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**COMPARISON OF ENVIRONMENTAL LEVELS OF** HAAS IN THE SOUTHERN AND NORTHERN **HEMISPHERES** 

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**NWRI Contribution No. 01-008** 

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Comparison of Environmental Levels of Chloroacetic Acids in the Southern and Northern Hemispheres A project funded by the Eurochlor program on "The Natural Chlorine Cycle"

#### Final Report on the Analysis of TCA and Other Chloroacetic Acids

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2

#### **NWRI CONTRIBUTION NO. 01-008**

#### **Management Perspective**

This manuscript is the final report on a comparison of the concentration levels of haloacetic acids between the northern and southern hemispheres. This study which addresses the business line of clean environment, it partially funded by Eurochlor, a European consortium of chlorine producers. The information presented augments the data available for haloacetic acid (HAA) concentrations in precipitation, soils and pine needles collected from Canadian locations and compared these with results from samples of similar matrices collected in Chile. Malawi and the UK. Precipitation results shown that HAA fluxes are greatest in Canadian rain and lowest in Malawi rain. However, Malawi rain consistently contained small amounts of monobromoacetic acid (MBA) whereas this compound was not detected in rain from Canada or Chile. The Canadian sites were in isolated locations, not susceptible to large inputs from nearby industrial activities. Soil samples from the UK were found to have the highest total HAA concentration levels, while those from Canada had the lowest. In addition, 1 cm slices from the first 10 cm of soil from all sites in Chile and Malawi were analysed. This allowed inspection of the distribution of the HAAs in soil. When there were high concentrations of HAAs in the soils, the most prominent HAA was the dichloroacetic acid (DCA) and its concentration along with the other HAAs gradually decreased with soil depth. In spruce needles, the monochloroacetic acid concentration levels were similar and low for samples from all countries. Both trichloroacetic and dichloroacetic acid concentration levels were low and similar for samples from Canada, Malawi and Chile. The UK samples had concentrations up to 10x greater.

These results indicate that at Canadian sites situated away from areas of high population densities, the concentration levels of HAAs present in soils and pine needles is similar to those of less industrialised areas, such as Malawi and Chile. In areas of high population and industrial densities high levels, HAA concentration levels similar to those found in Europe would be anticipated.

#### Sommaire à l'intention de la Direction

Le présent manuscrit est le rapport final d'une étude comparative des concentrations d'acides haloacétiques entre les hémisphères nord et sud. L'étude qui concerne le secteur d'activités « Environnement sain », est subventionné partiellement par Eurochlor, un consortium de producteurs de chlore. L'information présentée augmente la quantité de données disponible pour les concentrations d'acides haloacétiques (AHA) dans les précipitations, les sols et les aiguilles de pins prélevés à divers sites au Canada, et les compare avec les résultats provenant d'échantillons de matrices similaires prélevés au Chili, au Malawi et dans le RU. Les résultats obtenus avec les précipitations montrent que les flux d'AHA sont les plus élevés dans les eaux de pluie canadiennes et les plus faibles dans les eaux de pluie du Malawi. Cependant, ces dernières renfermaient régulièrement de petites quantités d'acide monobromacétique (AMBA), alors que ce composé n'a pas été décelé dans les eaux de pluie du Canada ou du Chili. Les sites canadiens étaient des endroits isolés, peu sensibles à des apports importants dus à des activités industrielles voisines. Des échantillons de sol du RU renfermaient les concentrations totales d'AHA les plus élevées, alors que ceux du Canada contenaient les plus faibles. On a également analysé des tranches de 1 cm dans les 10 premiers centimètres de sol à tous les sites du Chili et du Malawi. Cela a permis de déterminer la distribution des AHA dans le sol. Lorsqu'il y avait présence de fortes concentrations d'AHA dans le sol, l'AHA le plus abondant était l'acide dichloracétique (ADCA), dont la concentration tout comme celle des autres AHA diminuait graduellement avec la profondeur du sol. Dans les aiguilles d'épinettes, les concentrations d'acide monochloroacétique étaient comparables et faibles dans les échantillons de tous les pays. Les concentrations aussi bien d'acide trichloracétique que d'acide dichloracétique étaient comparables et faibles dans les échantillons du Canada, du Malawi et du Chili. Les échantillons du RU renfermaient des concentrations jusqu'à 10 fois supérieures.

Ces résultats montrent que, dans les régions canadiennes situées loin des zones fortement peuplées, les concentrations d'AHA dans les sols et les aiguilles d'épinettes sont du même ordre de grandeur que celles que l'on retrouve dans des zones moins industrialisées, comme au Malawi et au Chili. Dans les régions très peuplées et très industrialisées, on peut s'attendre à des concentrations élevées, comparables à celles décelées en Europe.

#### Abstract

Haloacetic acids are a series of compounds whose environmental concentration levels have been extensively studied in Europe. Their sources are believed to be both natural and anthropogenic. To better understand possible sources and contribute to the knowledge of the global distribution of these compounds, especially comparison of concentrations between the northern and southern hemispheres, samples of precipitation, soils and pine needles were collected from Canada, Malawi, Chile and the UK. Results from the precipitation samples indicate extreme HAA concentrations are most prevalent in Canadian samples especially for TCA. Malawi consistently has the highest MCA concentrations. The urban Chile site had higher concentrations of the CAAs than the rural site as noted in the comparison between Chapais (rural) and Algoma (more urban). Soil CAA concentration levels were highest in UK soils and lowest in Malawi soils, with Chile having higher levels than Canada. Soil samples from all sites from Malawi and Chile were also collected in 1 cm slices between 0-10 cm. This unique approach allowed determination of concentration levels of the CAAs with depth which varied from site to site. No chloroacetic acids were detected in pine needles collected from Malawi. UK samples had the highest concentrations of all CAAs (MCA: 2-18 ng/g; DCA: 2-38; TCA: 280-190 ng/g). Conifer needles from Canada and Chile contained CAAs at levels <16 ng/L. CAA levels in Canadian samples were found only in those from western Canada (Banff) but not in central Canada. The results indicate that concentration levels of HAAs are greatest in the industrialized northern hemisphere but there is significant amounts of these compounds in the less industrialized southern hemisphere.

