at Chicago, and *o,p'*-DDD concentrations decreased at Sleeping Bear Dunes. In the gas-phase, *p,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE, and *o,p'*-DDD concentrations showed decreasing trends at most sites, although shorter datasets resulted in a significant increasing trend of *o,p'*-DDT concentrations at Sleeping Bear Dunes and Sturgeon Point.

In general, most of the OCP half-lives listed in Table 3 are longer than those reported previously by Cortes et al. in 1998. With the additional eight years of data, the longer half-lives of OCPs that we now observe suggest that these concentrations are now approaching a steady state. In addition, with a longer sampling period, the calculated half-lives in our study showed lower relative standard errors compared to the previously reported results.

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A1.1.4 Executive Summaries for the active air sampling data of the project MONARPOP

Key Message

The air concentration data of the international project MONARPOP represent the first data from high altitude summits in the Alps and – since monitoring started only a few years ago – a baseline for future evaluations. Spatial differences in the concentrations of the Alpine region have been observed and clear evidence for the barrier effect of the Alps for long range transport of the compounds has been identified. Nevertheless, the detected concentrations at the Alpine summits give also evidence for the transport of POPs across the Alps - the detected concentrations show the same magnitudes as those from other remote or rural air monitoring sites.

Background

First results from the Alps revealed higher concentrations of POPs in spruce needles and forest soil at the highest sites of altitude profiles^{1,2}. Nevertheless, the information of the loads of POPs in mountain ranges, particularly in the Alps, has been scarce although they have properties that favour input and accumulation of such compounds. These include low temperatures in the high altitude ranges, an increase of precipitation with altitude and the barrier effects for long-range transported air masses indicated also by a clearly higher annual precipitation in the peripheral parts of the Alps. A further specific of the Alps (or difference to remote cold regions of the northern latitudes) is that they are located in central Europe surrounded by densely populated areas of high industrial and agricultural productivity.

Therefore, an initiative of ministries and institutes in Austria, Germany, Italy, Slovenia and Switzerland started the project MONARPOP in 2004 (see³)¹. The main objective of the project is to monitor POPs and other organic pollutants with respect to their long-range transport to remote regions in the Alps, prevalent source directions of their origin, the regional distribution of loads within the area of the Alps, the variation with altitude, an assessment of present pollutant stocks bound in forests of this region and possible biological effects of the detected loads. The project aims to provide information to decision makers and to establish a tool for future assessments of the success of the “Stockholm Convention”.

For sufficient spatial and altitudinal coverage, 40 remote alpine sites have been chosen in Austria, Germany, Italy, Slovenia and Switzerland. In addition, seven altitude profiles with several subplots were selected to investigate the vertical variation of POP-levels.

¹ co-founded by the EU INTERREG IIIb “Alpine Space Programme”, the Austrian Ministry for Agriculture, Forestry, Environment and Water Resources; Bavarian State Ministry of the Environment, Public Health and Consumer Protection; Swiss Federal Office for the Environment; Regional Agency for Environmental Protection of Lombardia; Regional Agency for Environmental Prevention and Protection of Veneto; Swiss Federal Office for the Environment; Swiss Federal Institute for Forest, Snow and Landscape Research; German Research Center for Environmental Health (GSF); German Federal Environment Agency; Umweltbundesamt (Austrian Federal Environment Agency); Slovenian Forestry Institute.

Three heavily instrumented sites above the timberline offer year-round air and deposition data.

The input of POPs is examined by measuring their concentration in air (with direction-specific active and with passive sampling devices), in deposition and needle samples. The present load of POPs in mountainous woodland ecosystems is estimated from needle, humus and topsoil concentrations. The sampled material is screened for detoxifying metabolic activities and dioxinlike effects (AhR-response).

The first project phase which ended in 2007 allowed to gain a good picture on the altitudinal and regional variation of the loads in the Alps (see results section below). The air and deposition monitoring at the three Alpine summits continues which secures a related future contribution to the “Effectiveness Evaluation” of the Stockholm Convention. In addition, specific questions that arose from the results, new aspects concerning POPs in the Alps not addressed by any studies so far and a more complete geographic coverage of the Alps are intended to be covered by a follow-up project.

Sampling

The active air sampling sites of MONARPOP represent three high altitude measurement sites located at three summits of the Alps, taking advantage of the infrastructures of well equipped meteorological stations to operate POP samplers. Weissfluhjoch (Switzerland; 2663 m a.s.l., coordinates: 9.8059 East, 46.8327 North), Zugspitze (Germany, 2650 m a.s.l.; coordinates: 10.9850 East, 47.4211 North) and Sonnblick (Austria; 3106 m a.s.l.; coordinates: 12.9575 East, 47.0539 North) were selected for this purpose (Figure 1).

They represent the top sites of three of the seven altitude profiles within a network of 40 remote sampling sites of the project. They are staffed around the year which ensures maintenance and immediate repair of the sampling equipment.

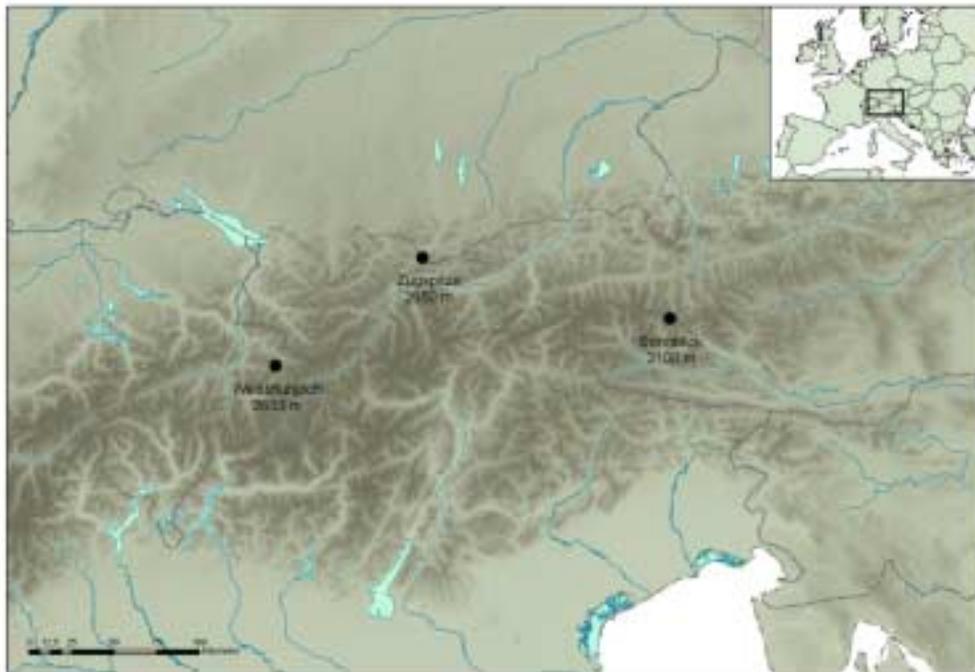


Figure 1: Active air sampling sites of MONARPOP

Air sampling is carried out continuously throughout the year (in subsequent three-months sampling periods) but separately according to source regions of the arriving air masses. Sampling is distributed between separate filters assigned to one of four source regions. Filters are switched according to daily trajectory forecasts. The selected source regions (possibly important for the Alps) are 1. the industrial regions of Germany, Great Britain, Belgium, The Netherlands in the Northwest of the Alps, 2. the industrial region of Czech Republic, Slovakia and Poland in the North East of the Alps and 3. the industrial region of the Po basin in Italy.

Existing air sampling techniques for POPs^{4,5} were modified^{6,7}. At every sampling site, two ambient air samplers, one low volume sampler (3 m³/h) coupled by a steering unit with a high volume sampler (8 m³/h) were equipped with four filter cartridges each. Three cartridges are assigned to the predefined source regions. The fourth cartridge collects air during so-called undefined weather situations, when air masses cannot be attributed to one of the three predefined source regions. Air masses are defined as attributed to a source region if their resident time over any of the predefined regions of interest was at least two days. The appropriate filter cartridges are activated through remote (internet) control based on daily meteorological trajectory forecasts specifically for each site which are carried out by the Austrian Central Institute for Meteorology and Geodynamics.



1...low volume sampler, 2...high volume sampler, 3...deposition samplers, 4...SPMD passive sampler

Figure 2: Sampling site at Mt. Zugspitze

To allow a comparability of the data all three sites are equipped with identical samplers and use the same sampling strategy. Several laboratories carry out the chemical analysis, but each lab analyses one group of compounds in all project samples independent from their national origin. Like that, full data comparability between the three sites has been achieved. For the “Effectiveness Evaluation” only data for the 12 POPs of the “Stockholm Convention” are requested: PCDD/F and PCB were sampled with the high volume samplers and analysed at the Umweltbundesamt in Vienna, while the chlorinated pesticides were sampled with the low volume samplers and analysed at the Helmholtz-Centre (former GSF) in Munich.

Sampling started in 2005. So far, data for the six continuous three-months sampling periods from December 2005 to July 2007 are available. The sampled period so far is too short to allow any time trend analyses. In the present contribution, annual means for the year 2006 for the three Alpine summits are compiled as basis data for future assessments and for comparisons with detected air concentrations from other monitoring programmes. The presented data are not split into source regions, but weighted means were calculated integrating the results from all source regions. This should facilitate the comparison with data from other monitoring programmes. In addition, longer time periods of monitoring will show if the identification of source regions so far that are associated with higher concentrations of some compounds can be repeated.

Sample analytical procedures

Analytical procedures for the PCDD/F and PCB:

The filter cartridges for ambient air sampling contained two polyurethane-foam (PUF) plugs and a glass fibre filter (GF). PUF plugs were precleaned by Soxhlet extraction with toluene and subsequently acetone for 24 hours each. After extraction, PUF plugs were dried in an exsiccator under vacuum and a gentle stream of nitrogen. Glass fibre filters were heated 12 h @ 250 °C. Precleaned PUF plugs and GFs were wrapped in aluminium foil and stored in airtight polyethylene bags in a refrigerator at app. 4° C until cartridge assembly. Before assembling the filter cartridge, GFs were spiked with ¹³C-labelled 1,2,3,4-TCDD and PCB 47. Filter cartridges were sealed with end caps and stored under cool conditions until sampling.

The glass fibre filters and PUF plugs from active air samplers were spiked with 17 ¹³C-labelled PCDD/F congeners, 12 ¹³C-labelled dioxin-like PCBs and six ¹³C-labelled indicator PCBs. The extraction was carried out in a Soxhlet extractor with toluene. The further clean-up comprised treatment with concentrated sulphuric acid adsorbed on Celite followed by a multilayer silica column and an alumina column. The latter was also used to separate PCB from PCDD/F. For recovery calculation one ¹³C-labelled standard was added to each fraction prior to injection.

The PCDD/F and PCB analysis was performed with a high resolution mass spectrometer Finnigan MAT 95 (Thermo Electron GmbH, Bremen, Germany) coupled to a Agilent 6890 gas chromatograph (Agilent Technologies, Waldbronn, Germany) equipped with a cool injection system by Gerstel GmbH (Mühlheim/Ruhr, Germany). PCDD/F have been analysed using a J&W (Agilent Technologies) DB5 column and a DBDIOXIN column, PCBs using a DB5ms column. The mass spectrometer was operated in single ion mode at a mass resolution of 8000 to 10000. The identification and quantification was done by isotope dilution method according to EPA 1613.

Analytical procedures for the chloropesticides:

Glass cartridges were filled with 50 g XAD and glass wool was placed on the top to reduce blank values. These cartridges were Soxhlet extracted with a 3:1 *n*-hexane/acetone mixture for 24 hours and 3 µl ¹³C-PCB was added as a sampling standard. Cartridges were sealed hermetically and transported to the deployment sites. Exposed XAD cartridges were Soxhlet-extracted after spiking with a mixture of ¹³C labelled PAH and chloropesticide standards (Cambridge Isotope Laboratories, USA). The extracts were reduced and split in four parts. One quarter was stored at -20 °C until further delivery, while another quarter was stored at -20 °C as a backup sample. The rest was eluted with a mixture *n*-hexane/dichloromethane 1:1 on a mixed column filled with 10 g silica gel, 5 g Al₂O₃ and 2 g Na₂SO₄ from the bottom to the top. After that, the extracts were eluted through a C18 modified silica column with ACN followed by the concentration of the eluate to 0.2 ml under nitrogen stream at 45°C. The extracts were transferred into vials and spiked with PCT. Finally the eluates were concentrated to 20 µl and the vials were stored at -20 °C until analytical analysis.

The compounds were determined by high resolution gas chromatography (HRGC) using a Rtx–Dioxin2 column (Restek, Germany). The GC was coupled to a high resolution mass spectrometer MAT95 (Thermo Electron GmbH, Germany) operating in single ion monitoring mode.

Data comparability

All steps, from sampling strategy to chemical analysis secure data comparability. Site selection criteria have been designed to allow the selection of comparable remote sites. The sampling strategy and equipment is the same for all three sites. Sample preparation and analysis is carried out for all the samples in the same laboratory – analysis in different labs is split according to groups of compounds and not according to national origin of the samples. So, sample preparation of the HV samplers and PCDD/F and PCB analysis is carried out at the Umweltbundesamt GmbH, in Vienna, sample preparation of the LV samplers and analysis of the chloropesticides at the Helmholtz Centre (former GSF) in Munich.

Both labs are accredited under international systems and participate frequently in international round robins (see related UNEP questionnaire). By that, they strictly need to follow predefined QA/QC regimes.

Data storage.

The project data are stored centrally at the Umweltbundesamt GmbH. This includes the certified original lab data sheets, the recalculated final data and metadata information.

Results.

Since the project started in 2004, the publication activity started short time ago (in 2007). Therefore, not too many of the findings are already available in the literature.

One of the most significant results of the project is the clear documentation of the barrier effect of the Alps for the long range transport of POPs. Concentrations were higher in the peripheral parts of the Alps than in the more shielded central parts. Which of the peripheral parts (north, south, east, west) had higher concentrations varied from compound to compound. With the location of the Alps in the centre of Europe these findings give also general indications for such differences on a larger geographic scale.

