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Identification of Volatile and Extractable Chloroorganics in Rain and Snow

KRZYSZTOF LANIEWSKI,[†]
HANS BORÉN,[†] AND
ANDERS GRIMVALL^{*,‡}

Department of Water and Environmental Studies and

*Department of Mathematics, Linköping University,
SE-581 83 Linköping, Sweden*

Organics enriched from samples of rain, snow, and glacier ice were analyzed to determine the chemical structure of the chloroorganic compounds that were most abundant in such media. Gas chromatography with atomic emission detection (GC-AED) was used to provide an overview of the presence of volatile and extractable chloroorganics at four sites in Europe and one site in Antarctica. Real samples and isomer-specific standards were then analyzed by gas chromatography with mass-spectrometric detection (GC-MS) to identify and confirm the structure of the chloroorganics that had been detected in the GC-AED analysis. The results revealed that of the volatile chloroorganics found in the samples, dichloronitromethane, a compound not previously reported to occur in the ambient environment, was often present in the highest concentration (up to 130 ng L⁻¹). Chlorobenzenes were detected mainly as 1,4-dichlorobenzene and minor amounts of 1,3- and 1,2-dichlorobenzene and one isomer of tetrachlorobenzene (1,2,4,5- or 1,2,3,5-tetrachlorobenzene). Chlorinated alkyl phosphates, which were normally responsible for the largest peaks in the chlorine-specific chromatograms of hexane- or ether-extractable compounds, were present as tris(2-chloroethyl)phosphate, tris(1-chloro-2-propyl)phosphate, and one of the isomers bis(1-chloro-2-propyl)(3-chloro-1-propyl)phosphate or bis(1-chloro-2-propyl)(2-chloro-1-propyl)phosphate. All of the chloroorganic compounds mentioned, i.e., dichloronitromethane, chlorobenzenes, and chlorinated alkyl phosphates, were detected at relatively remote sites in the northern hemisphere, whereas only chlorobenzenes were found in a reference sample of snow from Antarctica.

Introduction

Most of the studies of chloroorganics in rain and snow have dealt primarily with compounds that have long been recognized as harmful environmental pollutants. Some investigators have made relatively broad analyses of priority pollutants (1–5), whereas others have undertaken more specific studies of PCBs (6–10), chlorinated dioxins (11, 12), chlorophenols (13), or pesticides, such as DDT, lindane, and dieldrin (14, 15). A number of scientists have studied the occurrence of chlorinated C₂–C₄ hydrocarbons (3, 16, 17) and haloacetic acids (3, 18–22) in precipitation. Recently, the first results regarding chlorinated alkyl phosphates in rain and snow were published (23–25).

* Corresponding author phone: +46 13 281482; fax +46 13 100746; e-mail: angri@mai.liu.se.

[†] Department of Water and Environmental Studies.

[‡] Department of Mathematics.

In an attempt to detect chloroorganic compounds that may have been overlooked in previous studies of such substances in rain and snow, Laniewski and co-workers (25) determined the group parameters AOX (adsorbable organic halogens) and EOX (extractable organic halogens) and applied GC-AED (gas chromatography-atomic emission detection) and GC-MS (gas chromatography-mass spectrometry) to analyze specific compounds. The cited study revealed that chloroorganics that are not normally analyzed were often responsible for the largest peaks in the chromatograms recorded in the chlorine channel of the atomic emission detector. In particular, chlorinated alkyl phosphates, chlorobenzenes, and an unknown volatile compound were found to be among the most abundant chloroorganics in the fractions of volatiles and extractables.

The present study focused on chloroorganics that can be enriched by using purge-and-trap techniques or liquid-liquid extraction with hexane or diethyl ether. Organic extracts of such compounds were derived from samples of rain, snow, and glacier ice, and the presence of chloroorganic compounds was examined by using a combination of GC-AED and GC-MS. The main objectives of our investigation were as follows:

(i) to determine the structure of the volatile and extractable precipitation-borne compounds that produce the largest peaks in chromatograms recorded in the chlorine channel of an AED system;

(ii) to undertake a special study of the presence of chlorobenzenes and chlorinated alkyl phosphates in precipitation.

To facilitate general conclusions regarding the presence of chloroorganics in rain and snow, the analyzed samples were selected to represent both urban and remote areas.

Experimental Section

Sampling. Snow samples from Sweden and Poland were collected after individual snowfalls by pushing 5-L polypropylene jars into fresh loose snow packs of sufficient depth, i.e., 20–50 cm deep, avoiding the snow that was close to the ice on lakes or the ground. The sample from Antarctica was collected by pushing 2-L polyethylene bottles into the snowpack just below the surface. The ambient temperature during snow sampling was below 0 °C. A sample from a glacier in Sweden was obtained by sawing a block of ice out of a layer formed several hundred years ago. Dating was based on annual growth of the glacier (26).