#### Résumé

Les acides haloacétiques sont une série de composés dont les concentrations environnementales ont fait l'objet d'études poussées en Europe. On pense que leurs sources sont à la fois naturelles et anthropiques. Pour mieux comprendre quelles sont les possibles sources et la distribution mondiale de ces composés, notamment par des études comparatives des concentrations entre les hémisphères nord et sud, on a prélevé des échantillons de précipitations, de sols et d'aiguilles de pins au Canada, au Malawi, au Chili et au RU. Les résultats des analyses de ces échantillons montrent que les concentrations extrêmes d'AHA, particulièrement d'ATCA, se retrouvent le plus fréquemment dans les échantillons canadiens. C'est au Malawi que les concentrations d'AMCA sont systématiquement les plus élevées. Au Chili, les concentrations d'ACA étaient plus élevées dans le site urbain que dans les sites ruraux, comme en fait foi la comparaison entre Chapais (rural) et Algoma (plus urbain). Les concentrations d'ACA étaient les plus élevées dans les sols du RU et les plus faibles dans ceux du Malawi, le Chili présentant des concentrations plus élevées que le Canada. Des échantillons de sol ont également été prélevés au Malawi et au Chili en tranches de 1 cm d'épaisseur dans les 10 premiers centimètres de sol. Cette méthode particulière a permis de mesurer les concentrations des ACA en fonction de la profondeur, lesquelles variaient d'un site à l'autre. On n'a pas décelé d'acide chloracétique dans les aiguilles de pins analysées au Malawi. Les échantillons du RU renfermaient les plus fortes concentrations de l'ensemble des ACA (AMCA : 2-18 ng/g; ADCA : 2-38; ATCA : 280-190 ng/g). Les aiguilles des conifères du Canada et du Chili avaient des teneurs en CAA < 16 ng/L.. Des ACA ont été décelés uniquement dans les échantillons de l'ouest du Canada (Banff); il n'y en avait pas dans les échantillons du centre du Canada. Les résultats montrent que les concentrations d'AHA sont maximales dans l'hémisphère nord industrialisé, mais il existe des quantités significatives de ces composés dans l'hémisphère sud moins industrialisé.

#### **INTRODUCTION**

Trichloroacetic acid (TCA) has been detected in air, precipitation, soils and plants in Europe and North America as well as in glacier ice in the Arctic and Antarctic. It appears to be ubiquitous in the environment. However, the source of atmospheric TCA is still a matter of active debate (Juuti and Hoekstra 1998; Reimann et al. 1996, Laniewski et al 1998). Detection of TCA in Antarctic ice and snow at similar levels to those in northern Sweden (von Sydow et al. 1999) indicated a natural source because the main anthropogenic precursor, tetrachloroethene is present at much lower levels in the Southern hemisphere. However recent calculations by Franklin (2000) show that because of lower atmospheric OH radical concentrations and precipitation, the measured TCA levels can be explained by anthropogenic precursors. Measurements of TCA in atmospheric compartments are very limited outside of Europe and are especially lacking in the southern hemisphere. There are gaps in the geographical extent and temporal resolution of the existing environmental measurements of TCA. Most measurements of TCA in air or precipitation have been made in central and northern Europe; by comparison there are only limited measurements for North America (Scott et al. 2000). Asia or the southern hemisphere. This makes it difficult to infer sources from the current body of data.

The general objective of this project was to gather more information on the environmental levels of TCA and other chloroacetic acids in the southern hemisphere, an area for which there are few measurements to date. Measurements of TCA in precipitation and conifer needles were compared with the large database for TCA in these matrices in Europe. Measurements of TCA in non-agricultural surface soils in the southern hemisphere as well as in Canada and the UK were used to assess whether prevailing levels could be explained by atmospheric deposition or *in situ* formation (Hoekstra *et al*, 1999).

#### SAMPLE COLLECTION AND ANALYSIS

Sites: Sample collection sites for Canada, Malawi and Chile are shown In Fig. 1.

**Precipitation:** Sampling kits consisting of new polyethylene (PE) bottles, ultraclean "blank" water and 50x50x15 cm stainless steel collectors were sent to H. Bootsma (Senga Bay, Malawi) and R. Barra (Concepción, Chile) in early January 1999. Samples were collected in the open containers set out during rain events (<24 hrs) and about 1L was transferred to PE bottles and frozen. Samples were shipped frozen to NWRI where they were stored at  $-20^{\circ}$ C until analysis. Sampling at Senga Bay (rural location) began in late January and continued to the end of March 1999. In Chile, precipitation samples were collected at two sites near Concepción . Site A was located in the city of Concepción (downtown  $36^{\circ}50'$  S,  $73^{\circ}3'$  W) and site B in a rural area about 50 km from Concepción ( $36^{\circ}41'$  S,  $72^{\circ}26'$ W) removed from industrial activity. Sampling was delayed due to unusually dry weather in Concepción in the period January to May 1999. Samples were collected during the winter season from late May until early September. Almost all samples were duplicates of each rain event, some were in triplicate. Canadian precipitation samples were collected at Saturna Island (an island on the British Columbia

coast), Algoma (near Sault Ste. Marie, Ontario) and Chapais (in northern Quebec). The samples were provided by the Canadian Atmospheric Precipitation Monitoring Network of the Meteorological Service of Canada. All precipitation volumes were provided by local onsite observers.

Soil samples: Soil collections of 0-10 cm (including rooted portions of plants at the surface) and in subsurface soils 10-20 cm were made in Malawi (3), Chile (11) and Canada (2). In addition soil cores (0-10 cm depth, 1 cm slices) were collected at all Chilean sites by Dr. Barra's group in July and August 1999, where all sites were non agricultural and remote from urban areas. Similar collections were made in Malawi during March 1999. In the UK, soils (0-10cm) were collected at rural sites in December 1999 near Lancaster. In addition 4 archived soils from Rothamstead Agricultural Research Station, dating from 1865, 1881, 1944 and 1956, were provided by Kevin Jones (University of Lancaster). The coordinates of all sites are given in Appendix I.

Canadian soil samples (0-10 and 10-20 cm) were collected from 2 locations, one rural and the other urban. Samples from each of the two sub locations were analyzed using different techniques in the screening- drying process. The samples from the rural site were the most heterogeneous, containing the most unsievable material. Two additional sites were sampled later, one is a rural site near Grimbsy, Ontario, and one near coastal Labrador but only the 0-10 cm upper level was collected.

A technician, Katia Ramirez, from Dr. Barra's lab, who worked at NWRI for 4 weeks from late September to mid-October 1999, helped extract and analyse the Chilean precipitation and bulk soil samples.