These results were obtained by the studied soil and spruce needle compartments of a large number of sites. The air concentration and the deposition measurements at the three Alpine summits did – simply by the limited number of sites – not allow such a significant conclusion. Since these observed regional differences are not based on the core media of the GMP they are not further elucidated here.

The detected active air concentrations of POPs at the Alpine summits document well an existing air transport of these compounds across the Alps – although reduced according to the enhanced deposition of POPs at the peripheral parts. Even compounds like Mirex – never used in central Europe – could be frequently detected in the air at the summits.

Table 1 gives an overview of the detected mean concentrations of the 12 Convention POPs (except Toxaphen and Chlordane) at the Alpine summits. Since monitoring started

in 2005 no time series can be given so far. The data of the first completely available monitoring year 2006 are provided. These results allow a first basis of what can be recently detected at high altitudes at remote sites of the Alps. This allows comparison with data from other monitoring programs and regions, gives indications for the long range transport of POPs across the Alps, at least for those compounds that are no more used in the studied and neighboring countries since many years. Lower, medium and upper bounds were calculated for the various concentrations by replacing values below the detection limit with zero, the half or full detection limit, respectively.

Table 1: Mean atmospheric POP concentrations (2006) on the three Alpine summits measured in MONARPOP (lower–medium–upper boundary)

	unit *	Weissfluhjoch (CH)	Zugspitze (DE)	Sonnblick (AT)
∑DDT (all six isomers)	pg/m ³	4.89	6.95–6.97–7.00	1.92–1.93–1.93
Aldrine	pg/m ³	0.00–0.01–0.02	0.00–0.01–0.02	0.00–0.01–0.02
Dieldrine	pg/m ³	2.51	1.53–1.54–1.54	1.52
Endrine	pg/m ³	0.04–0.06–0.07	0.05–0.08–0.10	0.03–0.06–0.08
Mirex	pg/m ³	0.09	0.07–0.07–0.08	0.07
Hexachlorobenzene	pg/m ³	88.98	63.56	64.90
Heptachlor	pg/m ³	0.06	0.03–0.05–0.06	0.03–0.04–0.04
PCDD/F	fg/m ³	254	329	97
PCDD/F in TEQ _{WHO}	fg/m ³	3.26–6.88–10.50	2.02–3.39–4.75	1.79–3.04–4.29
∑12 dl-PCB	fg/m ³	4231	1735	950
∑12 dl-PCB in TEQ _{WHO}	fg/m ³	0.76–1.17–1.59	0.47–0.54–0.62	0.13–0.25–0.36
∑ 6 indicator PCB	pg/m ³	43.67	24.85	12.53

* at 0 °C and 1013 mPa

It can be seen that the air concentrations measured at the three Alpine summits show the same magnitude to those from the AMAP and EMEP stations. For PCB and DDT the means are higher in the Alps than at sites of the northern latitudes but lower than at the central European EMEP site Kosetice. The PCB concentrations are similar to those measured in the northern AMAP and EMEP sites some years ago. The PCB air concentrations decrease from the western site (Weissfluhjoch, CH) to the most eastern site (Sonnblick, A), a result that is confirmed by the regional distribution of PCB concentrations in the forest soil and needles of the numerous MONARPOP sites. Also for PCDD/F, the observed mean air concentration differences (higher concentrations at the Zugspitze in the northern periphery of the Alps in Germany than at the centrally located other two sites) are in line with the significant higher concentrations in studied soils and needles from the sites of the Northern fringes of the Alps compared to the central sites.

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A1.2 National Programs and ‘snap-shot’ studies for POPs in Air

A1.2.1 Executive Summary of Atmospheric Persistent Organic Pollutants (POPs) Measured under the Northern Contaminants Program (NCP) (Canada) and the National Oceanic and Atmospheric Administration (NOAA) (U.S.A.): Special study of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in air at Alert and POPs air concentrations measured at NCP satellite stations of Tagish (Canada), Little Fox Lake (Canada), Kinngait (Canada), Amderma (Russia), Dunai (Russia) and Valkarkai (Russia); and NOAA station of Barrow (Alaska, U. S. A.)

Key Message

Air concentrations of POPs were measured at seven satellite Arctic stations, with 4 stations in Canada (within the WEOG region) and 3 in Russia. Sampling was conducted at these satellite stations between 1992 and 2003; for varying periods of 2 months to approximately 2 years. Although temporal trends cannot be derived from these short-term measurements, re-initiation of sampling at these locations/regions would allow for assessing changes in air concentrations over time. This is exemplified by measurements conducted at Kinngait (1994-1995 and 2001-2002), Baffin Island, in the Eastern Canadian Arctic. Significant decline in air concentrations of the HCH isomers, chlordanes and dieldrin were observed by comparison of air concentrations between 1995 and 2001. Changes in air concentrations of Σ DDT and Σ PCB were not significant compared to those observed over the same period at Alert (82°30'N, 62°20'W) in the Canadian High Arctic.

Fifteen air samples collected from Alert during the winter of 2000/2001 were analyzed for polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) under a special study. Only particle phase concentrations were reported. The air concentrations of PCDD/Fs measured at Alert were much lower than those observed at Ny-Ålesund and Rörvik.

Background

The Canadian-operated Northern Contaminants Program (NCP) has conducted atmospheric monitoring of persistent organic pollutants (POPs) in the Canadian and Russian Arctic since 1992. The master station for air sampling under NCP is located at Alert, Nunavut, Canada, at which long-term continuous measurements of atmospheric POPs is operated. Long-term temporal trends measured at Alert are summarized in the Executive Summary of POPs in the Atmosphere: Evaluation based upon long-term POP monitoring of the European Monitoring and Evaluation Programme (UNECE-EMEP) and the Arctic monitoring and Assessment programme (AMAP).

(a) NCP and NOAA Satellite Stations

NCP also conducts air sampling for POPs at six satellite Arctic stations in Canada (Tagish, Little Fox Lake and Kinngait) and in Russia (Amderma, Dunai and Valkarkai). NOAA (U.S.A.) operated air measurements of POPs at Barrow, Alaska, in 2002/03, following the same operation, analysis, sample/data handling, quality assurance/ quality control (QA/QC) protocols as NCP. Air concentrations of POPs measured at Barrow are therefore also summarized in this report. The locations of these stations are shown in Figure 1 and site details are given in Table 1. Air measurements of POPs at these satellite stations were conducted at differing time intervals ranging from 2 months to about 2 years. A sampling timeline is given in Figure 1. Despite the short sampling times and measurements have not been continuous at the satellite stations, changes in air concentrations at a specific location may be determine in the future if air sampling were restarted. Spatial variations in air concentrations observed at these locations may also be useful in determining different source region of influence to the different Arctic regions. The current report will summarize air concentrations of POPs measured at these locations.

Out of the 12 priority POPs, only chlordane, dichlorodiphenyltrichloroethane (DDT), dieldrin, endrin, heptachlor, mirex, polychlorobiphenyls (PCBs), hexachlorobenzene (HCB) were measured at the satellite stations. Note that HCB generally experiences breakthrough (more than 33.3 % of the sampled amount was found on the second polyurethane foam (PUF) plug in the sampling train) in approximately 30 % of all samples. Therefore, the air concentrations reported here for HCB may be underestimated. Air concentrations of mirex, endrin and heptachlor were usually found to be below detection limits at all stations and are not reported here. Besides the priority POPs, air concentrations of hexachlorocyclohexane (HCHs) are also included in the current report.

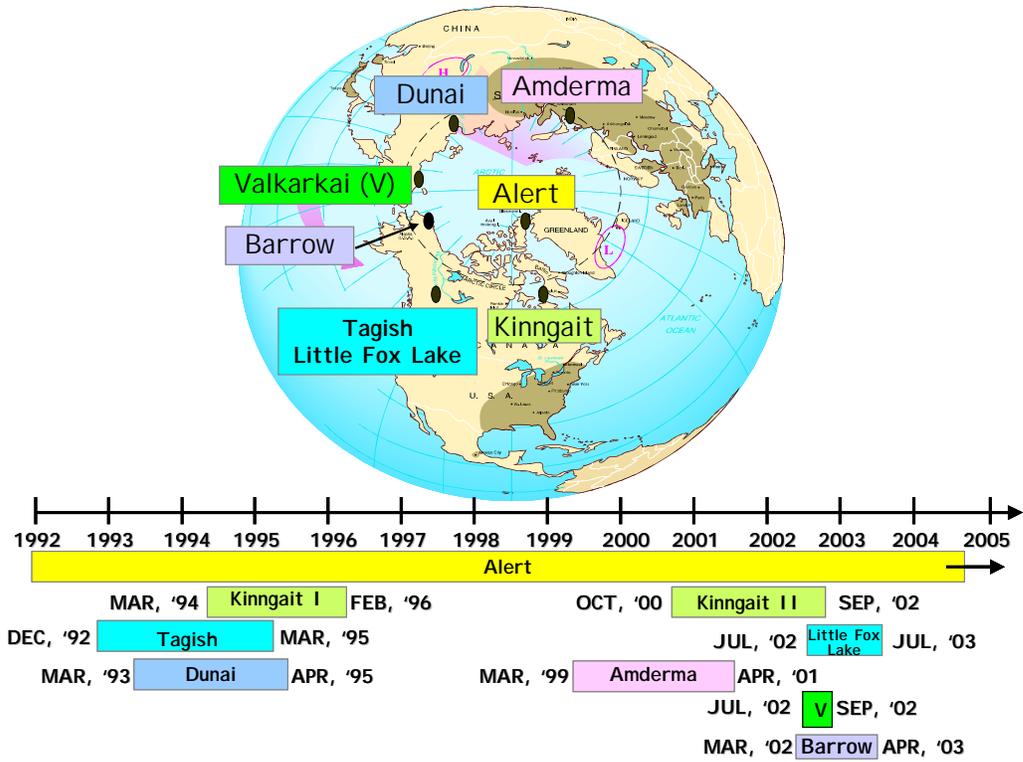


Figure 1. NCP Station Map and Sampling Timeline

Table 1: NCP and NOAA Satellite Stations

Station name	Program	Country	Location	Elevation (m a.s.l.)	Monitoring period
Tagish	NCP	Canada	60° 20' N 134° 12' W	~1000	1992/12/05 – 1995/03/30
Little Fox Lake	NCP	Canada	61° 21' N 135° 38' W	1128	2002/07/07 – 2003/07/06
Kinngait	NCP	Canada	64° 13' N 76° 32' W	119	I: 1994/03/15 – 1996/02/25 II: 2000/10/16 – 2002/09/06
Amderma	NCP	Russia	69° 43' N 61° 37' E	Sea Level	1999/03/28 – 2001/04/02
Dunai	NCP	Russia	74° 6' N 124° 30' E	Sea Level	1993/03/09 – 1995/04/31
Valkarkai	NCP	Russia	70° 5' N 170° 56' E	Sea Level	2002/07/29 – 2002/09/30
Barrow	NOAA	Alaska, U.S.A.	71° 19' N 156° 37' W	9	2002/03/19 – 2003/04/23

(b) Special Study: Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) at Alert

PCDD/Fs were analyzed in 15 air samples collected from Alert during the winter of 2000/2001. Only particle-bound PCDD/Fs were analyzed in this study. Therefore, air concentrations reported here are only particle-phase concentrations. However, atmospheric phase distribution at average ambient temperature (-28.2 °C) estimated using the Junge-Pankow adsorption model and the adsorption model based on octanol-air partition coefficients have shown that most PCDD/F congeners would be particle-bound during the sampling period; with particle fractions > 90 %. Air concentrations of PCDD/Fs measured at Alert are compared with those measured at Ny-Ålesund, Svalbard/Norway, in 1995 (Schlabach et al., 1996) and Rörvik, Sweden, in January-March 1989 (n=3) and May 1990 (n=5) (Tysklind et al., 1993).

Sampling

At each station, approximately 13000 m³ of air is drawn through a custom-made high volume air sampler every week. The sampling media used include a 20 cm glass fiber filter (GFF), which traps the particle-bound chemicals, and two polyurethane foam (PUF) plugs (20 cm dia × 4 cm thick each), which collect the vapour-phase chemicals. A field blank was obtained every 4 weeks by handling a GFF and a PUF in exactly the same way as a sample without air flow.

Sample Analytical Procedures

In each sample, the GFF and the PUFs were extracted separately with Soxhlet for 24 h with dichloromethane and hexane, respectively. After concentration using rotary evaporation to approximately 40 mL, half of each extract was archived. The remainder of the sample was cleaned-up and analyzed for polychlorinated biphenyls (PCBs), organochlorine pesticides (OCs), and polycyclic aromatic hydrocarbons (PAHs). Detailed description of clean-up and analytical methods can be found elsewhere (Fellin et al., 1996; Halsall et al., 1998). OCs and PCBs were analyzed using a high resolution gas chromatograph (HRGC) with electron capture detection (ECD), equipped with a 60 m × 0.25 mm i.d. DB-5 column. Although particle and vapour-phase concentrations were separately analyzed at all the satellite stations, for data comparability to other stations, total (gas+particle) concentrations are reported here.

For the analysis of PCDD/Fs, the filters collected from week 46 of 2000 (6-14/11/2000) to week 7 of 2001 (12-19/2/01) were cut into approximately half for the purpose of the special study. The filters were weighed before and after being cut. The concentrations were calculated by proportioning the air volume corresponding to the fraction of the filter being used for analysis. Halved filter used for analysis of PCDD/Fs were extracted for 16 - 20 h with toluene. Cleanup and analytical methods are given in Hung et al. (2002). The extracts were analyzed using gas chromatography-high-resolution mass spectrometry (GC-HRMS).