Bulk precipitation (rainfall) from Ireland was sampled by using a funnel-shaped, open collector made of stainless steel (surface area of 3 m², height of 1.5 m). The sampled precipitation was accumulated in 10-L glass bottles.

The samples of snow from Poland were brought directly to Linköping University in Sweden for prompt analysis. All other samples were transported frozen to the laboratory and then kept in a freezer until analyzed. The outer parts of the ice block from the glacier were removed by sawing out immediately before thawing. Information about sample types and sampling sites is summarized in Table 1.

Stripping Enrichment of Volatiles. Volatile chloroorganics with boiling points ranging from 80 to 350 °C were enriched by using a dynamic headspace technique (27). Samples of rain or melted snow or ice were purged with N₂ for 2 h at 60 °C. The compounds released were adsorbed on an activated carbon filter at 80 °C and then desorbed by extracting the filter with three portions of CH₂Cl₂ (10 + 5 + 5 µL). An internal standard, 1-chlorooctane, was added to the final extract.

Liquid-Liquid Extraction of Neutrals and Bases. Extractable neutrals and bases in rain and melted snow or ice

TABLE 1. Sample Types and Sampling Sites

medium	sampling site	site environment	position	sampling occasion	sample size
rain	Mace Head, Republic of Ireland	seashore in remote area	53°20'N 09°54'W	March 1996	10 L
snow	city of Gdansk, Poland	densely built area	54°22'N 18°35'E	January 1996	10 L ^a
				January 1997	5 L ^a
snow	Lakes: Järnlunden, Stora Rängen, Övre Föllingen, southern Sweden	ice-covered lake in rural area	58°12'N 15°37'E 58°18'N 15°40'E 58°00'N 15°31'E	January 1997	10 L ^a 10 L ^a 10 L ^a
snow	Queen Maud's Land, Antarctica	snow and ice	72°51'S 04°21'E	December 1996– February 1997	4 L ^a
ice	the Mårma Glacier, northern Sweden	ice and rocks in remote area	68°10'N 18°40'E	January 1996	2.5 kg ^b

^a Snow volume before thawing. ^b Before removal of the outer parts.

were enriched by liquid–liquid extraction. Prior to the extraction, the original samples were concentrated 50–100 times by rotary evaporation at 40 °C, and the pH was adjusted to 9.9 by addition of NaOH. The concentrates obtained were then extracted with hexane and thereafter with diethyl ether. The hexane and ether phases were evaporated to a small volume (100 µL) under a gentle stream of N₂. An internal standard, 1-chlorooctane, was added to the final extracts.

Gas Chromatographic Analyses. The GC-AED analyses were carried out on a Hewlett-Packard 5890 GC system equipped with an HP 5921A atomic emission detector. Carbon, chlorine, bromine, nitrogen, and oxygen were monitored at wavelengths of 496, 479, 478, 174, and 777 nm, respectively. Gas chromatographic conditions: SGE BPX5 column (5% phenyl equivalent modified siloxane, 24 m × 0.32 mm, 0.5 µm phase thickness); carrier gas helium, at a flow rate of 40 cm/s; splitless injection, splitless time 1 min; injector temperature 250 °C; temperature program, 40 °C for 5 min, 5 °C/min, and 250 °C for 10 min.

The GC-MS analyses in full scan or selected ion monitoring (SIM) mode were performed on a Hewlett-Packard 6890 GC system combined with an HP 5973 mass selective detector and equipped with an HP-5MS column (5% phenyl methyl silicone, 30 m × 0.25 mm, 0.25 µm phase thickness). Helium was used as a carrier gas, at a flow rate of 40 cm/s. Injection conditions: split or pulsed splitless injection. All other conditions were identical to those of the GC-AED analysis.

Blank Tests. All solvents were of analytical grade (Merck) and distilled before use. The purity of the distilled solvents was ascertained by GC-AED and GC-MS analyses of extracts of solvents evaporated to a small volume. The risk of contaminating the precipitation samples during preparation and analysis was examined by analyzing ultrapure water (Millipore Milli-Q) treated in the same manner as the real samples.

Detection and Quantification. An internal standard (1-chlorooctane) was added to the final extracts to monitor both retention times and the chromatographic response in each run and to estimate concentrations of detected compounds. Quantification was based on the response to chlorine (wavelength 479 nm) in the AED system, and a detection limit of 0.5–1 ng L⁻¹ was achieved for all the reference substances. Tris(2-chloroethyl)phosphate was found in both volatile and extractable fractions.