Conifer needle samples: Samples representing annual growth were collected in Malawi, Chile, the UK and Canada. All needles were sampled at approximately 1.5 m above the ground and collection was limited to first year's growth; recognized by lighter colour at the end of each branch. Duplicate samples were taken at most sites. Needles were transported in coolers and stored at -20°C until the time of analysis. All sites were non agricultural and remote from urban.

Southern hemisphere pine needles (*Pinus radiata*) were collected in 8 Chilean locations at altitudes ranging from 120 to 1385 m a.s.l. at the same sites as soil samples. In Malawi, conifer samples (species not yet identified) were collected at one forested location. In Canada, pine needle samples were collected in southern Ontario from in a "green belt" area between Burlington and Guelph (Ont) at the same site as soils in February 2000. For comparison we have included a second set of samples of White Spruce (*Picea glauca*) and Subalpine Fir (*Abies lasiocarpa*) obtained in March 1998 from sites in Banff National Park in the Rocky Mountains. In the UK conifer (pine) samples were collected by Dr. Kevin Jones' group in December 1999 near the University of Lancaster.

#### Chemical analysis:

Determination of HAAs: All the samples received were analyzed for TCA as well as dichloro- (DCA), and monochloroacetic acid (MCA). Precipitation samples were analysed as described by Scott and Alaee (1998) with minor modifications. In brief: TCA,

along with MCA and DCA were determined in evapo-concentrated samples (50 mL) after in situ derivatization with 2,4-difluoroaniline in the presence of the dicyclohexylcarbodiimide to yield fluoroanilides (Scott and Alaee 1998). A surrogate recovery standard of <sup>13</sup>C-trichloroacetic acid was added to each sample following evaporation. After removing the ethyl acetate cosolvent, the residue was taken up in toluene and passed through 7.5 g activated silica gel. The following ions were used for quantiation: MCA- 205, 207 &129 amu; DCA- 239, 241 & 156 amu; TCA- 273, 275 & 156 amu; and TFA - 225 and 156 amu. The major ions used for the <sup>13</sup>C-trichloroacetic acid were 274, 276 and 157amu.

Soil samples were treated by one of two procedures. All samples were thawed over night prior to treatment. Originally, samples were air dried then sieved through a 5mm screen then ~5g weighed into 50 mL of Milli-O treated water whose pH was adjusted to 10, spiked with <sup>13</sup>C-trichloroacetic, then vigourously stirred for 30 min. The contents were then placed into a 250mL centrifuge bottle and centrifuged at 1200 rpm for 25 min and the supernatant transferred to a 125 mL flask. The pH was then adjusted to  $\sim$ 1, left overnight in a cooler (4°C) and analyzed, as described for precipitation, the following day. The second procedure skipped drying and seiving steps so as to limit possible air borne contamination. The soil sample was placed in 50 mL of the Milli-O water, spiked with <sup>13</sup>C-trichloroacetic and the pH was adjusted to ~10 then stirred vigorously for 1 hr, centrifuged, decanted and the supernatant's pH adjusted to ~1 before being left over night prior to derivatization as described for the precipitation samples. Recoveries of <sup>13</sup>C-trichloroacetic acid were consistently >90% by this procedure. As the <sup>13</sup>C-TCA surrogate contributed measurable ion intensities at 273, 275 and 156 amu, these amounts determined in blanks were subtracted from the intensities of those in the Extraction of air-dried and moist soils gave similar recovery results. All samples. Chilean bulk soil samples were analyzed air dried and extracted with alkaline water while remaining soils were extracted without drying. Only two samples, both from the UK, presented analytical difficulties, with the extracts forming a thick emulsion which inhibited normal workup of the samples. For these two samples only, the organic liquid phase was left for 16 hr and passed through a silica gel column then the effluent analyzed. The recoveries for the added <sup>13</sup>C TCA in these samples were about 10%, so the concentrations were multiplied by a factor of 10. Additional soils from these two samples were air dried prior to analysis. This facilitated analysis of one of the samples from the two sites. The other still presented difficulties, in that the <sup>13</sup>C-TCA was a factor of 10 lower than anticipated. Samples from these 2 sites did not contain concentration maxima given later in the text. All samples were extracted and analyzed in duplicate.

Conifer needles (3g) were plucked from branches in the laboratory and were rinsed 2x with ultra clean water. The needle samples were frozen with liquid nitrogen then ground to a fine powder and sonicated with water. An aliquot (10 ml) of purified water was then added to the powder in a 50 ml centrifuge tube, 50 ng of the internal standard (perfluoropropionic acid; PFPA) was added, and the mixture was ultrasonicated for 60 min at 25°C. The sample was then centrifuged for 10 min or until most of the green colour had been removed from solution. A 5 mL aliquot was removed from the supernatant and derviatized as described for precipitation. Recoveries of PFBA were >90%.

TCA, DCA, and MCA in precipitation and bulk soils were analyzed by GC-MS (selected ion monitoring) using an HP5890 series GC and 5971 MSD equipped with an HP-5MS fused silica capillary column (30m x 0.25 mm i.d). This procedure has been shown to give equivalent results to other methods for HAAs (von Sydow 1999). Soil slices were analyzed on an HP5973 MSD using similar conditions. GC-MS analyses of HAAs in conifer samples were carried out using a MDN-5 (Supelco) column (0.25 um x 30 m) and a Varian Saturn ion-trap MS operating in selective ion storage mode for MCA, DCA, and TCA. Quantitation was performed by comparing the response of the internal standard to the response of the HAAs in each sample and comparing that to the relative response of a spiked standard (approx 25 ng of all HAAs) that was run on each day with 6 samples and a blank. Pine needle HAA concentrations were reported as ng/g wet weight.

Other analyses: Moisture content of soils and conifer needles were determined so that results could be expressed on both fresh and dry weight basis. Physical characteristics of the soils, as determined using standard methods (Folk, 1974) are given in Appendix II. Soil pH range was determined by making a slurry of each soil then taking the pH over several hours, noting any increase or decrease of this measure.

Quality assurance: Recoveries of <sup>13</sup>C-trichloroacetic acid from precipitation and soil samples were consistently >90% by this procedure. Extraction of spiked pine needle samples revealed no major interferences, and recovery of PFPA was >90%. Analysis of spiked water samples (2.5 to 50 ng) revealed a linear response ( $r^2>0.9$ ) for all HAAs over the range of interest using the Varian Saturn MS and similar linearity was found with the GC-MSD over the same mass range.