Data Comparability

Except for the analysis of PCDD/Fs, all samples taken at the NCP satellite stations and at the Barrow station of NOAA reported here were collected and handled following the NCP protocol and analyzed by the same laboratory, namely Freshwater Institute, Department of Fisheries and Oceans, Canada. Quality assurance measures included the calculation of method detection limits (MDLs) for each sampling year (average blank value of each sampling medium (filter or PUFs) plus three standard deviations from the mean), inclusion of recovery and internal standards in each sample extract, analysis of EPA standard reference materials, and routine reanalysis of extracts. To retain the maximum amount of information, samples with concentrations below MDLs are included in all analysis. Samples that were found to be below instrument detection limits (IDL) were replaced with 2/3 IDL of the corresponding compound.

PCDD/Fs were analyzed by the Analysis and Air Quality Division, Environmental Technology Center, Environment Canada.

Both laboratories participate in international intercalibration studies for POPs and perform well in these studies.

Data Storage

Air concentration data reported under this program have not been blank- or recovery-corrected. A statistical database in SAS called the Research Data Management and Quality Control System (RDMQTM) with an extensive flagging system is used to track and calculate all air concentration data and quality control information. Data are submitted to the Arctic Monitoring and Assessment Programme (AMAP) Database, hosted by the Norwegian Institute for Air Research (NILU), and are also included in the National Atmospheric Chemistry (NAtChem) database operated by Environment Canada.

Results

Air Concentrations of POPs Measured at NCP and NOAA Satellite Stations

Table 2 summarizes the annual average air concentrations of POPs measured at the NCP satellite stations and at the NOAA station of Barrow.

Table 2. Arithmetic mean (range) of atmospheric POPs at NCP Satellite Stations and NOAA Barrow Station (filter + PUF)

(pg/m ³)	Kinngait I		Kinngait II	
	1994	1995	2001	2002 ^e
HCB ^a	55.4 (15.6 - 123)	63.4 (28.1-123)	57.8 (7.29-112)	46.7 (4.37-86.3)
α-HCH	78.4 (19.3 -193)	71.2 (31.6-112)	25.4 (2.66-66.1)	27.1(8.22-55.4)
β-HCH	0.59 (0.03 - 2.39)	0.29 (0.04-0.57)	0.13 (0.03-0.49)	0.21 (0.02-1.57)
γ-HCH	14.0 (2.25 – 39.3)	9.38 (3.07-26.8)	4.73 (2.22-17.5)	3.07 (1.22-7.44)
Σchlordanes ^b	3.64 (1.28-7.74)	2.28 (1.03-3.56)	1.18 (0.49-2.42)	0.83 (0.25-1.87)
dieldrin	1.63 (0.60-3.96)	1.45 (0.53-2.16)	0.46 (0.13-1.06)	0.39 (0.03-0.93)
ΣDDT ^c	1.61 (0.64-3.27)	1.35 (0.62-2.82)	1.24 (0.57-2.75)	0.63 (0.15-1.79)
ΣPCB ^d	5.58 (2.93-8.77)	5.62 (1.92-14.81)	5.90 (2.4-19.1)	3.9 (0.82-17.1)

(pg/m ³)	Tagish		Little Fox Lake	Barrow
	1993	1994	2002/07/07 – 2003/07/06	2002/03/19 – 2003/04/23
HCB ^a	41.8 (10-138)	55.0 (0.34-901)	66.7 (12.8-118)	47 (13-125)
α-HCH	79.3 (24-160)	78.0 (0.25-757)	47.6 (16.9-86.9)	19 (6.0-37)
β-HCH	1.08 (0.09-3.06)	0.47 (0.02-7.99)	0.19 (0.02-0.85)	0.33 (0.041-0.80)
γ-HCH	11.0(3.33-25.1)	13.2 (0.18-138)	4.50 (1.72-10.2)	2.7 (0.89-5.8)
Σchlordanes ^b	2.89 (1.07-6.62)	3.20 (0.26-30.5)	1.03 (0.51-1.51)	0.99 (0.29-2.6)
dieldrin	0.93 (0.37-2.15)	1.28 (0.04-20.6)	0.31 (0.11-0.60)	1.0 (0.10-3.7)
ΣDDT ^c	1.39 (0.26-3.21)	2.01 (0.43-25.6)	0.93 (0.28-1.55)	1.2 (0.48-4.4)
ΣPCB ^d	3.65 (0.92-8.25)	4.45 (0.86-46.9)	4.09 (0.75-10.6)	17 (8.6-47)

^a HCB breakthrough in ~30 % of all samples taken, mean concentrations may be underestimated.

^b Σchlordanes = Sum of c-chlordane, t-chlordane, c-nonachlor and t-nonachlor

^c ΣDDT = Sum of o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD, o,p'-DDT and p,p'-DDT

^d ΣPCB = AMAP sum of 10 PCBs (PCB 28, 31, 52, 101, 105, 118, 138, 153, 156 and 180)

^e Only samples from 2001/1/15 to 2002/09/06 collected were included in deriving means and ranges.

^f For the Russian stations of Amderma and Dunai, annual sampling cycles started and ended in March. Annual values were therefore derived from one full year of sampling from the start date. For Valkarkai, values were derived from the 5 PUF samples taken during the summer of 2002 due to relatively high GFF field blanks.

Con't Table 2. Arithmetic mean (range) of atmospheric POPs at NCP Satellite Stations and NOAA Barrow Station (filter + PUF)

(pg/m ³)	Amderma ^f		Dunai ^f		Valkarkai ^f
	1999/03/27 – 2000/03/28	2000/03/27 – 2001/04/02	1993/03/09 – 1994/03/14	1994/03/14 – 1995/04/31	2002/07/29 – 2002/09/30
HCB ^a	41 (15.3-96.8)	34.5 (12.4-74.1)	57.0 (18.7-173)	63.8 (30.8-104)	76 (27-104)
α-HCH	24.2 (5.25-78.0)	20.3 (2.33-39.6)	44.9 (0.63-102)	54.6 (4.37-144)	64 (60-75)
β-HCH	0.29 (0.04-1.91)	0.17 (0.04-1.50)	0.92 (0.06-4.73)	0.56 (0.04-11.7)	2.4 (0.26-9.5)
γ-HCH	8.10 (0.79-24.2)	7.24 (1.01-23.8)	10.4 (0.02-22.8)	10.3 (0.17-35.7)	7.4 (4.6-16)
Σchlordanes ^b	1.01 (0.31-1.84)	0.83 (0.13-1.61)	2.26 (0.11-6.03)	2.08 (0.28-8.56)	1.8 (1.4-2.8)
dieldrin	0.69 (0.06-1.42)	0.65 (0.02-1.85)	1.06 (0.02-2.04)	1.33 (0.20-5.29)	0.60 (0.26-0.89)
ΣDDT ^c	2.17 (0.83-5.89)	4.72 (0.45-52.8)	0.98 (0.24-2.04)	1.30 (0.45-5.34)	23 (5.5-77)
ΣPCB ^d	7.82 (2.94-109)	4.72 (1.35-10.2)	8.10 (0.54-22.6)	5.88 (2.09-18.0)	161 (104-296)

^a HCB breakthrough in ~30 % of all samples taken, mean concentrations may be underestimated.

^b Σchlordanes = Sum of c-chlordane, t-chlordane, c-nonachlor and t-nonachlor

^c ΣDDT = Sum of o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD, o,p'-DDT and p,p'-DDT

^d ΣPCB = AMAP sum of 10 PCBs (PCB 28, 31, 52, 101, 105, 118, 138, 153, 156 and 180)

^e Only samples from 2001/1/15 to 2002/09/06 collected were included in deriving means and ranges.

^f For the Russian stations of Amderma and Dunai, annual sampling cycles started and ended in March. Annual values were therefore derived from one full year of sampling from the start date. For Valkarkai, values were derived from the 5 PUF samples taken during the summer of 2002 due to relatively high GFF field blanks.

Since measurements at these stations were for one or two years only (except for Valkarkai where measurements only occurred for 2 months in 2002) and not continuous, it is not possible to derive temporal trends for these locations. However, if atmospheric measurements were to be restarted at these locations/regions, it will be possible to estimate changes in atmospheric concentrations of POPs over time.

As an example, atmospheric measurements at Kinngait were conducted in 1994-1995 and again in 2001-2002. The relative changes in POP air concentrations at this station can be compared with those observed at long-term measurement stations, such as Alert, as shown in Table 2.

Table 2. Comparisons of concentration change between 1995 and 2001 at Kinngait and at Alert

	Kinngait			Alert		
	1995 (pg/m ³)	2001 (pg/m ³)	% changed ^e	1995 (pg/m ³)	2001 (pg/m ³)	% changed ^e
HCB ^a	63.4	57.8	-8.8	60.8	68.5	12.8
α-HCH	71.2	25.4	-64.3	52.8	20.1	-62.0
β-HCH	0.29	0.13	-54.2	0.14	0.08	-43.0
γ-HCH	9.38	4.73	-49.5	7.89	6.81	-13.7
Σchlordanes ^b	2.28	1.18	-48.4	2.61	0.95	-63.7
dieldrin	1.45	0.46	-68.5	1.19	0.49	-59.0
ΣDDT ^c	1.35	1.24	-7.8	1.18	0.58	-50.4
ΣPCB ^d	5.62	5.90	5.0	5.12	2.19	-57.3

^a HCB breakthrough in ~30 % of all samples taken, mean concentrations may be underestimated.

^b Σchlordanes = Sum of c-chlordane, t-chlordane, c-nonachlor and t-nonachlor

^c ΣDDT = Sum of o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD, o,p'-DDT and p,p'-DDT

^d ΣPCB = AMAP sum of 10 PCBs (PCB 28, 31, 52, 101, 105, 118, 138, 153, 156 and 180)

^e % change = $\frac{(\text{annual average concentration in 2001} - \text{annual average concentration in 1995})}{\text{annual average concentration in 1995}} \times 100\%$, a positive

value indicates an increase while a negative value indicates a decrease in air concentrations

It can be seen that the past-used chemical of HCB does not show a significant change in air concentration between 1995 and 2001 at either Kinngait or Alert. Both stations show significant declines in air concentrations of the HCH isomers, chlordanes and dieldrin between 1995 and 2001. The decline in air concentration of lindane (γ-HCH) was relatively faster at Kinngait than at Alert which may reflect the input of lindane from Eurasian sources sustaining air concentrations at Alert. On the other hand, the atmospheric concentrations of ΣDDT and ΣPCB did not change significantly at Kinngait while those at Alert have declined 50.4 % and 57.3 %, respectively, from 1995.

PCDD/Fs measured at Alert

In this special study, weekly filter samples, representing air-borne particles, at Alert, Nunavut, collected between 2000/11/06 and 2001/02/19 have been analyzed for PCDD/Fs. The data has been published in Hung et al. (2002). The 15 samples analyzed were deliberately selected such that the sampling periods coincided with the occurrence of the Arctic Haze (December to April) when air-borne particulate concentrations are generally high at Alert. A total of seventeen 2,3,7,8-substituted dioxin and furan congeners were analyzed. Table 3 summarizes the results from this study and compares measured results to those observed at Ny-Ålesund and Rörvik. The air concentrations of PCDD/Fs at Alert are much lower than at the other two locations. Although both Alert and Ny-Ålesund are located in the high Arctic, the latter is a destination for cruise ships in spring and summer and is closer to Eurasian sources than Alert.

Table 3. Comparison of arithmetic mean (fg/m^3) (range) of atmospheric PCDD/F measured at Alert, Ny-Ålesund and Rörvik^a

	Total PCDD^b	Total PCDF^c
Alert filter only (2000/11/06 - 2001/02/19)	2.76 (n.d. - 13.1)	9.65 (n.d. - 46.5)
Ny-Ålesund, Norway (1995/4/21-1995/5/17) ^d	28	76
Ny-Ålesund, Norway (1995/7/21-1995/08/23) ^d	16	51
Rörvik, Sweden (background air only) ^e	220 – 470	84 – 240

^a All concentrations, other than those from Alert, are total concentrations (vapour + particle phases).

^b Total PCDD = 2,3,7,8-TCDD + 1,2,3,7,8-P5CDD + 1,2,3,4,7,8-H6CDD + 1,2,3,6,7,8-H6CDD + 1,2,3,7,8,9-H6CDD + 1,2,3,4,6,7,8-H7CDD + OCDD

^c Total PCDF = 2,3,7,8-TCDF + 1,2,3,7,8-P5CDF + 2,3,4,7,8-P5CDF + 1,2,3,4,7,8-H6CDF + 1,2,3,6,7,8-H6CDF + 2,3,4,6,7,8-H6CDF + 1,2,3,7,8,9-H6CDF + 1,2,3,4,6,7,8-H7CDF + 1,2,3,4,7,8,9-H7CDF + OCDF

^d Schlabach et al., 1996. For sample taken during 1995/4/21-1995/5/17, recoveries of H6CDD/F were low (20 %); and those of H7CDD/F and OCDD/F were unacceptable (0-4 %).

^e Tysklind et al., 1993.

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A1.2.2 Australian National Dioxins Program: Dioxins in ambient air in Australia in 2002-2003

Key Message

Dioxin levels in ambient air were measured at various locations in Australia including metropolitan, agricultural and remote reference sites (a total of 10 sites). Sampling was conducted over a twelve-month period from approximately September 2002 to September 2003, in order to establish possible seasonal variations in dioxin concentrations.

A strong seasonal cycle in PCDD/PCDF concentrations, both as mass concentrations and TEQ was observed, with a winter concentration maximum in all of the major population centres studied. At urban sites, annual mean concentrations, expressed as middle bound TEQs, ranged between 9 fg TEQ_{DF} m⁻³ and 17 fg TEQ_{DF} m⁻³. Extremely low

PCDD/PCDF concentrations were observed in clean marine air and also in rural locations removed from the major urban centres (typically less than 2 fg TEQ_{DF} m⁻³).

For the urban locations, the PCB concentrations appeared to be more location specific than the PCDD/PCDF concentrations.