Synthesis of Di- and Trichloronitromethane. Chlorinated nitromethanes were synthesized by mixing nitromethane (CH₃NO₂; 4 × 10⁻³ mol) and sodium hypochlorite (NaClO; 4 × 10⁻³ mol) in 50 mL of water. Immediately after mixing, 10 mL of the solution was extracted with 2 × 2 mL of CH₂Cl₂. After 30 min, an additional 10 mL of the reaction mixture was extracted. Another portion of NaClO (2 × 10⁻³ mol) was then added to the remaining 30 mL of the reaction mixture, and a third 10-mL portion of this mixture was extracted with CH₂Cl₂. The chromatograms obtained upon GC-MS analysis of the CH₂Cl₂ extracts showed that trichlo-

ronitromethane was the main chlorination product in all three of the analyzed extracts. A small peak representing dichloronitromethane appeared when analyzing the last extract.

Results

The chromatograms recorded in the chlorine channel of the GC-AED system showed that only a few compounds in the analyzed precipitation samples produced distinct peaks, measured as chlorine, at a detection level of 0.5–1 ng L⁻¹. It had previously been reported that the chloroorganics normally present at ppt levels are chlorinated nitrogen compounds, chlorobenzenes, or chlorinated alkyl phosphates (25), hence we focused our attention on these three groups of compounds. However, it should be also mentioned that other chloroorganics, such as lindane and chlorofluorocarbons that have at least six carbon atoms, occasionally occurred in the lower ppt range. In addition, a relatively large amount of a chlorinated organometallic compound was detected in one of the analyzed samples.

Chlorinated Nitrogen Compounds. Identification. We have previously reported that extracts obtained by stripping enrichment of organics in rain and snow can contain comparatively large amounts of a compound that is active in the chlorine channel of a GC-AED system and produces CHCl₂ fragments upon GC-MS analysis (25). The present study confirmed the occurrence of such a compound. The GC-AED chromatogram in Figure 1A shows that, when a wavelength (479 nm) characteristic of chlorine was monitored, a significant peak appeared shortly after the solvent peak (retention time 5.475 min). Examination of so-called snapshots of emission spectra provided further evidence that this peak was caused by a chlorine-containing compound. The mass spectrum of the same compound (Figure 2) displays a cluster of three peaks (*m/z* 83, 85, and 87) that probably represent the formation of CHCl₂ fragments. A pair of peaks at *m/z* 48 and 50 might be attributed to CHCl fragments, and a peak at *m/z* 30 suggests that NO or CH₂NH₂ fragments were formed. GC-AED chromatograms recorded at wavelengths characteristic of nitrogen (Figure 1B) and oxygen (not shown) indicated that the investigated compound did contain the former element and probably also the latter. Together, the cited observations raised the question of whether the unknown chloroorganic compound could be dichloronitromethane (CHCl₂NO₂).

GC-MS analysis of reaction products of aqueous chlorination of nitromethane showed that trichloronitromethane was the main product and that dichloronitromethane was also formed. Moreover, the unknown chloroorganic had practically the same mass spectrum and retention time as the synthesized dichloronitromethane (Figures 2–4).

Occurrence. Dichloronitromethane was the most abundant volatile chloroorganic in all of the samples from Poland, Sweden, and Ireland. The highest concentration (130 ng L⁻¹) was observed in a rainwater sample from Ireland,

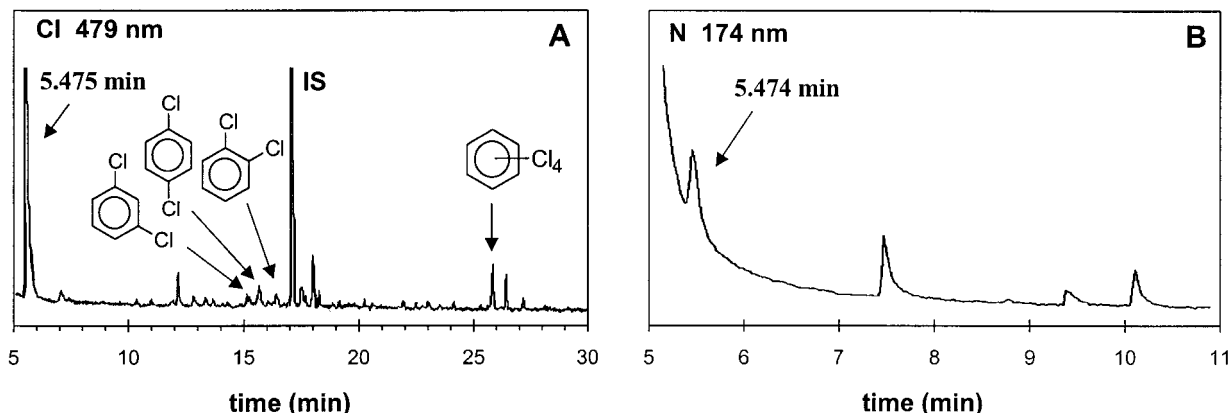


FIGURE 1. Chromatograms recorded during GC-AED analysis of a stripping extract derived from snow collected in the city of Gdansk, Poland. The two chromatograms show the response to chlorine (A) and nitrogen (B) measured at wavelengths of 479 and 174 nm, respectively.