The method detection limit based on a mean level of the blank plus 3 times the standard deviation of the blank (Keith 1991) were estimated to be 1 ng/L for precipitation (based on a 1 L sample), 1 ng/g for soils (based on a 10 g sample) and 2 ng/g for conifer needles for all CAAs. Concentrations below the MDL but above the level of the blank were assigned a value of half the detection limit for calculation of means.

#### RESULTS

**Precipitation:** In Malawi samples, low concentrations of TCA and substantial levels of MCA and DCA were detected in all rainfall analyzed (Table 1(a), and Figure 2(a)). TCA, DCA and MCA were detectable in most samples from Chile (Table 1(b) and Figure 2(b)) and the proportions of each chloroacetic acid were approximately the same in all samples with TCA>>DCA>MCA. The concentrations and proportions of the chloroacetic acids in Chile were generally lower than in Malawi or than in Canadian samples collected in 1999 from rural locations in central Ontario (Table 1(c) and Figure 3).

TCA was found frequently in many of the Malawi samples whereas it is found infrequently in the Canadian samples, although this is not obvious in Figures 2 & 3. On the other hand, these samples from Malawi, although only a small sample set, did not have the high extremes of TCA that are encountered in the Canadian rainfall samples, e.g. <10 ng/L to 2400 ng/L. Both Chapais and Saturna Island are relatively remote sites reflecting background levels of haloacetic acids with Saturna Island being influenced by weather patterns off the Pacific Ocean. Algoma is closer to industrialized areas of southern Ontario and mid-western USA.

The samples from Malawi have higher amounts of MCA and similar or lower amounts of TCA than the Chilean or Canadian samples. The Malawi samples have a similar pattern of MCA>DCA>TCA as that observed by Reimann et al (1996) in rainwater in Zurich and Apthal in Switzerland. The TCA levels in Malawi were very low, on par with lowest levels in remote regions of Canada (Scott *et al* 2000).

Further analysis of the results from Chile shows that both locations had higher proportions of TCA than DCA and MCA. However, during the winter sampling period there were few consistent differences between TCA levels at the downtown Concepción site and a rural site (Figure 2). The observation of elevated TCA in Chilean samples is quite different although not unprecedented; higher amounts of TCA than MCA were also observed at the Algoma site. Von Sydow et al. (1999) found a somewhat similar proportions of TCA to MCA in snow/firn from Antarctica (Dronning Maud Land). The CAA pattern in the Chilean samples is quite different from Switzerland, where MCA predominates in precipitation (Reimann et al. 1996). Overall, the levels of TCA in the Chilean samples appear to be at the low end of the range observed in Canada (Scott et al. 2000) and in western Europe (Reimann et al. 1996).

Soil samples: Method development work was conducted on the Canadian soils. At the two sites, there were minimal differences in the concentrations when using the wet or dry techniques, as shown in Table 2 for the more urban site. In these Canadian samples, DCA was present at moderate amounts with lesser amounts of TCA and MCA. The rural site contained MCA and DCA with TCA found in 2 of the 8 repeats analyzed. Appendix III lists the HAA values for the 4 Canadian sites by site including values for soils from Grimsby and Labrador. The Labrador samples contained small amounts of DCA and MCA (<5ng/g) but no measurable amounts of TCA . The Grimsby soil contained 2.2ng/g of TCA and 10x this concentration level for the other two chloroacetic acids.

Table 3 lists the mean concentration of each CAA of soils for 0-10 and 10-20 cm depth samples. DCA was the most prominent CAA at all sites with concentrations averaging 22 ng/g (dry weight) at 0-10 cm and 5.4 ng/g at 10-20 cm. MCA and TCA concentrations were generally lower than those of DCA, although variation was high, and did not show significant differences with depth. One Chilean site, Risopatron, was omitted from the results because levels of all CAAs were much higher in both the 0-10 and 10-20 cm samples than at other sites. This site receives the most precipitation of all sites analyzed.

Samples were collected from 3 (X2) locations in Malawi at depths identical to those from Chile. DCA was the most prominent CAA, detected at both depths at all sites with an average concentration of 14 ng/g with a range of 55 to 3 ng/g (Table 2). TCA was found at 3 sites with an average concentration of 7 ng/g at these sites or a 2 ng/g average at all 6 sites. These values ranged from 9 to 1 ng/g. MCA concentration levels were comparable to those of TCA, being detected at 4 of the 6 sites with a range for 10 to 1 ng/g.

The average HAA values for all countries for the 0-10 cm depth of soils for all sites investigated are shown in Table 4. In this table, the averages of the slice values for

Malawi and Chile are used. The 1999 samples from the UK contained the highest mean values for MCA, DCA and TCA (Appendix IV). In the two samples which contained the highest levels of MCA and DCA, which were also the most difficult to analyze, no measurable TCA was found. This may be the result of bacterial action which has been found to explain the disappearance of CAAs in freshwater systems (Ellis *et al*, 2001). Concentration levels in the soil samples analyzed from Malawi are lower than in Canada or Chile. The samples from Malawi were from rural areas (a National Park, tree plantation and rain forest) and can be considered representative of undisturbed soils.

Four archived UK soil samples were analyzed. These were for the years of 1865, 1881, 1944 and 1956. The 1865 sample contained the highest levels of the CAAs, greater than the content of any of the 1999 samples. Analysis of another portion of the 1865 soil produced similar results. It is suggested that this sample has somehow become contaminated. The other samples contain increasing concentration levels of the HAAs with the highest values found in the 1955 sample (Figure 4), but at levels less than in the samples collected during 1999.

Analysis of the soils slices from all sites in Malawi and Chile, provides an insight as to the distribution of the CAAs in the top 10 cm of the soils. These values are listed in Table 5 along with the values for the 0-10 cm from Table 4. As the amount of soil used in each analysis is the same as the bulk soil analysis, the sensitivity is increased by a factor of 10, and since these were analyzed on a more modern MSD, the sensitivity is enhanced by a factor greater than 2X. Except for 3 sites, (Chile sites 8 and 11 and Malawi site 3) there is agreement with the bulk measurement for the 0-10 cm sections and the average of the slice values. Those samples in which there are differences involve the TCA concentrations. A possible explanation is that the bulk sample analyzed was not representative of the entire sample. Concentration levels for TCA from Chilean sites 8 and 11 indicate that there is slightly more in the 10-20 cm sample than the 0-10 cm sample. The slice samples from site 8 contain detectable amounts of TCA whereas the slices from site 11 do not. However, in both instances, the values from the slices indicate an increase in CAA concentration with increasing depth. The other sites have decreasing concentrations of TCA with depth or a similar amounts in all slices. Several sites have very high concentrations of CAAs (>100 ng/g), but this decreases with depth and the most abundant HAA being DCA. The results listed in Table 5, are shown as graphs in Appendix V. Samples from sites 10 and 11 (both depths) were analyzed using both extraction techniques, and the two sets of results agreed.