Background

This study aimed to characterise dioxin levels in ambient air in Australia during 2002-2003, at various locations including metropolitan, agricultural and remote reference sites. The study formed a component of the Australian National Dioxins Program, which also included measurement of dioxin-like chemicals in human milk, human blood, aquatic environments and soils. There are 12 technical reports available at:

<http://www.environment.gov.au/settlements/chemicals/dioxins/reports.html>

Sampling

Sampling for this report was conducted over a twelve-month period to establish possible seasonal variations in dioxin concentration. The basic sampling period was one month except for two locations where the sampling period was two months. The ten measurement sites represented metropolitan, agricultural and remote area air sheds, with eight of the ten sites situated at existing air-monitoring facilities. Samples were collected using high-volume samplers incorporating particulate and gas phase traps. Particulate phase collections were based on one-week exposure periods.

Samplers used in the ambient air study were designed and constructed to collect both gas and particle phase dioxins and dioxin-like PCBs using established semi-volatile species collection methodologies. Samplers utilised open face quartz fibre filters for the condensed phase. The gas traps, used in conjunction with the filters, were constructed from a medium-density PUF (polyurethane foam) plug, a layer of XAD-2 resin and second PUF plug in a glass housing. The first PUF plug in each trap was pre-spiked using a range of isotopically-labelled surrogate standards for determination of sampling loss.

There was a duplicate sampler at one site, for eleven samplers deployed overall. The majority of samplers were operated at flow rates between 160-200 std. L min⁻¹ (std. refers to standard volume, or reduced to STP). An additional high-volume sampler utilising a larger-inlet trap system, and operating at approximately 1 m³ min⁻¹, was constructed for Cape Grim in Tasmania and operated from March 2003 to August 2003.

Samplers in Queensland were operated at around 73 std. L min⁻¹. The sampled air volume was determined weekly, using built-in calibrated gas meters (or orifice plate for the Cape Grim high-volume sampler).

Sampling sites used for the ambient sampling project represent three broad geographic regions of northern Australia, south-eastern Australia and south-west Western Australia, and priority air sheds represented include Darwin, south-east Queensland, Sydney, Port Phillip and Perth, with the later addition of Adelaide.

The nominal start date for the ambient program was 1 September 2002 and the end date for sampling was 31 August 2003 with trap changes nominally at the end of each calendar month. The sampling program for Netley, SA, was incorporated as an addition to the main sampling program after the start of the main program. It was commissioned in January 2003 and ran until January 2004.

Sample analytical procedures

All gas trap components were prepared for sampling at AGAL, Sydney. This comprised clean-up, a batch blank verification analysis, XAD-2 packing, spiking and trap assembly. Details are included in the full technical report.

Analyses, at the ultra-trace level, of toxic polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs or furans) and co-planar polychlorinated biphenyls (PCBs) were conducted by the-then Australian Government Analytical Laboratories (AGAL) Sydney (now known as the National Measurement Institute). The analytical methodology for the determination utilised isotopic dilution techniques and was modified from those described by the US EPA methods 1613B, 1668A and TO9A. Analyses for dioxins, and dioxin-like compounds, was performed using a high resolution Gas Chromatograph - high resolution Mass Spectrometer HRGC-HRMS (ThermoQuest Finnigan MAT95XL) that has a sensitivity for 2,3,7,8-TCDD of better than 10 fg with a signal to noise ratio of 10:1. Data were collated and processed at CSIRO Atmospheric Research.

The reference laboratory selected for analysing the duplicate quality control samples was the Ministry of the Environment, Laboratory Services Branch, Ontario, Canada (MOE). Five collocated samples plus three samples from the normal sample stream that were split into two aliquots after extraction and clean-up at AGAL (primary analysts) were analysed by MOE Canada.

Data comparability

Quality control procedures were established and documented before the start of the sampling program and included a wide range of checks on both sampling and analytical procedures (eg field blanks, collocated samples and replicate analyses). The data quality assurance plan for the study is included in the technical report. In general, data collection and analysis went smoothly and most data quality goals were attained. Two filters from Queensland were lost in the mail - these represented only small fractions of the monthly samples for those sites and resulting concentrations could be substantially corrected. Also two months' samples (June - July) from the Sydney site, were analysed with incorrect filter and gas trap combinations; however, these data were also substantially correctable using separate gas and filter analyses for the complementary filter and trap combination, retaining effective monthly samples for that site (and providing some limited qualitative information on phase partitioning).

Data storage

The raw analytical data are held by the authors of the report. Electronic copies of the technical reports are held by the Australian Government Department of the Environment, Water, Heritage and the Arts (DEWHA).

Results

Concentrations of 17 dioxin and furan congeners, the total (tetra to octa CDD/F) homologue groups, the 12 dioxin-like PCB congeners and a suite of inorganic and light organic aerosol components were determined for an annual cycle.

A clear, seasonal cycle in PCDD/PCDF concentrations was found, both as mass concentrations and TEQ, with a winter concentration maximum in all of the major population centres studied, from Perth, through Adelaide, Melbourne, Sydney and as far north as Brisbane. The period of enhanced loadings was shorter in Queensland than further south. Neither of the rural locations, in north-east Victoria and in south-east Queensland, showed winter increases as strong as those seen in the urban locations.

The seasonal variation in PCDD/PCDF concentration, correlation with aerosol non-sea-salt potassium (nssK), a tracer for biomass burning, and association of PCDD/PCDF with nssK by factor analysis, indicate that residential wood smoke may contribute to this winter enhancement. The congener patterns found in this study show strong resemblances to the congener concentration patterns found in a study of wood smoke emissions from Australian residential wood heaters, by Gras et al. (2002) and to homologue patterns reported for emissions from Christchurch and Masterton, NZ during winter by Buckland et al. (1999).

Despite the winter enhancement in PCDD/PCDF, overall annual mean concentrations in the major cities were still relatively low by comparison to levels reported in other countries. The annual mean concentrations, expressed as middle bound TEQs, were around 14 fg TEQ_{DF} m⁻³ at the two Perth locations, 9 fg TEQ_{DF} m⁻³ for Brisbane, around 15 fg TEQ_{DF} m⁻³ for Sydney, 17 fg TEQ_{DF} m⁻³ for Melbourne and 15 fg TEQ_{DF} m⁻³ for Adelaide.

Extremely low PCDD/PCDF concentrations were observed in clean marine air and also in rural locations removed from the major urban centres (typically less than 2 fg TEQ_{DF} m⁻³). This indicates a very clean regional background, with the major sources being local and associated with the urban population. The very low concentrations of dioxins in Southern Ocean air, in Australian rural locations, and urban locations in summer point to predominantly local sources for the observed dioxins.

The relative contributions of TEQ_{DF} and TEQ_P vary across the different locations. For the urban locations the PCB concentrations appear to be more location specific than the PCDD/PCDF concentrations. The SA site, Netley, has the highest dioxin-like PCB levels in ambient air of the locations studied and the highest fraction of PCBs in the TEQ_{DF&P}.

During the study period bushfire activity was very strong in both south-eastern and south-western Australia, notably over the summer of 2002-2003. Smoke from bushfire burning was reported from a number of sampling locations including Wattleup, Duncraig, Boorolite and Alphington. PCDD/PCDF concentrations do not show elevations as strong

as those observed during winter, suggesting significant composition differences between smoke from open biomass burning and that from domestic burning.

Concentrations of dioxin-like PCBs in general did not correlate strongly with those of PCDD/PCDFs and were generally higher in the warmer seasons, compared with the winter maxima for the PCDD/PCDFs. PCB169 shows positive correlation with the PCDD/PCDFs and the smoke tracers. The general lack of correlation between concentrations of the dioxin-like PCBs and the dioxins, points to different sources or transformation histories for these species.

A1.2.3 Atmospheric Measurements of Persistent Organic Pollutants in Spain contributed to the Effectiveness Evaluation and Global Monitoring Plan of the Stockholm Convention on POPs by the Ministry of the Environment Rural and Marine Affairs² and the XVPCA in Catalonia.

Key Message

A large number of sporadic atmospheric measurements of POPs in air are available for Spain, only one regional program has operated continuously since 1994 measuring PCDD/F and more recently coplanar PCBs and PAHs in air. In 2008 a long term monitoring plan under the the SC NIP has been established. The available data on PCDD/F show a clear spatial difference from background to industrial and traffic locations. Limited work on temporal trends seems to indicate a decrease in maximum and average values for PCDD/F in 1994-2004.

Background

In the framework of the implementation of the Spanish NIP for the SC and at the initiative of the Division of Air Quality and Industrial Environment of the the Ministry of the Environment Rural and Marine Affairs a long term POPs monitoring plan is being established in cooperation with CSIC (Consejo Superior de Investigaciones Cientificas/ National Research Council) and CIEMAT (Research Center on Energy Environment and Technology) for air sampling and CNSA- I.S. Carlos III for human samples. In spring 08 five passive air samplers have been deployed at each of the 12 EMEP stations in Spain, soil samples have been also analyzed for these sites, other sites will be included in subsequent deployments. The monitoring plan intends to be long term and help identify background levels and seasonal variation at remote sites in the framework of the GMP.

The XVPCA³ is an air quality monitoring system established in 1983 (law 22/1983 of 21 November) and amended by 1986 (Order of 20 June 1986). Administratively it falls under the Department of the Environment and Housing of the Government of Catalonia⁴, Measurements of PCDDs/PCDFs in air have been carried out by the XVPCA since 1994 and since 2003 coplanar PCBs are also measured. Monitoring campaigns with high volume samplers are deployed four times a year obtaining two winter and two summer samples in urban, suburban and rural sites distributed over 15 Air Quality Zones (AQZ).

² This document has been produced (19 November 2008) for the ROG WEOG on effectiveness evaluation of the SC by the Subdirección General de Calidad del Aire y Medio Industrial of the Ministerio de Medio Ambiente Medio Rural y Marino, in Madrid in cooperation with the Departament de Medi Ambient i Habitatge , Generalitat de Catalunya .

³ Xarxa de Vigilancia i Previsió de la Contaminació Atmosfèrica, Red de Vigilancia y Previsión de la Contaminación Atmosférica de Cataluña, Network for Monitoring and Forecasting Air Pollution in Catalonia .Direcció General de Qualitat Ambiental, Departament de Medi Ambient i Habitatge , Generalitat de Catalunya.

⁴ Catalonia is one of the 19 Autonomous Communities (Comunidades Autonomas) that make Spain Andalucía, Aragón, Asturias, Baleares, Canarias, Cantabria, Castilla León, Castilla la Mancha, Cataluña, Ceuta, Extremadura, Galicia, Madrid, Melilla, Murcia, Navarra, País Vasco , Rioja and Valencia.

A few sampling stations have been maintained over the complete period others are moved with the objective of characterizing the 15 AQZ in Catalonia and the different types of environments typified by dominant emission: background, traffic , industrial and land use: urban, suburban and rural in each of them.

In the period 2005-07 three AQZ have been studied : 1 (área de Barcelona), 2 (Vallès-Baix Llobregat) and 4 (camp de Tarragona).

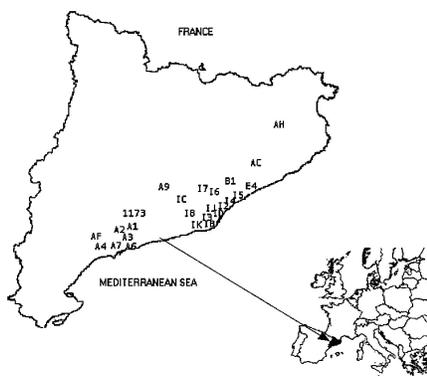


Figure 1 Map showing the region monitored by XVPCA and some of the stations (Abad et al 2002)

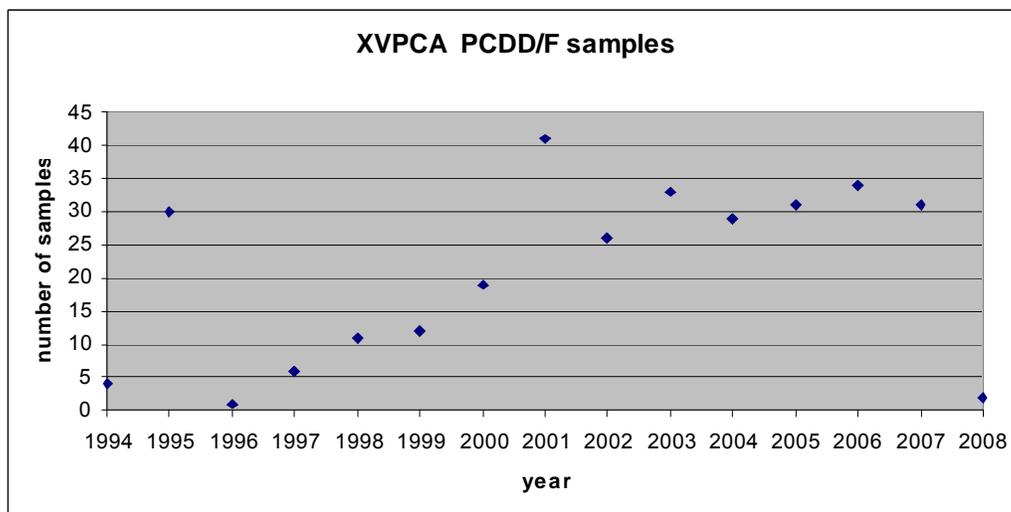


Figure 2: Total number of 24h high volume air samples per year with reported measurements of PCDD/F.

The royal decree 812/2007 of 22 June concerning monitoring and management of air quality in relation with arsenic, mercury, nickel and PAHs establishes the monitoring of benzo(a)pyrene and XVPCA has measured it since 2007.

Concerning the monitoring strategy over the period 1994-2004 the sampling points were selected to represent highly populated areas, industrial , traffic and background.

From 2005 the objective of the XVPCA for PCDD/PCDFs , coplanar PCBs and PAHs is to characterize the 15 AQZ in which the territory is divided. For each zone baseline values in background, traffic and industrial areas will be measured as well as its seasonal variation.

This document presents a summary of the PCDD/F data in air obtained by XVPCA (Catalonia, Spain) in the period 1994-2008.