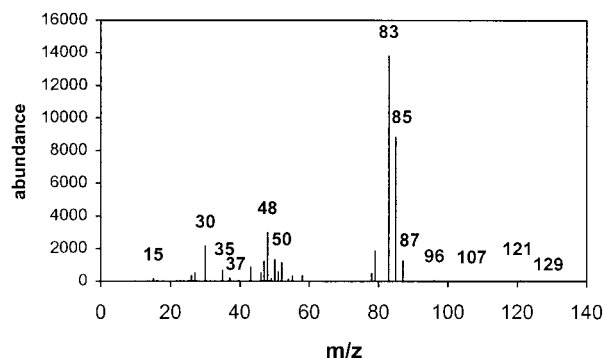


FIGURE 2. Mass spectrum of the chloroorganic compound that was most abundant in the stripping extract of a snow sample collected in the city of Gdansk, Poland.

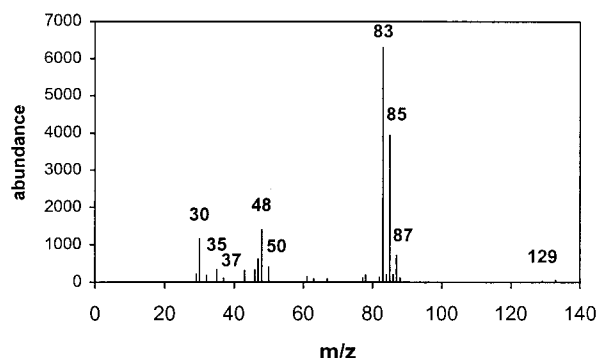


FIGURE 3. Mass spectrum of dichloronitromethane synthesized through aqueous chlorination of nitromethane with sodium hypochlorite.

whereas the Swedish snow samples contained an average of 10 ng L^{-1} . The amount of dichloronitromethane was below the detection level ($<0.5 \text{ ng L}^{-1}$) in glacier ice from northern Sweden and in the reference sample of snow from Antarctica, and this compound was not detected in any of the blank samples. Trichloronitromethane was not found in any of the analyzed samples.

Chlorobenzenes. Identification. We have previously reported that dichlorobenzene can occur in extracts obtained by stripping of precipitation and that the isomer that was most abundant in such extracts had the same retention time as 1,4-dichlorobenzene (23, 25). In the present study, it was noted that the chromatograms recorded in the chlorine channel of the AED system often contained small peaks that might represent other isomers of dichlorobenzene (Figure 1A). GC-MS analysis in the full scan mode confirmed this conjecture, and analysis of model compounds showed that all three isomers, i.e., 1,2-, 1,3-, and 1,4-dichlorobenzene, were present in stripping extracts of precipitation. The presence of one isomer of tetrachlorobenzene was demonstrated by GC-MS analysis in the full scan mode as well as by monitoring of selected ions (m/z 214, 216, and 218). Analysis of model compounds showed that the detected isomer was 1,2,4,5- or 1,2,3,5-tetrachlorobenzene. Pentachlorobenzene was found in the analyzed extracts. However, this compound was also detected in the blank samples, thus it was uncertain whether it had actually been present in the original precipitation samples.

Occurrence. Chlorobenzenes were found to be ubiquitous in precipitation. All of the analyzed samples contained the three possible isomers of dichlorobenzene, and 1,4-dichlorobenzene was invariably present in higher concentrations (up to 5 ng L^{-1}) than 1,2- and 1,3-dichlorobenzene. The detected isomer of tetrachlorobenzene, was also present

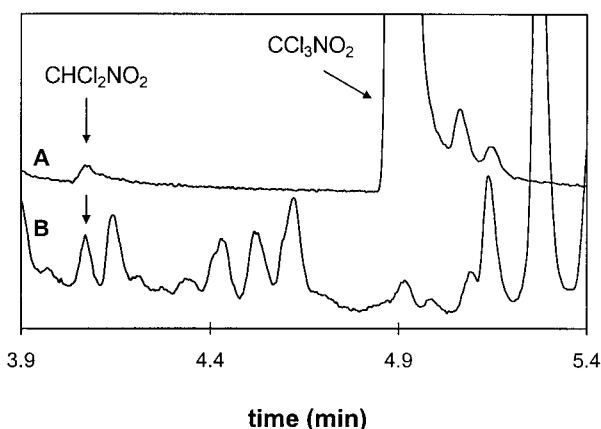


FIGURE 4. GC-MS-TIC (total ion current) chromatograms of extracts obtained from aqueous chlorination of nitromethane (A) and from Mace Head rainwater, Ireland (B).

in all analyzed samples. None of the chlorobenzenes were found in any of the blank samples.