The levels of TCA in soils observed in this study are generally within the range found in rural soils in Germany (Frank 1988) of <1-380 ng/g dry wt. A report on TCA in soils from southern Russia gives values of less than 1 ng/g fresh weight (Weissflog et al. 1999) however it is not clear if the methodology used to generate those results, which involved heating the sample to produce CHCl<sub>3</sub> and measuring the headspace concentrations, is comparable to that used in the present work.

**Conifer samples:** Levels of HAAs in all conifer samples analyzed to date have been near detection limits. There was always good agreement among duplicates. In Chilean pine needle samples only MCA was consistently detected and only 2 of the 8 sites had concentrations above the minimum detectable level (MDL). Because of the low results

we have also reported mean values <MDL in Table 6, e.g. for DCA. TCA was < 1 ng/g in all samples from Chile and the Canadian west. Needles from central Ontario contained either 2 or 3 ng/g of the CAAs which is equal to or slightly lower than found in the needles from Malawi.

The concentrations of CAAs detected in conifer needles from Canada, Chile and Malawi are much lower than reported in Europe and proportions of TCA/DCA/MCA differ. TCA concentrations in the range of 2-150 ng/g fresh weight have been measured in Finland and in Central Europe (Juuti et al. 1993; 1996; Norokorpi and Frank 1995) and these are in the same range as measured in the UK samples. Proportions of TCA to MCA in samples from Finland varied but were typically 3:1, similar to those determined in the UK samples. Even sites in northern Finland had much higher TCA concentrations (median 22 ng/g) than those in Chile. However, a recent study of DCA in pine needles from Finland reported lower levels than other studies, with concentrations ranging from 0.3-3.8 ng/g fresh wt (Sinkkonen et al. 1998).

The differences may be due to sample type and to time of year of sampling. Sampling occurred in late winter in western Canada (March) as well as in Chile (July) but during October in central Canada. Some authors have reported that TCA concentrations in conifer needles were highest in summer and autumn (Frank 1991). The samples from this study were thus collected following a long period of relatively low sunlight irradiation which could be important assuming that TCA was formed from sunlight photolysis of precursors.

Juuti et al. (1996) found lower TCA levels in first year needles compared to 2 year old pine needles. Our decision to collect annual (first year) growth was made as a means of controlling for the factor of age which is expected to be significant. They are useful to show recent exposure, however, older needles may be more useful for geographical comparisons especially since few studies have made the distinction between old and new growth.

#### SUMMARY AND CONCLUSIONS

The results of this study, show some interesting differences in TCA levels and patterns of CAAs between southern hemisphere and north temperate zone urban and remote sites as well as interesting difference between Europe (UK) and the other parts of the world. To our knowledge the dataset is the largest on CAAs developed outside of central and northern Europe where most measurements for precipitation, plants and soil have been made. The results suggest that Central Europe has higher levels of CAAs in precipitation, soil and plants than other locations. If the HAAs are a direct result of atmospheric burden, there is considerably more CAAs in the air in Europe than the comparatively more sparsely populated and less industrialized other regions of the globe.

The results also show some interesting differences in TCA levels and patterns of CAAs between southern hemisphere and north temperate zone urban and remote sites. The pattern of TCA/DCA/MCA in Chile was similar to that observed by Von Sydow et al. (1999) for the CAAs in snow/firn from Antarctica although DCA was greater than MCA in Chile. Von Sydow et al. concluded that TCA had a natural source based on the profile in Antarctic firn and the observations in Chile, where precipitation is influenced

by the large expanse of the south Pacific, may reflect similar predominance of natural sources. The CAA pattern in the southern hemisphere is clearly not uniform because the results from Malawi differ from those in Chile or Antarctica.

Levels of CAAs in soils were within the range reported by others although the number of studies is limited. As anticipated, the upper 10 cm of the soil contained greater amount of the CAAs than the next 10-20 cm levels. The concentrations of CAAs detected in conifer needles (Chile and western Canada) were generally much lower than reported in Europe and proportions of TCA/DCA/MCA differ. The low proportion of TCA in Chile and the Rocky Mountains of Canada is particularly interesting. However, some differences could be due to sampling season and sample type. For e.g. we used annual growth for conifers while other studies have used conifer needles of undefined age.

#### REFERENCES

Ellis, D., M.I. Hanson, P.K. Sibley, T. Shadid, N.A. Fineberg, K.R. Solomon, D.C.G. Muir, S.A. Mabury, 2001, Chemosph., 42, 309-318.

Folk, R.L., 1974, "Petrology of Sedimentary Rocks", Hemphill Publishing Co., Austin, Texas.

Frank, H. 1991. Ambio 20: 13-18.

Frank, H. 1988. Nachr. Chem. Tech. Lab. 36, 889-901.

Franklin. J., Intern. Symposium on Haloacetic acids and shortchain halocarbons: Sources and fate in the environment, Toronto, Aug27-29, 2000.

Hoekstra, E.J. and E.W.B. DeLeer. 1993. In Contaminated Soil. Kluwer Publ. Pp. 215-244.

Hoekstra, E.J., E.W.B. de Leer, and U. A. Th. Brinkman, Chemosph. 1999, 38, 2875-2883.

Juuti, S. and E.J. Hoekstra, 1998. Atmos. Environ. 32, 3059.

Juuti, S., Y. Norokorpi, T. Helle and J. Ruuskanen. 1996. Sci Total Environ. 180:117-124.

Juuti, S., Y. Norokorpi, and J. Ruuskanen. Chemosphere 30: 439-448.

Keith, L.H. Environmental sampling and analysis: A practical guide. Lewis Publishers. CRC Press Inc. Boca Raton, Florida. 1991.