Sampling

Sampling PCDD/PCDFs and coplanar PCBs

The sampling device consists of a high volume sampler (HVS). A quartz filter (yielding PM10 samples) is placed on the HVS head followed by a pre-cleaned polyurethane foam (PUF) as an adsorbent. The process was controlled by spiking the PUF with CSS standard solution formed by 37Cl-2,3,7,8-TCDD, 13C12-1,2,3,7,8-PeCDF, 13C12-1,2,3,7,8,9-HxCDF and 13C12-1,2,3,4,7,8,9-HpCDF. The HVS was connected to a vacuum pump and between 1000 and 1600 m³ of air mass was collected in 24 h at a sampling flow rate of 45–68 m³/h

Sampling of PAHs

PAHs are sampled following the norm UNE-EN 12341 to determine the PM10 fraction. Sampling time is 24h.

Sample analytical procedures

Analytical procedures to determine PCDD/PCDFs and coplanar PCBs EPA 1613 standard solutions in nonane (CS-1 to CS-5, PAR, LCS, ISS and CSS, Wellington Labs., Guelph, Ontario, Canada) were used for instrument calibration, quantification, recovery and quality control. Solvents (acetone, dichloromethane, toluene, ethyl acetate, n-hexane and cyclohexane) for organic trace analysis were purchased from Merck (Darmstadt, Germany). The cleanup procedure was based on the use of the Power Prepk system (FMS, Massachusetts, USA). The automated system cleanup employs multilayer silica, basic alumina and PX -21 carbon adsorbents, prepackaged in Teflon columns and hermetically sealed.

EN-1948 standard solutions in nonane (Wellington Labs., Guelph, Ontario, Canada) were used for instrument calibration, quantification and quality control. For PCB, standards from WP series in nonane (Wellington Labs., Guelph, Ontario, Canada) were used. Solvents for organic trace analysis were purchased from Rathburn (Walkerburn, Scotland), J.T. Baker (Deventer, The Netherlands), SDS (Peypin, France) and Fluka (Neu-Ulm, Switzerland).

The clean-up procedure was carried out in a multilayer silica column and Envi-Carb SPEcarbon tubes (Supelco, Bellefonte, PA, USA). For planar PCB a further fractionation was performed in a pyrenil PYE column (Cosmosil 5PYE, 4.6x250 mm, 5 µm, Nacalai Tesque, Japan), that allows to separate planar PCBs from the bulk of PCBs.

Instrumental analysis was performed by HRGC/HRMS on a GC 8000 Series gas chromatograph (Carlo Erba Instruments, Milan, Italy) coupled to an Autospec Ultima mass spectrometer (Micromass, Manchester, UK), using a positive electron ionization (EI+) source and operating in the SIM mode at 10,000 resolving power (10% valley definition). The two most abundant ions in the [M-Cl]⁺ cluster were monitored at a 50-ms dwell time and a delay time of 20 ms.

Chromatographic separation was achieved with a DB-5 (J&W Scientific, California, USA) / RTX-5MS (Restek, fused-silica capillary column (60 m#0.25 mm ID, 0.25-m film thickness) with helium as carrier gas, in the splitless injection mode (1–2 :L). As a confirmation, a DBDIOXIN (J&W Scientific) fused-silica capillary column (60 m#0.25 mm ID, 0.25-m film thickness) was employed when required. Chromatographic windows for each group of PCDD/PCDF homologues, from tetra- to octachlorinated, were defined on the DB-5 GC column. Planar PCB analysis were performed in a DB-Dioxin (J&W Scientific) fused-silica column (60 m, 0.25 mm i.d., 0.25 µm film).

Quantification was carried out by the isotopic dilution. Relative response factors (RRF) for the individual isomers were obtained by analyzing CS-1 to CS-5 standard solution mixtures. The recoveries of labeled standards were calculated using a mixture of two labeled PCDDs (ISS mixture) and 4 labeled PCB added before the HRGC-HRMS analysis.

Data comparability

The two laboratories (CSIC⁵ and IQS⁶) that work with XVPCA for the monitoring of PCDDs/PCDFs and coplanar PCBs in air are accredited to comply with ISO 17025. IQS is accredited by the Spanish National Body for Accreditation since 1999. IQS participates in international inter laboratory exercises (International inter calibration Study, organized by Dr. Bert van Bavel) for environmental matrices every year.

⁵ www.iiqab.csic.es

⁶ www.iqs.url.es

Data storage.

Data are reported to the Department of the Environment and Housing of the Government of Catalonia in TEQ per sample of 24h , The data concerning each measured congener for each sample are stored at the laboratory. No long term sample storage is operational at this point

Results.

The stations are classified (according to EU guidelines) by land use (Urban, Suburban, Rural) and type of emission sources (Industrial, Traffic, Background).

The results for PCDD/Fs obtained in 1994-2007 for different types of location show the following ranges,

Spatial variation

Industrial locations: from 3 to 1000 fg I-TEQ/m³, with an average at 88 fg I-TEQ/m³.

Traffic locations: from 5 to 1400 fg I-TEQ/m³, with an average at 122 fg I-TEQ/m³.

Background locations: from 4 to 250 fg I-TEQ/m³, with an average at 33 fg I-TEQ/m³. Study of air samples in Camp de Tarragona area show the following trends:

Rural and background areas were also studied. Eight samples collected in three different sites revealed overall results ranging from 5 to 45 fg I-TEQ/m³ with a mean of 28 fg I-TEQ/m³, whereas background stations presented concentrations of 8 to 28 fg I-TEQ/m³ (Abad et al 2007)

Seasonal variation

PCDD/F levels are higher in winter (8.25-72.7 fg TEQ/m³) than in summer(3.04-10.4 fg TEQ/m³). This difference can be due to an increase of sources in winter, lower dispersion than in summer and lower concentrations of OH radicals in winter.

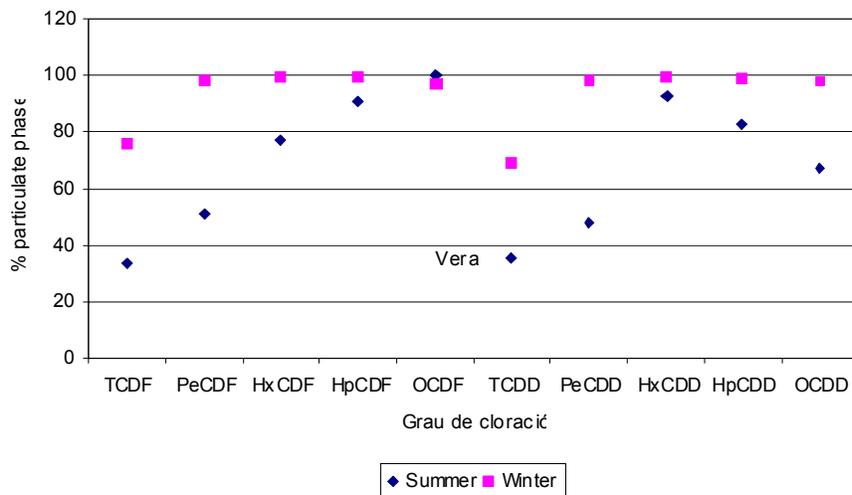


Figure 3 Distribution of PCDD/F between particulate phase and vapor phase is different in winter and in summer. In summer, lower chlorination PCDD/Fs are mostly in vapor phase. The fraction present in the particulate phase increases with the chlorination degree. In winter, TCDD and TCDF still show a significant proportion in the vapor phase (30-40%), while the other homologues are mainly detected in the particulate phase. Considering total values, 61% of TEQ are detected in the particulate phase in the summer, while this amount increases to 97% in the winter.

Homologue profiles are quite similar in the different locations from the Camp de Tarragona area. For furans, the profile is characterized by higher concentrations of the low -chlorination homologues. For dioxins, maximum concentrations are detected in the penta- and hexa-homologues in the summer, while in winter the concentration is increased with the chlorination degree.

Temporal trends

Temporal trends in the data set have been explored in Abad 2004 who publishes the following results in fg I TEQ /m³

	Max	Average	Min
1994-95	954	181	11
1997-98	405	171	18
1999-00	357	109	5
2001-02	223	72	10

Table 1 Temporal variation in maximum, average and minimum concentration values (fg I TEQ /m³) for PCDD/F in air 1994-2002 Abad et al 2004. p283

A more recent study including more data has been published in 2007 (Abad et al 2007) and includes the following results

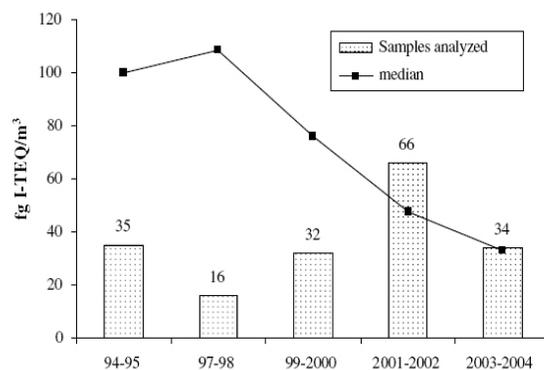


Fig. 1. Ambient air 2,3,7,8-PCDD/F concentration trend in Catalonia (Spain).

Figure 4. The PCDD/F concentration trend in Catalonian ambient air. A noticeable decrease of the median values occurred during the sampling period. A decline of about 70% was observed from 1997–1998 to 2003–2004 (Figure1 in Abad et al 2007).

The time series of PCDD/F concentrations in air corresponding to 10 stations of XVPCA with at least 10 data points in the interval 1994–2008 are presented in figures 5 to 14 below. The values are represented in ln (fg I-TEQ/m³).

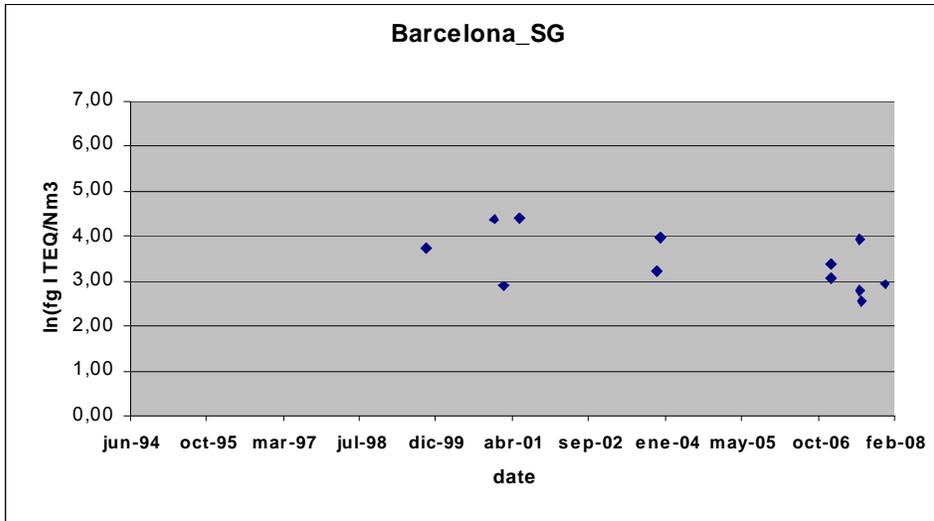


Figure 5: Station code: 08019044, Name: Barcelona-Gracia-St. Gervasi
 UTM : 429.316,00 4.583.565,00 Type: Urban - Traffic

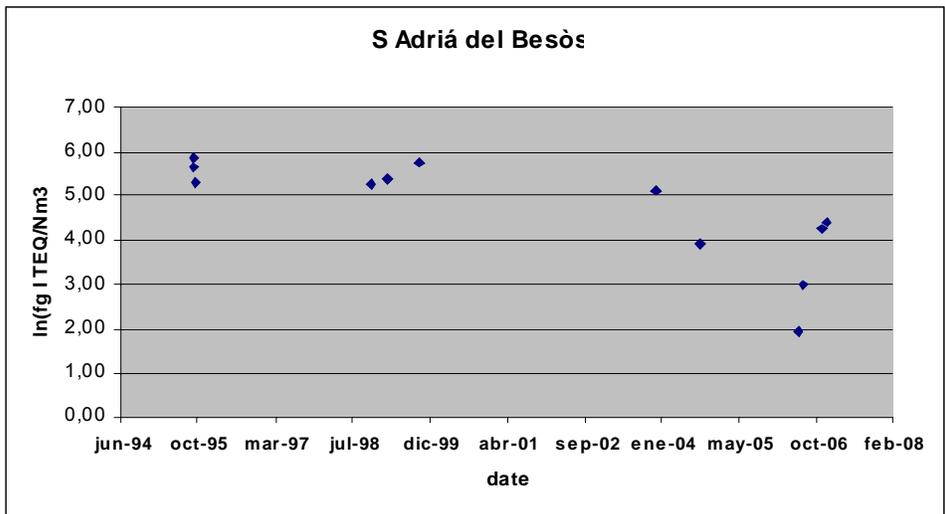


Figure 6: Station code: 08194008 Name: S. Adria del Besòs
 UTM: 435.106,00 4.586.503,00 Type : Suburban - Traffic

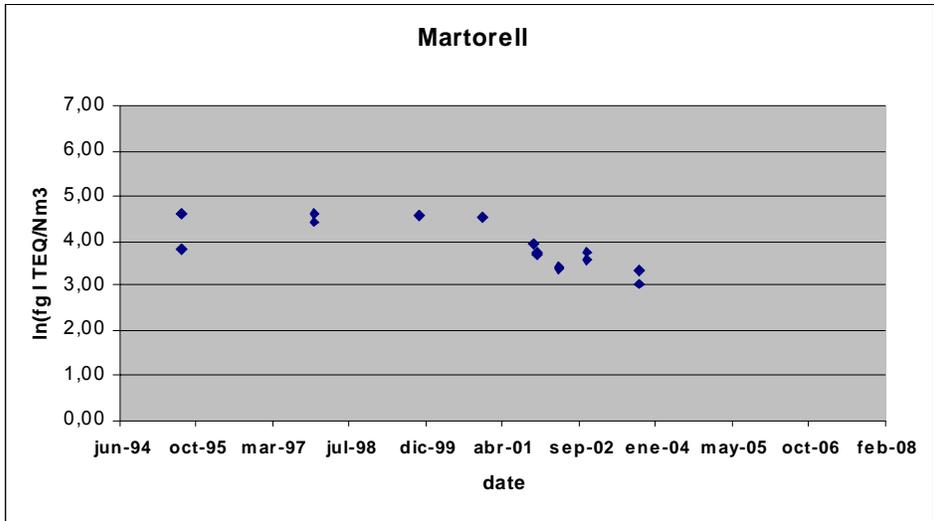


Figure 7: Station code 08114006 Name: Martorell
 UTM : 410.945,43 4.593.043,05 Type: Suburban - Industrial