Chlorinated Alkyl Phosphates. Identification. It has already been reported elsewhere (23–25) that tris(2-chloroethyl)phosphate can occur in rain and snow. The GC-AED runs in the present study showed that extracts obtained by liquid-liquid extraction of precipitation normally contained a chlorinated compound with a retention time that was identical to that of tris(2-chloroethyl)phosphate (Figure 5). Moreover, the model compound and the organochlorine detected in precipitation had almost identical mass spectra in the GC-MS analysis in the full scan mode.

Closer examination of the chromatogram A in Figure 5 and other chromatograms recorded in the chlorine channel

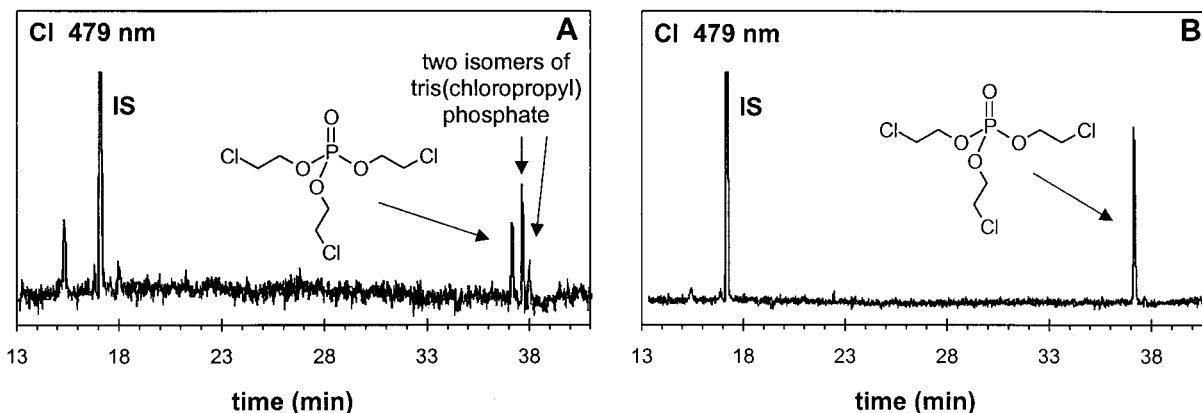


FIGURE 5. GC-AED chromatograms of organics enriched from snow by hexane extraction (A) followed by diethyl ether extraction (B). The sample was collected on the ice of Lake Järnlunden in southern Sweden. The response to chlorine in the AED system was monitored at 479 nm.

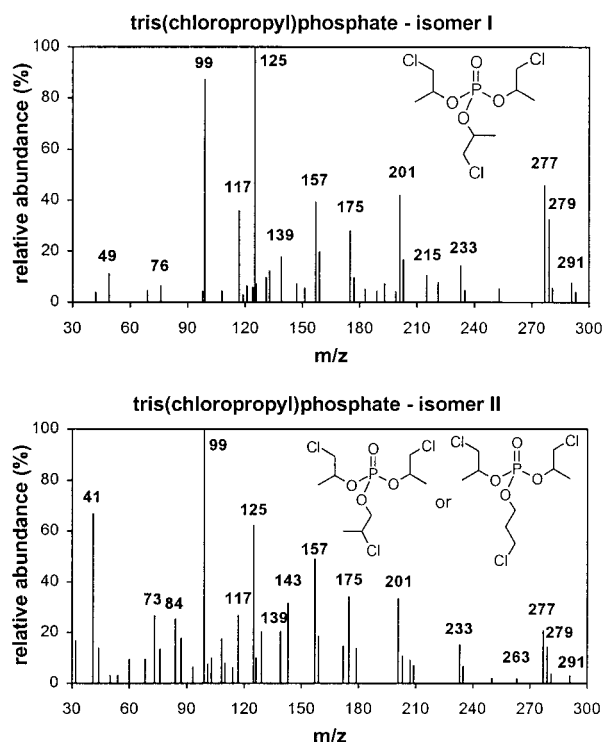


FIGURE 6. Mass spectra of two isomers of tris(chloropropyl)-phosphate found in an ice sample from the Mårma Glacier in northern Sweden.