Laniewski, K., H. Borén, A. Grimvall, S. Jonsson, L. von Sydow, In Naturally Produced Organohalogens, 1995, Kluwer Academic Press, Dordrecht, The Netherlands; pp113-129. Reimann, S., K. Grob and H.Frank. Chloroacetic acids in rainwater. Environ. Sci. Technol. 30:2340-2344

Scott, B.F., D. MacTavish, C. Spencer, W. Strachan, D.C.G. Muir, 2000, Environ. Sci. Technol., 34, 4266-4272.

Scott, B.F. and M. Alaee. 1998. Water Qual. Res. J. Canada, 33, 279-293.

Sinkkonen, S., T. Rantio, J. Paasivirta, M. Alanko and M. Lahtiperä. 1998. Chemosphere 37:2653-2664

Von Sydow, L., A. B. Grimvall, H.B. Borén, K. Laniewski and A.T. Nielsen, 2000, Environ. Sci. Technol., 34, 3115-3118.

Von Sydow, L.M. 1999. PhD Thesis. Linköping University. Sweden.

Weissflog, L., M. Manz, P. Popp, N. Elansky, A. Arabov, E. Putz and G. Schüürman, 1999, Environ. Pollut., 104:359-364.

Table 1. HAA concentrations in precipitation of countries studied (ng/L)

•

(a) MAL	AWI										
Sample date	3-Feb	Feb11	13-Feb	19-Feb	20-Feb	Feb25	26-Feb	9-Mar	12-Mar	16-Mar	17-Ma
MCA	1100	680	370	850	1200	1300	1300	270	490	380	1400
DCA	65	120	78	161	130	440	140	26	100	980	280
TCA	20	57	5	33	22	42	24		44	56	21
(b) CHIL	E										
Urban	May27	June 11	June 4	June 17	June 21	July 1	July 13	July 20	July 30		
MCA	67	61	69	6	53	22	87	61	51		
DĊA	93	25	42	87	25	27	21	29	43		
TCA	360	330	60	980	95	120	75	92	520		
Rural	May 29	June16	June 22	Jüne 26	July 5	July 16	July 30	Aug 31	Sept 13		
MCA	77	94	7	34	18	12	19	18	11		
DCA	33	210	32	27	20	17		18	24		
TCA	400	720	110	94	330	81		190	80		
(c) ČAN	IADA										
			ŚA	<b>TURNA IS</b>	LAND (Pa	cific influe	ence)				
	2-Feb	19-Feb	26-Feb	18-Mar	29-Mar	26-Apr	12-May	30-May			
MCA						20	79				
DCA	37	36	43	210	26	55	100				
TCA		32	69	150			51	310			
				CHAR	PAIS (Inlar	nd)					
	2-Ma	ar 5-1	Mar 2	3-Mar	8-Арг	19-May	<b>22-Ma</b>	ý 3-J	ul t	3-Jul	
MCA		:	9	53	76	160	250	43	3	20	
DCA	60	2	28	190	110	160	1400	80	)	41	
TCA	27			36	91	-	160	16	0	63	
				ALGO	MA (Inlan	id)					
	1-Mar	7-Apr	7-May	25-May	8-Jun	27-Jun					
MCA					97						
DĊA	510	220	1100	50	160	240					
TCA	170	160	740		480	2400					

•..

Table 2. Comparison between dry sieved soil and wet extracted soil CAA results (ng/g) at more urban site

	dry 0-10 cm	wet 0-10 cm	dry 10-20 cm	wet 10-20 cm
MCA	10	10	4	3
DCA	60	100	20	8
TCA	10	4	7	<2

#### Table 3. Concentrations of chloroacetic acids in bulk 0-10 cm and 10-20 cm Chilean, Malawi and Canadian soils (ng/g dry weight)

	Number of sites			0-10 cm			10-20 cm	
			Mean	min	max	mean	min	max
Chile	11	MCA	4.9	2.0	9.0	7.7	1.7	41
		DCA	11	0.3	39	15	0.3	46
		TCA	22	0.3	152	5.4	0.3	21
Canada	2	MCA	10	<1	39	<1	<1	<1
		DCA	19	<1	100	3	<1	4
		TCA	5.4	<1	19	4	<1	20
Malawi	3	MCA	8.2	<1	10	3.6	<1	10
		DCA	23	5	55	10	3	30
		TCA	2.6	<1	9	<1	<1	3

.

	Canada	Chile	Malawi	UK
# sites	4	11	3	5
MCA	8.1	7.2	3.7	49
(range)	2.3-10	2-30 <b>1.6-69</b> *	na-7.5 <b>2.8-25</b> *	3-180
DCA	26.3	68.0	23.2	128
(range)	3-100	nd-642 <b>2.7-1300</b> *	5-37 5.0-300*	4-320
TCA	4.9	4.7	3.8	8.5
(range)	nd-10	nd-44 <b>nd-89</b> *	nd-7.5 <b>nd-22*</b>	nd-29

Table 4. Average Concentrations of HAAs in 0-10 cm Layer of Soils (ng/g)

\* based on 1 cm slice results

nd = below detection limits

•.