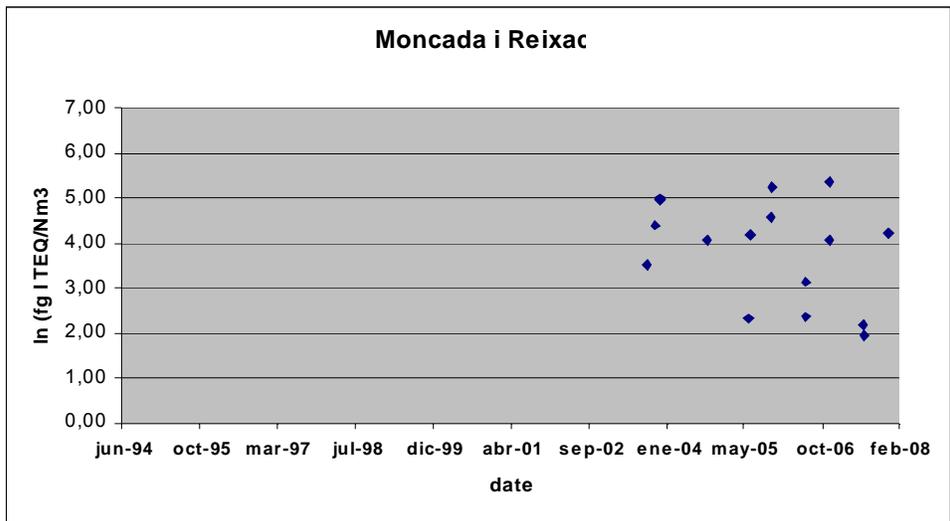


Figure 8: Station code: 08125012 Name: Montcada i Reixac-Ajuntament
 UTM : 432.340,00 4.592.790,00 Type: Suburban - Industrial

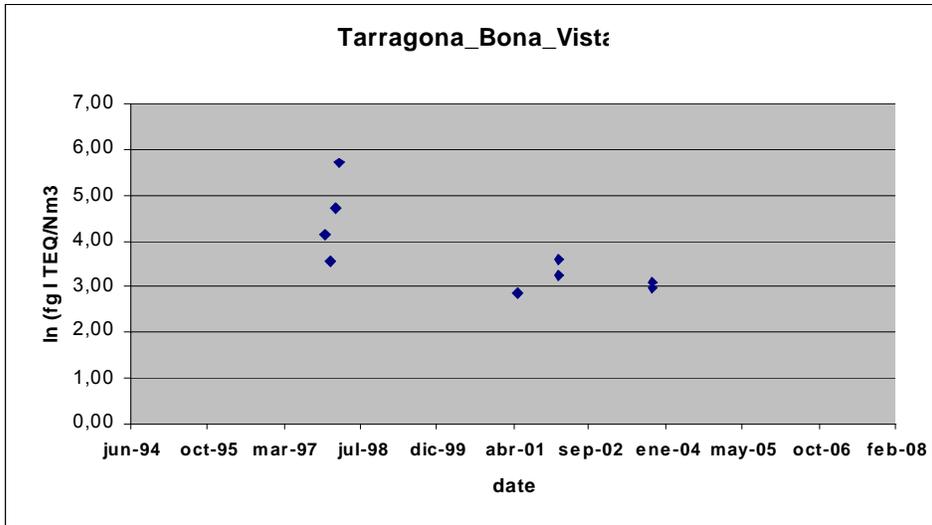


Figure 11: Station code: 43148003 Name Tarragona-Bonavista
 UTM: 348.300,00 4.553.400,00 Type : Suburban - Industrial

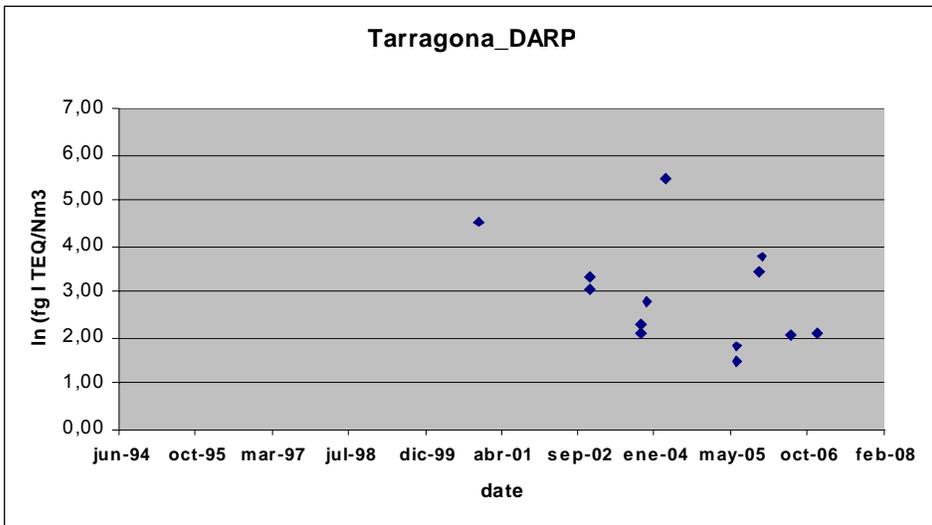


Figure 12: Station code: 43148026 Name: Tarragona-DARP
 UTM: 352.910,00 4.554.085,00 Type: Urban – Background

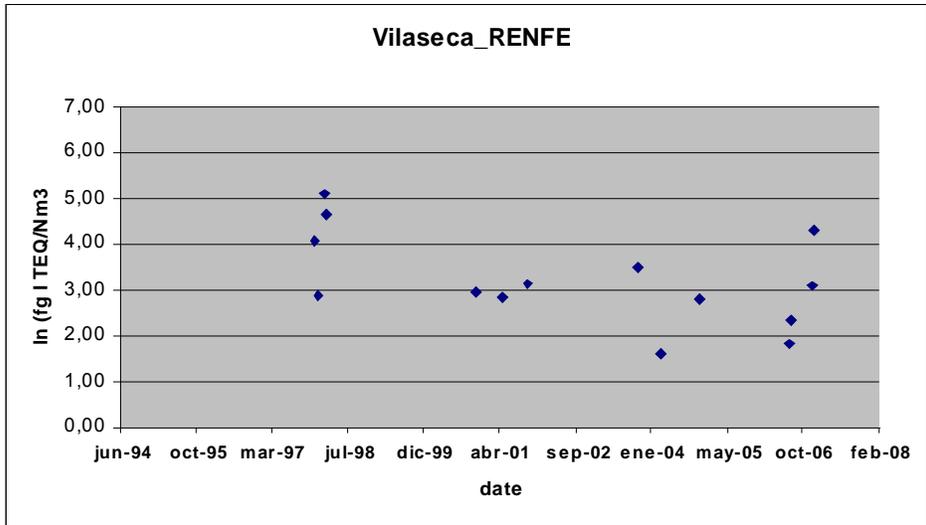


Figure 13: Station code 43171001 Name: Vilaseca (estació RENFE)
 UTM: 344.920,00 4.553.050,00 Type : Suburban - Industrial

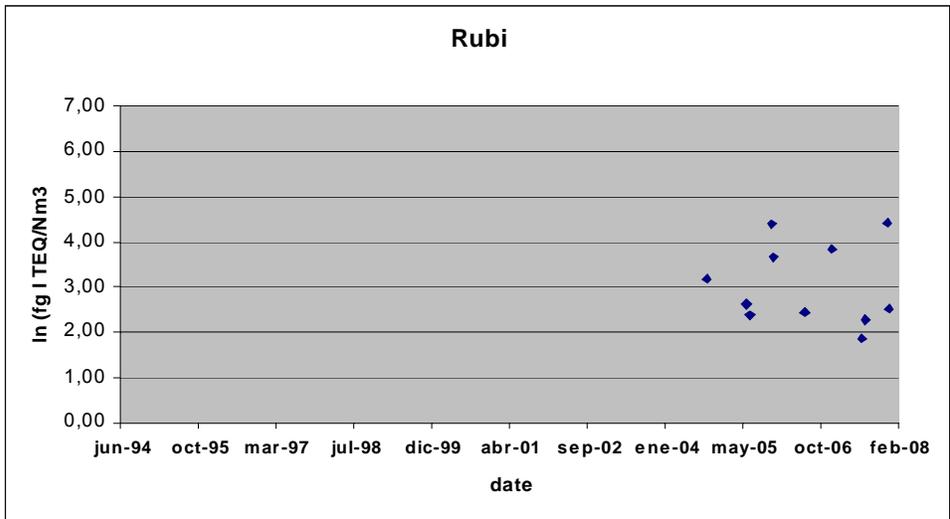


Figure 14: Station code: 08184006 Name: Rubi (ca N'Oriol)
 UTM: 420.180,00 4.594.022,00 Type: Suburban – Background

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A1.2.4 New Zealand: Ambient Concentrations of Selected
Organochlorines in Air

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A1.2.5 UK: The UK Toxic Organic Micro Pollutants (TOMPs)
Program: Air Monitoring of Dioxins/Furans, PCB and PAHs

Key Message

TOMPs (Toxic Organic Micro Pollutants) is a monitoring network funded by the Department for Environment Food and Rural Affairs (DEFRA), to monitor the concentration of PAHs, PCBs, and PCDD/Fs within the U.K. The network was set up in 1990, with Lancaster University (LU) becoming the main contractor in 2004. The sites include; Manchester, Middlesbrough, High Muffles, Hazelrigg, London and Stoke Ferry.

Ambient Air Sampling Under TOMPs

TOMPs sites consist of three urban sites in London (LON), Manchester (MAN), and Middlesbrough (MB), two rural sites at High Muffles (HM) and Stoke Ferry (SF), and one semirural site at Hazelrigg (HR) (see Figure 1). At the rural and semirural sites, samplers are located away from major roads, whereas at the urban sites, samplers are located in the city center on the roof of a building.



Figure 1. Longest-running TOMPS sites discussed in this paper. Urban sites: London (1991–2006), Manchester (1991–2006), and Middlesbrough (1993–2006). Rural sites: High Muffles (1997–2006) and Stoke Ferry (1997–2006). Semirural site: Hazelrigg (1992–2006).

Data are now available for these two longest-running sites for a time period of 16 years, and data for other sites for time periods of between 10 and 15 years (see Figure 1). It is rare to get long time-series like this, especially where the sampling and analysis methods have been consistent throughout the study.

Analytical Methodology for TOMPs

Samples are collected every two weeks with high-volume air samplers, using a glass fiber filter to collect the particle-bound compounds and using two in-line polyurethane foam plugs to collect the gas-phase compounds. Typical air volumes collected over a two-week period are 500–700 m³. Extracts are pooled before analysis to obtain quarterly data (Jan–March (Q1), April–June (Q2), July–Sept (Q3), and Oct–Dec (Q4)).

PUF plugs are pre-extracted with dichloromethane (DCM) for 48 hr using a Soxhlet apparatus. GFFs are pre-combusted at 450°C. Each air sample (gas + particle) is spiked with a recovery standard of ¹³C₁₂-labeled PCB congeners (¹³C₁₂ PCB 28, 52, 101, 138, 153, 180, 209) and with an isotope dilution/recovery standard containing ¹³C₁₂-labelled PCDD/Fs and individually extracted in a Buchi extraction unit for 18 hours with hexane and 6 hours with toluene. The extracts are concentrated using rota-evaporation and nitrogen-evaporation. The 6 hexane fractions of each quarter are then bulked together. The samples are transferred into a 250ml round bottom flask using hexane. If necessary this can then be rotary evaporated to 2ml for splitting. The toluene fractions are then bulked in the same way using hexane. The hexane fraction is then split: 10% is used for the PAHs analysis, 40% for the analysis and 50% is archived. The toluene fraction is also split: 10% is discarded, 40% is analysed and 50% is archived. The toluene and hexane fractions are archived in the same vial. The extracts are then eluted through a multilayer 20 mm id acid silica column containing a small layer of sodium sulphate, 1 g activated silica (Merck Silica 60), 2 g of basic silica (Merck Silica 60), 1 g of activated silica (Merck Silica 60), 4 g of acid silica (Merck Silica 60), 1 g activated silica and a small layer of sodium sulphate (all baked at 450°C overnight), followed by an acid digestion concentrated H₂SO₄, for 2 days and a second multicolumn. The extracts are eluted through gel permeation columns containing 6 g of Biobeads SX 3 and concentrated to 0.5 mL. The concentrated samples are finally fractionated using basic alumina, the PCDD/Fs fractions are eluted with 30ml Hexane/DCM 1:1 and evaporated. The samples are transferred using hexane to injection vial; 15µl of nonane with a ³⁷Cl₆-labelled was added as injection standard and the extract reduced to 15µl using nitrogen blowing system. All samples are analyzed by GC-HRMS using HP6890 GC and a VG Autospec Ultima mass spectrometer, tuned to 10,000 resolving power and running in selected ion monitoring mode. Total PCDD/Fs homologue groups and individual congeners are separated using a 60m DB5MS capillary column. Quantification is achieved using an isotope dilution method.