of the AED system revealed the presence of two more chlorinated compounds eluting just after tris(2-chloroethyl)-phosphate. Scott and co-workers (24) have reported that tris(chloropropyl)phosphates can occur in precipitation, and GC-MS analysis in the full scan mode indicated that the organochlorines detected in our samples were two isomers of that compound (Figure 6). Standards of different isomers of tris(chloropropyl)phosphate were not commercially available, and the GC-MS library did not provide any isomer-specific information, hence identification of the two isomers was based on general theories of mass spectrometry. As can be seen in Figure 6, *isomer I* produced a relatively intense ion cluster (m/z 277, 279, and 281) that is characteristic of losses of CH_2Cl fragments at branching points in isopropyl structures. The absence of the ion m/z 263, which is characteristic of α -cleavage and loss of $\text{CH}_2\text{CH}_2\text{Cl}$ or $\text{CH}_3\text{-CHCl}$ fragments, indicated strongly that all three of the side carbon chains of *isomer I* were 1-chloro-2-propyl. Thus, *isomer I* was identified as the flame retardant tris(1-chloro-

2-propyl)phosphate (CAS No. 13674-84-5). The mass spectrum of *isomer II* differed from that of *isomer I* in two important respects: the ion cluster characteristic of CH_2Cl losses at branching points was weaker, and a clearly visible peak at m/z 263 indicated α -cleavage and loss of $\text{CH}_2\text{CH}_2\text{Cl}$ or CH_3CHCl fragments from 3-chloro-1-propyl or 2-chloro-1-propyl structures, respectively. Comparison of major ions and retention times with those reported in a study of chloroalkyl phosphates in wastewater (28) indicated that *isomer II* was the nonregistered compound bis(1-chloro-2-propyl)(3-chloro-1-propyl)phosphate. However, the registered compound bis(1-chloro-2-propyl)(2-chloro-1-propyl)-phosphate (CAS No. 76025-08-6) may also produce a similar mass spectrum.

Occurrence. Tris(2-chloroethyl)phosphate was present in all of the analyzed samples from the northern hemisphere. Normally, it was also the most abundant chloroorganic compound in the fraction of extractable organics. Interestingly, the highest concentration (21 ng L^{-1}) was observed in the sample of glacier ice from northern Sweden; in comparison, concentrations in the other samples ranged from 1 to 17 ng L^{-1} . GC-AED analysis of hexane and ether extracts of snow from Antarctica did not indicate the presence of tris(2-chloroethyl)phosphate at that site. Furthermore, that compound was not found in Milli-Q water that had been evaporated and extracted in the same manner as the precipitation samples. GC-MS-SIM analysis of the diethyl ether extract of ice from the Mårma Glacier confirmed the results of the GC-AED analysis, whereas the GC-MS-SIM response to the extract of Antarctica snow was below that of Milli-Q water, which was used as a blank.

GC-AED analysis showed that the hexane and ether extracts of samples from Sweden contained both of the investigated isomers of tris(chloropropyl)phosphate, whereas rainwater from Ireland and snow from Gdansk, Poland, contained only tris(1-chloro-2-propyl)phosphate. The highest concentrations of tris(1-chloro-2-propyl)phosphate and bis(1-chloro-2-propyl)(3-chloro-1-propyl)phosphate or bis(1-chloro-2-propyl)(2-chloro-1-propyl)phosphate were 3.0 and 1.5 ng L^{-1} , respectively. The amount of tris(chloropropyl)-phosphate in the reference sample of snow from Antarctica and in the blank sample of Milli-Q water was below the detection level of the GC-AED analysis. To further investigate the presence of that compound at remote sites, hexane extracts of Milli-Q water, snow from Antarctica and ice from the Mårma Glacier were also analyzed by GC-MS-SIM. The diagrams shown in Figure 7 confirmed that two isomers of tris(chloropropyl)phosphate were present in the ice sample, whereas the response to the extract of Antarctica snow was almost identical to that of Milli-Q water.