(a) Chile Site & Altitude	Conc. in 0-10cm sample											Average conc. of slices
Central												
311E 1 1395m		0-1 cm	1-2 cm	2-3 cm	3-4 cm	4-5 cm	5.6 cm	6-7 cm	7-8 cm	8.0 cm	0.1000	
MCA	5	10.3	9.1	3.9	6.1	5.1	66	87	57	7 9	65	70
DCA	6	11.3	12.3	7	7.6	6.8	6.9	9.5	6.9	7.3	5.9	8.2
TCA	bdl	2.7	1.8	3.3	0	3.6	0	0	0	0	0	1.1
SITE 2												
700m		0-1 cm	1-2 cm	2-3 cm	3-4 cm	4-5 cm	5-6 cm	6-7 cm	7-8 cm	8-9 cm	9-10cm	
MCA	4	2.4	2.7	2.9	2.4	2.8	2.9	2.7	1.6	2.6	3	2.6
DCA	15	13	13	9.2	7.3	9.3	6.2	5.9	3.3	-3.5	5.1	7.6
TCA	bdl	1.3	0	0	3,5	0	0	0.5	1.8	1.4	0	0.9
SITE 3		0.1.000	1 0 am	2.2 am	2 4 am	4.5.000	E C am	67.000	7.0	0.0	0.40	
345m MCA	e	0-1 Cm 1 0	1-2 Cm	2-3 Cm	3-4 Cm	4-5 Cm	0-0 Cm	0-7 CM	1-8 Cm	8-9 CM	9-10cm	<u> </u>
	20	200.0	21.0	135.0	12:5	73 A	10.1 69.6	9,1 12 2	10.4	0.2 21.7	3.0 0.2	9.5
TCA	12	14.5	6.7	4.4	4.5	0.0	0.0	0.0	0.0	0.0	9.3 0.0	3.0
SITE 4												
500 m		0-1 cm	1-2 cm	2-3 cm	3-4 cm	4-5 cm	5-6 cm	6-7 cm	7-8 cm	8-9 cm	9-10cm	
MCA	4.7	6.2	5.0	4.8	5.2	4.3	4.4	5.1	4.3	4.7	4.8	4.9
DCA	5.1	6.6	4.1	4.8	6.3	4.8	4.6	5.1	5.7	5.5	10.9	5.8
TCA	4.6	0.0	0.0	0.9	1.5	4.0	0.0	1.0	0.0	0.8	0.0	0.8
SITE 5												
770 m		0-1 cm	1-2 cm	2-3 cm	3-4 cm	4-5 cm	5-6 cm	6-7 cm	7-8 cm	8-9 cm	9-10cm	
MCA	3	16	10	8.65	6.2	7.2	9.5	9.6	13	10.3	6.7	9.7
DCA	3.8	14.5	7.7	7.15	4.1	5.2	8	7	7.7	9.5	6.6	7.7
TCA	bdl	0	0	0	3.5	2.3	0	0	0	0	0	0.6
SITE 6		<b>6</b> 4	4.0				<b>c o</b>		-		• • •	
1300 m	•	0-1 cm	1-2 cm	2-3 cm	3-4 cm	-4-5 cm	5-6 cm	6-7 cm	7-8 cm	8-9 cm	9-10cm	
	9 40	5.Z 7	1.4	1.2	0.4	1.1	15	14 55	14	12.8	10.4	10.0
TCA	bdi	0	9.8 0	0	2.4	0.3	4.1	25 0.4	29.5 1.9	0	32.9 0	18.9 0.9
Northern												
SHE /		0 4 <i></i>	i 0	0.0	<b>3</b> /	A E	E Č 🛶	67	7 0	0.0	0.40	
	2	U-1 CM	1-2 CM	2-3 CM	3-4 CM	4-5 CM	ີວ-ວ cm	0-7 CM	/-୪ CM ସୁ ₄	8-9 cm	9-10cm	• •
	2 6	2.U 0.7	3.Z	3.5	1.9 20	2.4 12	1.0 6.5	2.0 1 E	∠.4 ∡Ω	Z. I A 4	1.7	2.4
TCA	62	4,1 1 2	34	4.5	2. <del>5</del> 4 1		0.0	4.0 0.0	4.9 0.0	4.1	∠.0 0.0	3.3 4 0
	~		<b>v</b> . •	v. v	4. 4	0.0	0.0	<b>v</b> .v	0.0	0.0	0.0	1.0

Table 5. Concentrations of haloacetic acids in 1 cm soil sections (ng/g)

SITE 8												
4450m	average	0-1 cm	1-2 cm	2-3 cm	3-4 cm	4-5 cm	5-6 cm	6-7 cm	7-8 cm	8-9 cm	9-10cm	
MCA	3	20	17	31	25	24	31	37	44	29	25	28.3
DCA	3	154	93	140	170	170	251	190	280	320	250	201.8
TCA	bdl	11	10	15	17	18	17	14	31	51	34	21.8
SITE 9												
4300m		0-1 cm	1-2 cm	2-3 cm	3-4 cm	4-5 cm	5-6 cm	6-7 cm	7-8 cm	8-9 cm	9-10cm	
MCA	4	7	16	4.9	6.6	3.9	3.9	4.3	5.9	3.2	8.7	6.4
DCA	3.8	5	4.7	4.8	5.4	4.3	6.1	5.5	5.8	4.3	5.3	5.1
TCA	bdl	6.3	Ó	4.6	3.9	5.2	0.0	0.0	0.0	0.0	0.0	2.0
Southern	ı											
SITE 10												
145 m		0-1 cm	1-2 cm	2-3 cm	3-4 cm	4-5 cm	5-6 cm	6-7 cm	7-8 cm	8-9 cm	9-10cm	
MCA	30	47	45	60	69	39	36	45	33	26	33	43.3
DCA	642	1300	847	1200	1400	650	620	490	380	151	180	721.8
TCA	44	89	36	74	52	19	18	13	11	0	5.1	31.7
SITE 11												
700 m		0-1 cm	1-2 cm	2-3 cm	3-4 cm	4-5 cm	5-6 cm	6-7 cm	7-8 cm	8-9 cm	9-10cm	
MCA	13	24.7	16.2	19.5	9.2	10.0	31.7	23.1	27.1	16,5	22.9	20.1
DCA	11	30.3	30	32.6	22.3	17.7	62.0	64.7	73.6	42.7	70.9	44.7
TCA	20											bdl
(b) Malawi												
SITE 1												
		0-1 cm	1-2 cm	2-3 cm	3-4 cm	4-5 cm	5-6 cm	6-7 cm	7-8 cm	8-9 cm	9-10cm	
MCA	7.5	5.6	5.5	5.6	9.2	9.9	8	16.3	9.2	12.2	25	10.7
DCA	28	29	28	27	38	32	20	32	22.4	18.8	23.1	27
TCA	7.5	5.7	4.8	5.4	9.3	8.2	2.7	4.3	5,6	4.1	3.8	5.4
SITE 2		0.4	4.0		0.4				~ ~	• •		
	25	0-1 cm	1-2 CM	2-3 cm	3-4 CM	4-5 CM	1 5-6 CM	6-7 cm	/-8 cm	8-9 cm	9-10cm	
MCA DCA	3.5 bal	0.0 10 0	4.5	0.0	5.4 0.4	11.1	5.7	3.1	2.8	3.0	3.7	5.1
	DO	10.8	10.8	8.4	8.1	8.2	10.4	7.3	6.9	5.0	5.6	7.9
ICA	DOI											
SITE 3		Ő 1 öm	1_2 000	2_2 ~~	3.1	A-E am	5.6 cm	67.~~	7 0		0 10	
MCA	4 0	0-1 UII 24 E	17 4	17 C	10 UIII	12.2	10-000m 70	10-7 CM	1-0 CM	0-9 CM	40	
	1.0	24.0	160	17.0	10.0	13.3	(50 07	10.1	10.3	12	01 400	14.8
	30.3 641	- <b>3</b> 00	001	100	100	114	31 70	33 E 0	91	14U 214	120	143
ICA	pai	22.3	9.1	12.3	12	1.1	(.2	<b>J.</b> Z	0.2	11	12.6	10.6