Data comparability

A number of steps are taken to obtain data that would allow an assessment of the accuracy and reliability of the data. Recoveries are monitored by quantifying 20 ¹³C₁₂-labelled PCDD/F isotope dilution standards, using the injection standard as an internal standard. Analytical blanks, consisting of anhydrous sodium sulphate kept in jars similar to those used for samples and stored with the samples until analysis, are included at a rate of one blank for every 5 samples. The method detection limit is calculated as 3 times the standard deviation of the concentrations found in the analytical blanks. If the concentrations in the blanks are below the instrumental detection limit, then the method detection limit was defined as equal to the instrumental detection limit. The average recoveries ranged between 61 and 101%. The criteria for the quantification of analytes

were a retention time found within 2s of the standard, isotope ratio found within 20% of standard and a signal to noise ratio of at least 3. All results were blank corrected.

Data storage.

The data are reported to DEFRA and published on the UK air quality website (www.airquality.co.uk). Archived samples for each year (50% of the samples) are stored in the freezer in the laboratory at Lancaster University. More information can be found at <http://www.lec.lancs.ac.uk/cem/>.

Results.

PCDD/Fs. PCDD/Fs enter the environment from various combustion processes and as impurities from the manufacture and use of various chlorinated compounds. Considerable effort has been expended in the UK and elsewhere to try and quantify and rank these sources and their emissions into the environment, principally the atmosphere, so that cost-effective source reduction measures can be taken.

Statistical analysis of the time trends for the sum of PCDD/Fs was carried out to investigate the statistical significance of the decreasing trends and to calculate apparent half-lives. Assuming first-order kinetics, the concentration of the chemical in air is given as

$$C = C_0 e^{-kt} \quad \text{or}$$

$$\ln C = \ln C_0 - kt$$

where C is the concentration of the compound in air (ng m^{-3}), k is the rate constant, and t is time (years). Therefore, regressing the natural logarithm of the concentration against time should yield a straight line with intercept $\ln C_0$ and slope $-k$. Half-lives can then be calculated as $t_{1/2} = \ln 2/k$.

The first-order decay curves are shown in Figure 2. Out of the 6 regressions, 3 were statistically significant at Middleborough, Manchester and London. Regressions at High Muffle, Hazelrigg and Stoke Ferry were not statistically significant. This indicates that at more remote sites far from sources, the dioxins/furans signal is more weathered and influenced by meteorology and less dependent on source patterns. The time series for Stoke Ferry and High Muffle is shorter, and therefore the likelihood of detecting significant trends is decreased given the variability in the data. Half-lives range from 3.2 years at London to 11.1 years at Middleborough, with an average half-life of 6.3 years for the sum of PCDD/Fs at all sites.

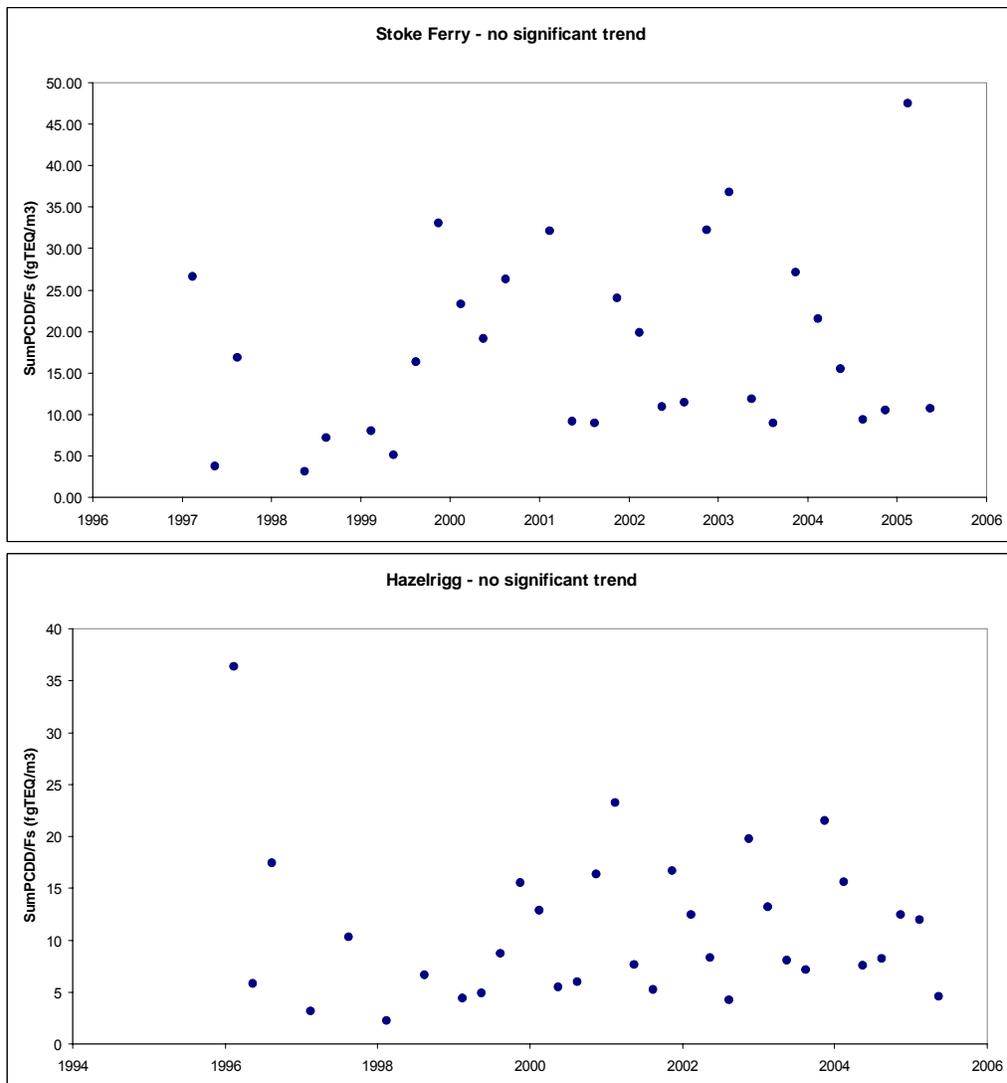


Figure 2. Half-lives curves for the sum of PCDD/Fs at all sites.

PAHs. Statistically significant half-lives ($p < 0.05$ for the slope of the regression) are reported. Out of the 74 regressions, 63 were statistically significant. Out of the 11 regressions that were not significant, eight were at the rural sites High Muffles and Stoke Ferry. The compound with the fewest significant decreasing trends is AC, for which only Hazelrigg and London showed a significant trend. Half-lives range from 2.2 years (AN at Middlesbrough) to 13.4 years (PHE at Manchester), with an average half-life of 5.9 years for all compounds at all sites. A more detailed description of the dataset can be found in Meijer et al. (2008).

PCBs Regression for half lives of PCBs were statistical significant at all sites. Half-lives range from 1.5 years at Stoke Ferry and 20 years at High Muffles.

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A1.2.6 USA: The U.S. EPA's National Dioxin Air Monitoring Network (NDAMN)

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Key Message

NDAMN has been the most comprehensive and extensive air monitoring program for dioxin-like compounds ever conducted in North America. Comprised of 34 geographically dispersed locations in the United States, it operated from June 1998 through December 2004 and collected ambient air measurements of PCDDs, PCDFs and coplanar PCBs in 24 rural and 7 remote sites. Additional data were collected at 3 urban locations to aid in the interpretation of data; however the primary focus of NDAMN was to establish background levels of dioxin-like compounds in air in agricultural and remote areas of the U.S. Sampling was on a quarterly basis and spanned various climate types and seasons. The information obtained from NDAMN has aided scientific understanding of the sources, fate, time-trends, and distribution of these compounds. Dioxin is present in extremely low concentrations (i.e., parts per quadrillion for PCDDs and PCDFs, and parts per trillion for coplanar PCBs). The analysis of data is ongoing, and currently reflects monitoring from 1998 to 2002. These data suggests that there has been little or no change in the amount of these compounds present in ambient air over this time period and in areas of the country that are distant from known anthropogenic source activities. Furthermore, these data support the hypothesis that urban areas are the primary sources of PCDDs, PCDFs, and PCBs present in ambient air over agricultural and remote regions. The uniform pattern of PCDD and PCDF congeners present in ambient air in cities, rural areas, and remote areas is forensic evidence that further associates the collective human activities of the urban environment with measurable contamination of dioxin in rural and remote areas hundreds of km away. In this context, cities can be viewed as regional sources. NDAMN data strongly suggest that mean contemporary background concentrations of dioxin TEQ (WHO-TEQ) in rural and remote areas are within a range of 6 to 15 fg m⁻³, and 0.1 to 3 fg m⁻³, respectively. Coplanar PCBs (WHO-TEQ) are within a range of 0.5-1.0 fg m⁻³ in rural areas, and 0.1-0.5 fg m⁻³ in remote areas.

Background

- Objectives of NDAMN: The National Dioxin Air Monitoring Network (NDAMN) was specifically designed to determine the long-term temporal trends and background air concentrations of PCDDs, PCDFs and coplanar PCBs over agricultural and remote regions of the United States. A secondary objective was to investigate latitudinal and seasonal variation of dioxin-like compounds in ambient air.
- Geographic boundaries: NDAMN was a nationally-based air monitoring network. Air monitoring locations were geographically dispersed throughout the U.S. (i.e., from California to Alaska, Texas to Michigan, and Florida to Vermont). The locations of sampling sites are shown in Figure 1. These locations covered a wide range of climatic conditions from tropical sub-humid to sub-Arctic climates. The idea behind the sampling configuration was to provide reasonable geographic coverage of the United States limited only by budgetary constraints. Funding was

sufficient for the operation and maintenance of 34 NDAMN stations over a period of 6 years.



NDAMN Sites

FIGURE 1 The relative locations of NDAMN stations. Station 2 was a collocated sampler used as a quality assurance procedure.

Ambient Air Sampling Under NDAMN

Long-term ambient air sampling was conducted with a Tisch Environmental® TE 1000PUF (polyurethane foam) sampler in accordance with EPA Method TO-9A as modified in the Quality Assurance Project Plan. The TE 1000PUF sampler consisted of a sampling head; a meter equipped with a magnehelic gauge to measure drop in pressure used to later calculate the air flow, and a blower type vacuum pump. The sampling head assembly consisted of a 10.16cm.i.d. quartz-fiber filter (QFF) and a 5.85cm (i.d.) by 12.7cm (length) glass sample cartridge containing a 5.08cm (length) PUF absorbent material. A regulated air flow was drawn into the top of the sampling head assembly by a vacuum pump, and the particle-bound phase of the contaminants in the air stream was collected on the QFF surface (porosity down to 0.1 μm), while the vapor phase was absorbed into the PUF. A second PUF in a glass cartridge and a QFF were placed into an inactive sampling head assembly at the site to serve as a field blank for quality assurance and quality control. Detection of the analytes in the field blank was an indication of contamination of the sample media prior to active sampling. Any sample in which the field blank exceeded 50% of the measurement results (data) of the active sampler was rejected. Inadvertent sample contamination could not be ruled out.

Each sampling moment consisted of 20-24 days of active sampling over a 28-day period, on a weekly schedule of 5 or 6 days of continuous operation followed by 1 or 2 days of inactivity. In this manner approximately 5000 to 8000 m^3 of air passed through

the sampling head assembly. This permitted sufficient sample volume so as to extend the limit of detection for individual congeners in air to parts per quadrillion (on a volume bases). The protocol was reviewed by a panel of outside experts in the air monitoring field to give further assurance that the sampling procedure would not generate artifactual data. Each week the QFF was harvested and a new QFF was placed in the sampler, yielding four QFFs per sampling moment. This was done to prevent saturation and clogging of the filter media with collected particles. Another benefit of changing the QFFs was the potential to reduce volatile loss of particle-bound dioxin which would have confounded the interpretation of results. The PUF was collected once at the end of the sampling moment. Field testing the sampling protocol indicated that the high sampling volume did not cause loss of sample from the PUF. Prior to sampling, the PUFs were commercially pre-cleaned by heating at 100 °C for 16 hrs, and then analytically determined to be free of dioxin contamination. The QFFs were also pre-cleaned of dioxins. Known quantities of ¹³C-labeled 1,2,3,4- TCDF and PCB-81 were added to the PUF as a quality assurance procedure. Both compounds were selected to represent the most volatile members of the class of analytes, and were intended to gauge any loss of sample during the duration of the sampling period. Four sample sets were generated for each sampling moment at each NDAMN site: one PUF filter from active sampling; one PUF field blank; one set of four QFFs from active sampling; and one set of four QFF field blanks. Daily meteorological measurements were recorded at each site. Harvested samples were packed in dry ice and sent to an EPA laboratory for sample extraction and chemical analysis. The harvested NDAMN samples were packaged with freezer packs and shipped overnight to an EPA laboratory for analysis.

Analytical Procedures for NDAMN

Samples were processed in analytical sets consisting of a group of 12: nine samples, one fortified laboratory control sample, and two method blanks. The QFFs from each individual field sample or field blank were combined with its corresponding PUF in a Soxhlet apparatus, fortified with the 17 ¹³C labeled 2,3,7,8-Cl substituted dioxins/furans and 7 ¹³C labeled coplanar PCBs (all twelve WHO coplanar PCB are analyzed after 2002) and extracted for 24 hours with toluene. The volume was reduced to 50 ml and the solvent exchanged to hexane. The extracts were then stirred for 3 hours with 50 grams of acidified silica and passed through acidified and basic silica gel. The volume was then reduced to less than 1 ml in a Zymark Turbovap II[®] and fractionated on PX-21 graphitized carbon. The dioxin fraction was then further “cleaned-up” on neutral alumina prior to analyses. All reagents were prepared according to procedures detailed in U.S.EPA Method 1613. The lowest calibration standard contained 50 fg of TCDD and 5 pg/μl of ¹³C-labeled surrogates. The samples were fortified to deliver 5 pg/μl from 20 μl of final sample volume. The lower ¹³C surrogate fortification level allowed for a more realistic approximation of the actual recovery of native analytes at the sub parts-per-trillion level and better approximates the behavior of trace levels of natives during sample processing and analyses. All analyses were performed on either a Kratos Concept[®] or a Micromass Ultraspec[®] high resolution mass spectrometer using isotope dilution. The HRMS was operated in the electron impact ionization mode using selected ion monitoring. Chromatographic separations were achieved using a Hewlett Packard 6890 Series II[®] high-resolution gas chromatograph, utilizing a 60 m x 0.32 mm (0.25 μm film

thickness) DB-5MS capillary column. The GC conditions were optimized to completely separate the various 2,3,7,8-Cl-substituted dioxins/furans: initial oven temperature, 130°C; injector temperature, 270° C; interface temperature, 275° C; temperature programming, time 1, 1.0 min, rate 1, 5° C/min, time 2, 15.0 min, rate 2, 6° C/min; temperature 3, 295° C; injector, splitless, 1.0 min; split flow, 30-40 ml/min; purge flow, 1-2 ml/ min; and temperature equilibration time, 2 min. The mass spectrometer was tuned and calibrated prior to all analyses. It was tuned to a minimum resolution of 10,000 ppm (10% valley) using $m/z = 330.9792$ (or any suitable reference peak) at full accelerating voltage of 8,000 V. Pertinent MS parameters were as follows: cycle time for each congener group, ~1.0 s; ESA sweep (analytes), 10 ppm; native ion dwell, ~100 ms; 13C-labeled ion dwell, ~35 ms; lock mass sweep, 200 ppm; lock mass dwell, 50 ms; ionization voltage, ~35 eV; source temperature, 250° C; accelerating voltage, 8,000 V; and trap current, 500 μ A.