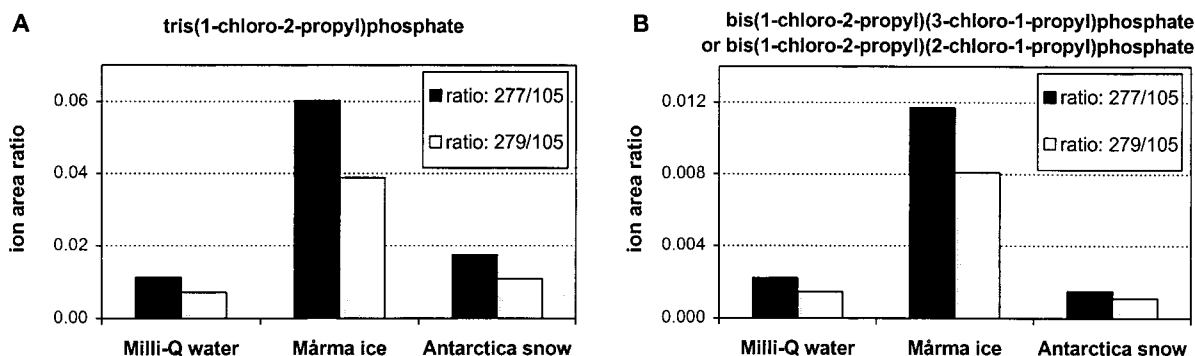


FIGURE 7. Formation of ions characteristic of tris(1-chloro-2-propyl)phosphate (A) and bis(1-chloro-2-propyl)(3-chloro-1-propyl)phosphate or bis(1-chloro-2-propyl)(2-chloro-1-propyl)phosphate (B) when hexane extracts of Milli-Q water, ice from the Mármá Glacier in Sweden and surface snow from Antarctica were subjected to GC-MS-SIM analysis. The bars represent the area ratios of the ions m/z 277 and 279 to m/z 105, which was characteristic of the internal standard 1-chlorooctane.

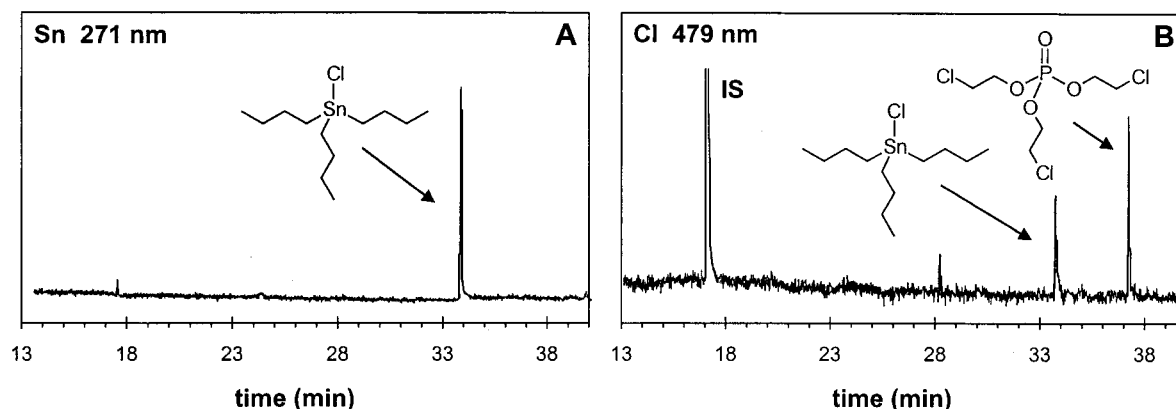


FIGURE 8. GC-AED analysis of a diethyl ether extract of a snow sample collected in the city of Gdansk, Poland. The chromatograms show the response in the tin channel (A) and the chlorine channel (B).

TABLE 2. Observations of Dichloronitromethane, Chlorobenzenes, and Chlorinated Alkyl Phosphates in Different Types of Precipitation Samples^a

compound	type of sample				
	snow southern Sweden	snow Gdansk, Poland	rainwater Mace Head, Ireland	glacier ice northern Sweden	surficial snow Antarctica
dichloronitromethane	+	+	+	—	—
1,4-dichlorobenzene	+	+	+	+	+
1,3-dichlorobenzene	+	+	+	+	+
1,2-dichlorobenzene	+	+	+	+	+
tetrachlorobenzene	+	+	+	+	+
tris(2-chloroethyl)phosphate	+	+	+	+	—
tris(1-chloro-2-propyl)phosphate	+	+	+	+	—
bis(1-chloro-2-propyl)(3-chloro-1-propyl)phosphate or bis(1-chloro-2-propyl)(2-chloro-1-propyl)phosphate	+	—	—	+	—
tributyltin chloride	—	+	—	—	—

^a Confirmed presence in at least one sample is indicated by "+", and "—" stands for not detected or inconclusive results.

Organometallic Compounds. The hexane and ether extracts of a snow sample collected in the city of Gdansk contained fairly large amounts of a chlorinated compound that was absent in all of the other extracts. GC-AED runs in the chlorine and tin channels, respectively, revealed the presence of an organotin compound (Figure 8). GC-MS analysis of the two extracts indicated that the detected compound was tributyltin chloride, and this was subsequently confirmed by GC-MS and GC-AED analyses of a standard solution of that compound.

Summarizing Table. Table 2 illustrates the presence of chloroorganics in different types of precipitation samples.