bdl = below detection limit

Table 6. Concentrations of	f CAAs in conifer sample	>S		
Location		MCA	DCA	ŤĊĂ
Chile (8 locations)	Mean (ng/g ww*)	4	1	<1
	Range	<2 - 16	<2	<2
	% >MDL of 2 ng/g	25%	0%	0%
Canada (15 locations in	Mean	2	1	<1
Banff Nat'l Park)	Range	<2-6	<2-3	<1
-	%>MDL of 2 ng/g	60%	13%	0%
Canada (2 locations near	Mean	3	2	2
Guelph ON)	Range	>2-3	>2-3	<2-3
-	% >MDL of 2 ng/g	100%	100%	50%
Malawi (2 locations)	Mean	4	2	3
	Range	3-5	<2-5	<2-6
	%>MDL of 2 ng/g	100%	25%	50%
UK (5 locations near	Mean	7	12	87
Lancaster)	Range	<2-18	2-38	28-190
	% >MDL of 2 ng/g	70%	100%	100%

\* ww = wet weight

#### Caption for Figures

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- Fig. 1. Sites for soil and precipitation sample collections
- Fig 2. Temporal trends of HAA concentration levels from samples collected from Chile and Malawi
- Fig 3. Temporal trends of HAA concentration levels from samples collected from Saturna Island, Algoma and Chapais, Canada
- Fig. 4. CAA concentrations in archived UK soils

# Sampling Sites

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Figure 1







## CANADA







Figure 3

## U.K.



Figure 4

#### **APPENDIX I**

Country	Site	Latitude	Longitude
Chile	1	37°20'S	71°37'W
	2	37°16'S	71°46'W
	3	37°14'S	71°57'W
	4	37°47'S	72044'W
	5	37°49'S	72°54'W
	6	37°48'S	73°2' W
	7	18°16'S	69°10'W
	8	18º10'S	69°12'W
	9	18°48'S	69°7' W
	10	44°3' S	72°21'W
	11	45°33'S	72°3'W
Malawi	1	13°08'S	33°58'E
	2	13°22.09'S	34°00.4'E
	3	13°22.12'S	34°00.2'E
Canada	Rural	43°24'0''N	80°6'36"W
	Urban	43°21'36"N	79°49'48"W
	Grimsby	43°10'48''N	79°33'36"W
	Labrador	53°44'12"N,	60°56'48"W
UK	1	55°1'N	2°43'W
	2	54°4'N	2°42W
	3	54°11'N	2°30'W
	4	54°12'N	2°22'W
	.5	54°13'N	2°41'W

### Coordinates for Soil Sample Sites

## APPENDIX II

## Physical Properties of Soils

Site	Loss on	Org C	Inorg C	Total C		Composition			
	Ignition (%)	%	%	%	Gravel 2000μ %	Sand 62.5μ %	Silt 3.91µ %	Clay <3.91μ %	рН
Chile 1	3.87	1.011	0.228	1.24	2.92	81.77	12.23	3,18	6.2
Chile 2	5.29	2.07	0.39	2.46	10.38	66.33	18.1	5.2	5.6
Chile 3	8.31	2.57	0.29	2.86	12.45	52.33	35.22	0	5.5
Chile 4	<b>9</b> .72	1.82	0.43	2.25	4.05	30.78	43.07	22.8	5.4
Chile 5	9.83	1.29	0.2	1.49	8.43	45.41	24.36	21.79	5.5
Chile 6	21.96	5.43	0.1	5.53	3.8	36.08	38.66	21.46	5.2
Chile 7	5.01	0.28	0.16	0.445	4.71	77.32	13.19	4.78	6.3
Chile 8	1,77	0.05	0.43	0.48	8.72	84.47	4.15	2.67	7.8
Chile 9	2.37	0.24	0.84	1.08	14.06	72.34	7.09	6.5	6.9
Chile 10	18.95	9.89	1.48	11.37	2.5	35.71	40.48	21.31	4.9
Chile 11	39.78	5.5	0.58	5.09	0.63	47.33	35.38	16.66	6.2
Malawi 1	20.9	1.26	0.89	2.15	1.45	63.83	34.72	0	5.7
Malawi 2	87.38	0.62	0.3	0.92	0	68.05	16.76	15.18	4.2
Malawi 3	37.11	1.68	0.37	2.05	1.6	75.42	8.98	14	6.6
ŰK 1	87.92	31.87	0.42	32.29					4.2
UK 2	14.47	2.89	0.32	3.22	0	28.54	46.94	24.52	4.3
<b>UK 3</b>	4.44	4.2	0.33	4,54	0	40.57	42.91	16.53	4.5
UK 4	21.12	<b>29.89</b>	0.3	30.18	0	3.89	58.76	37.35	5.6
ÜK 5	22.52	6.33	0.58	6.91	0	11,13	51.41	37.46	4.4
Grimsby	8.76	1.34	1.44	2.79	17.33	25.99	30.7	25.98	5.6
Labrador	0.99	0.02	0.45	0.469	0	95.35	3.1	1.55	5.3
Scott	10.98	1.41	1.26	2.68	0.88	22.95	55.87	20.3	6.9
Lawrence	8.57	1.53	3.51	5.03	42.1	37.52	41.51	16.39	7.6

### HAA Content of Canadian Soils (ng/g) (duplicate analysis) APPENDIX III

	<u>MCA</u>	<u>DCA</u>	<u>TCA</u>
<u>SITE</u>			
Rural	8	21	4
Urban (1)	10	59	7
Urban (2)	34	20	2
Labrador	2	3	<0.5

Burlington
Grimsby

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### APPENDIX IV

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#### HAA Concentrations in UK Soils

	UK Soil 1B	UK Soil 2A	UK Soil 2B	UK Soil 3A	UK Soil 3B	UK Soil 4A	UK Soil 5A	UK Soil 5B
TFA	2	5	5	5	9	3	0.9	0.8
MCA	160	11	11	2	4	180	9	13
DCA	320	110	170	3	5	320	42	56
TCA	<5	10	19	29	10	<5	<5	<5



Appendix V



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