Data comparability

The Quality Assurance and Quality Control procedures and criteria are described above. These procedures allow for accuracy and reproducibility of the data. Proper published methods were followed (U.S. EPA method TO9A for sampling, and U.S. EPA Method 1613 for analysis). Sample blanks were employed in the laboratory analysis and field blanks were used to assure that field sampling was not confounded by the introduction of inadvertent contamination of the sampling media.

Data storage.

Aliquots of sample extracts are stored in an archive maintained by the U.S. EPA Environmental Chemistry Laboratory in Bay St. Louis, MS. These samples are stored in freezers at 0°C.

Results.

Although three urban sites were included in NDAMN, the focus of the air monitoring network was to determine background concentrations of dioxin-like compounds in non-urban areas. Results of annual mean air measurements in rural and remote sampling sites are displayed in Table 1.

TABLE 1. Annual Mean Atmospheric TEQ_{DF} and TEQ_{PCB} Concentrations at Rural and Remote Sites in the United States (from the National Dioxin Ambient Air Monitoring Network)^a

location	units	1998/1999 ^b	2000	2001	2002
rural mean TEQ _{DF}	fg m ⁻³	10.43 (± 6.18) (7.25-13.60)	11.39 (± 8.6) (7.37-15.42)	10.40 (± 8.85) (6.37-14.43)	10.47 (± 6.85) (7.43-13.5)
remote mean TEQ _{DF}	fg m ⁻³	1.41 (± 0.94) (0.1-2.91)	0.99 (± 0.59) (0.36-1.61)	0.7 (± 0.25) (0.44-0.96)	1.07 (± 0.61) (0.50-1.63)
rural mean TEQ _{PCB}	fg m ⁻³	0.62 (± 0.28) (0.45-0.80)	0.69 (± 0.47) (0.46-0.91)	0.59 (± 0.31) (0.44-0.74)	0.70 (± 0.46) (0.49-0.92)
remote mean TEQ _{PCB}	fg m ⁻³	0.16 (± 0.01) (0.12-0.21)	0.22 (± 0.15) (0.06-0.38)	0.18 (± 0.11) (0.06-0.30)	0.32 (± 0.21) (0.13-0.52)
no. of sampling stations		8-23	26-30	30-31	34

<i>no. of valid samples</i>	98	99	119	136
<i>no. of sampling moments</i>	9	4	4	4

a (One standard deviation about the mean. Numbers in parentheses (...) are 95% confidence interval. b Includes 1998 sampling moments. The TEQ were calculated using the WHO 1998 toxic equivalence factors.

Results are displayed by years 1998/1999, 2000, 2001, and 2002. In 1998 there were only three sampling periods toward the end of the year; therefore, these results were merged with the 1999 data. At rural sites the mean annual TEQ_{DF} for each of the NDAMN sampling years was 10.43, 11.39, 10.40, and 10.47 fg m⁻³ for 1998/1999, 2000, 2001, and 2002, respectively. There was no statistically significant difference in the rural mean TEQ_{DF} air concentrations across the sampling years (at 0.05 level of significance), although the mean concentration in sampling year 2000 increased 10% relative to the other years. One standard deviation around the mean provides a close concordance of dispersion of these data indicating similar variability in TEQ_{DF} from year to year. The 95th percent confidence interval of the annual TEQ_{DF} concentration for rural areas of the United States suggests that the true annual mean falls within a range of 6.4-15.4 TEQ_{DF} fg m⁻³. Mean annual atmospheric TEQ_{DF} concentrations at remote sites were 1.41, 0.99, 0.7, and 1.07 fg m⁻³ in 1998/1999, 2000, 2001, and 2002, respectively. From 1998/1999 through 2001, there was an average annual reduction of about 0.36 fg m⁻³ per year in mean TEQ_{DF} air concentration at the remote sites. From 2001 to 2002, there was an increase of 0.37 fg m⁻³, suggesting an overall curvilinear trend line from 1998/1999 to 2002. When compared with rural NDAMN sites, the remote sites have average air TEQ_{DF} concentrations that are approximately a factor of 10 lower. The confidence intervals suggest that there is a 95% probability that the true mean annual atmospheric TEQ_{DF} concentration in remote areas of the United States is between 0.1 and 3 fg m⁻³. Global remote areas may have contemporary TEQ_{DF} air concentrations that are <3.0 fg m⁻³.

Figure 2 compares the mean PCDD/PCDF congener profile in ambient air at rural and remote sites. The rural and remote NDAMN sites displayed very similar and consistent distributional patterns of congeners from year to year. The 1,2,3,4,6,7,8-HpCDD and OCDD congeners dominated the congener profile. 1,2,3,4,6,7,8-HpCDD and OCDD ranged from 10.6 to 11.2% and 36 to 39% of the sum of PCDD + PCDF concentrations in rural air, respectively, with a central estimate of about 10% and 37%. In remote air these congeners ranged from 10 to 13% and 33.5 to 38.6%, respectively, with a central estimate of about 11% and 36%. The 1,2,3,4,6,7,8-HpCDF was the third most elevated congener in rural air, representing 1.9-2.7% of total PCDD/PCDF concentration. The fourth most abundant congener in rural and remote air was the OCDF, which represented approximately 2-6% of total PCDD/PCDF concentration. Together, these four congeners accounted for 50-55% of all PCDD and PCDF present in rural and remote air. All other congeners were less than 5% of total PCDD and PCDF concentration. The highly toxic congeners 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD were detected in 96% and 97% of the NDAMN rural samples, and only 49% and 60% in remote samples. When detected in both rural and remote NDAMN sites, the 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD constituted 0.1%, 0.04% and 0.3%, 0.3% of total PCDD/PCDF concentration, respectively. With regard to the mean TEQ_{DF}, there appear to be seven congeners that contribute approximately 80% of the TEQ_{DF} in the ambient air of rural and remote areas of the United States. Ranked in order, these congeners are 1,2,3,7,8-PeCDD; 2,3,4,7,8-

PeCDF; 1,2,3,4,6,7,8-HpCDD; 1,2,3,6,7,8-HxCDD; 1,2,3,7,8,9-HxCDD; 2,3,4,6,7,8-HxCDF, and 2,3,7,8-TCDD.

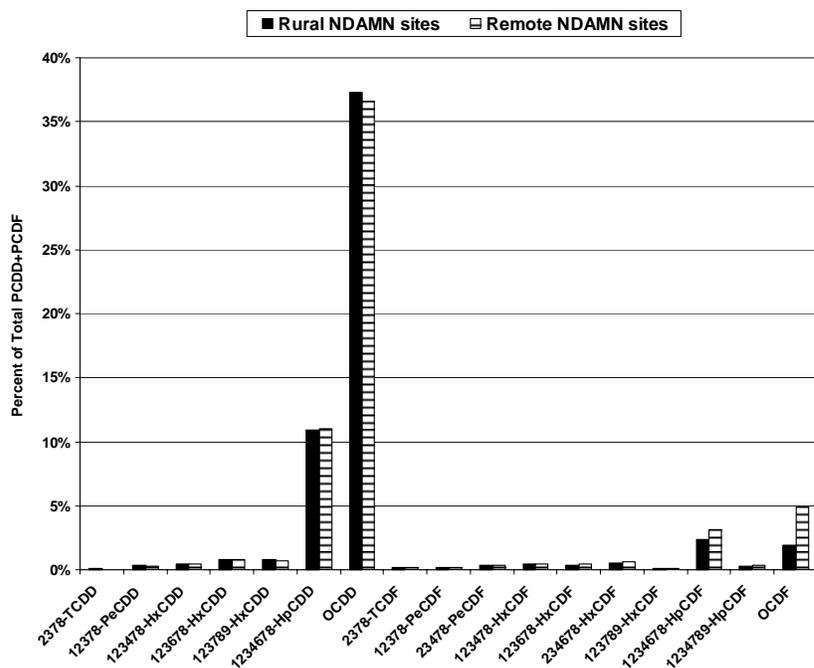


FIGURE 2 Mean PCDD, PCDF congener profile in ambient air at rural and remote NDAMN sites (profile based on dividing mean congener concentrations by sum of mean PCDD+PCDF concentration).

Seven cp-PCB congeners were routinely measured in ambient air at the NDAMN sites. These compounds were PCB-77, PCB-105, PCB-118, PCB-126, PCB-156, PCB-157, and PCB-169. Figure 3 shows the coplanar PCB congener profile for rural and remote locations. With the exception of PCB-169, all cp-PCB congeners were detected in 100% of the samples. PCB-169 was detected at a frequency of 92% in rural sites, but only 42% in remote sites. For the rural sites, there was close agreement in the mean annual air concentrations (TEQ_{PCB}) among the years 1998/1999, 2000, 2001, and 2002 (i.e., 0.62, 0.69, 0.59, and 0.7 $fg\ m^{-3}$, respectively). However, as is the case with PCDDs/PCDFs there was a marked increase (i.e., $\approx 13\%$) in the annual rural mean air concentration in 2000 as compared to the other sampling years. This can be seen in Figure 3. With regard to time-trends, there was no significant difference in the mean measurement of TEQ_{PCB} concentration in rural areas remained over the sampling years. The confidence intervals across the NDAMN sampling years suggest a 95% probability

that mean atmospheric concentrations in rural and remote areas of the United States are within the range of 0.5-1.0 fg m⁻³ TEQ_{PCB} and 0.1-0.5 fg m⁻³ TEQ_{PCB}, respectively. The cp-PCB congener distributional pattern (Figure 3) was relatively similar across the NDAMN sampling years at both rural and remote sites. Among the congeners measured, PCB-118 consistently had the highest concentration in air for all sampling years, followed in order by PCB-105, PCB-77, and PCB-156. Note that in the year 2000, PCBs-118, 77, and 105 significantly increased in comparison to 1998/1999, 2001, and 2002. In terms of the contribution to the TEQ, PCB-126 represents approximately 60%, and PCB-118 accounts for approximately 12-28% of the TEQ_{PCB}. When the TEQ_{PCB} is added to the TEQ_{DF}, they represent on average only 10-15% of the total TEQ air concentration.

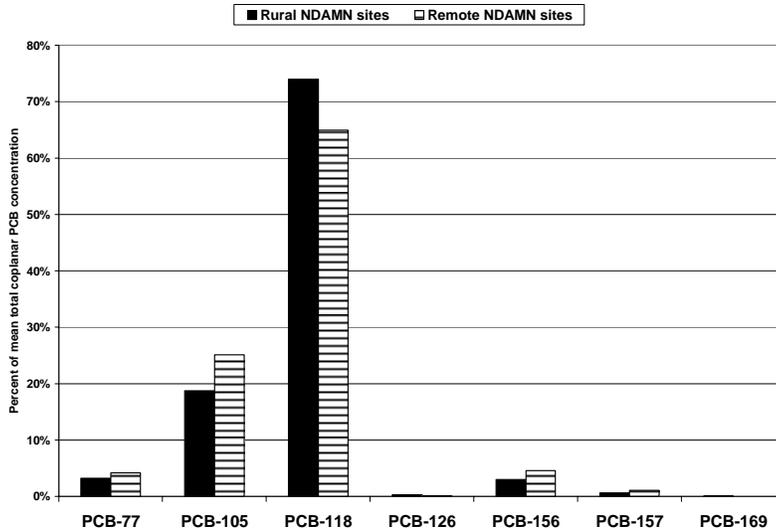


FIGURE 3 Mean coplanar PCB congener profiles from NDAMN for rural and remote areas (based on dividing mean congener concentrations by mean total coplanar PCB concentration).

Seasonal variability: Seasonal variability was able to be observed with quarterly air measurements of PCDDs, PCDFs, and cp-PCBs. The atmospheric concentrations of PCDDs and PCDFs were found to be higher in the fall and winter as compared to spring and summer. For the PCBs, the inverse was true, namely that concentrations were higher in the spring and summer as compared to the fall and winter. Regressing the mean quarterly TEQ_{DF} air concentration at all the NDAMN rural sites against the inverse of the mean atmospheric temperature (K), PCDDs and PCDFs are negatively correlated with temperature meaning that as atmospheric mean temperatures decrease, the concentrations of PCDD/PCDF in air increase. This correlation is statistically significant ($r^2 = 0.81$, at

0.0001 level of confidence). On the other hand, PCB measurements at NDAMN rural sites show a statistically significant positive and linear correlation with temperature ($r^2 = 0.56$, at 0.013 level of confidence).

Contact Information

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Special Note: A database of the results of detecting congener-specific PCDD, PCDF and coplanar PCB in ambient air at each sampling location, for each sampling moment and each sampling year will be publically available by July, 2008. Access to this database will be through U.S. EPA's Internet address: <http://www.epa.gov/NCEA>.

Citations

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