Discussion

Combined GC-AED and GC-MS proved to be an efficient method to reveal the chemical structure of the organochlo-

rine that were most abundant in the investigated samples of rain, snow, and ice. Almost all chloroorganics that were regularly present in concentrations of at least 1 ng L⁻¹ were identified.

The discovery that dichloronitromethane is very widespread in precipitation is by far the most remarkable finding of the present study. To the best of our knowledge, there are no reports suggesting that this compound has been detected in the ambient environment. Nevertheless, it is an indisputable fact that dichloronitromethane was present in all of our precipitation samples collected in southern Sweden, Poland, and Ireland. Furthermore, of all the volatile organochlorines detected, dichloronitromethane was usually found in the highest concentration. The comprehensive and unequivocal information regarding elemental composition, the mass spectrum, and retention time allowed the identification of

the chemical structure, and there were no indications whatsoever of blank problems or contamination of samples.

The absence of dichloronitromethane at the two most remote sampling sites indicates that anthropogenic sources predominate. Apart from that, there are few clues as to sources or precursors of the compound. Dichloronitromethane is not intentionally produced or manufactured on a large scale. However, it was recently shown that both mono- and dichloronitromethane can be formed during pyrolysis of organic matter in the presence of reactive chlorine (29). Hence, it cannot be excluded that uncontrolled formation of dichloronitromethane can take place, for example during incineration processes. Formation of dichloronitromethane during chlorine disinfection of drinking water or wastewater is possible but seems to be negligible (30).

The trichlorinated analogue of nitromethane (chloropicrin) is used as a fumigant in agriculture (31), and the same compound can also be a byproduct of aqueous chlorination of organic matter (32, 33). However, there is no obvious connection between the occurrence of di- and trichloronitromethane in the environment. It is not very plausible that trichloronitromethane is transformed to dichloronitromethane in the atmosphere (34, 35), and it is difficult to imagine that microbial dechlorination of trichloronitromethane under anaerobic conditions (36) could render dichloronitromethane the most abundant volatile chloroorganic in precipitation.

Haloalkyl phosphates are used as flame retardants in polymers (37, 38), and the occurrence of such compounds in rainwater samples has previously been noted by our study team (23, 25) and by Scott and co-workers (24), who analyzed samples collected in urban areas close to Lake Ontario in Canada. In addition, Aston and co-workers (39) found such compounds in pine needles in the Sierra Nevada Mountains in the United States. The results of the present study are novel in two respects: the structures of the two dominating isomers of tris(chloropropyl)phosphate are suggested; the presence of haloalkyl phosphates in the sample of glacier ice from northern Sweden strongly indicates that such compounds are subjected to long-range airborne transport. When planning this investigation, we assumed that any chloroorganics present in old glacier must have natural sources, because of the age of the ice sample (26). However, detection of lindane in the analyzed ice sample suggested that recent precipitation had contaminated older layers of ice. The concentrations of haloalkyl phosphates in surface snow from Antarctica were below or slightly above the limit of detection.

Dichlorobenzenes are used as fumigants and sanitizers and as intermediates in the manufacture of dyestuffs, insecticides, and pharmaceuticals (30). The presence of 1,2-, 1,3-, and 1,4-dichlorobenzene in rain and atmosphere from urban and suburban areas was documented more than a decade ago (40). The results of the present study showed that all three isomers of dichlorobenzene can also be found in precipitation collected at remote sites. Tetrachlorobenzene is an intermediate in the synthesis of 2,4,5-trichlorophenol and a metabolite of hexachlorobenzene and lindane (30). We are apparently the first to report that one of the isomers of tetrachlorobenzene, i.e., 1,2,4,5- or 1,2,3,5-tetrachlorobenzene, is widespread in rain and snow. It is most probably 1,2,4,5-tetrachlorobenzene, but at present stage the exact identity is not known.

Organotin compounds are used often as antifouling agents for ships, but we did not find any evidence that such substances are prevalent in precipitation. Tributyltin chloride was detected in only one of the samples, and that particular snow sample had been collected in the vicinity of a shipyard.

Acknowledgments

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Literature Cited

- (1) Strachan, W. M. J. *Environ. Sci. Technol.* **1985**, *19*, 677.
- (2) Strachan, W. M. J. *Environ. Toxicol. Chem.* **1988**, *22*, 871.
- (3) Schleyer, R.; Renner, I.; Mühlhausen, D. *WaBoLu-Hefte* **1991**, *5*, 31.
- (4) Hart, K. M.; Tremp, J.; Molnar, E.; Geiger, W. *Water Air Soil Pollut.* **1993**, *68*, 91.
- (5) Hoff, R. M.; Strachan, W. M. J.; Sweet, C. W.; Chan, C. H.; Shackleton, M.; Bidleman, T. F.; Brice, K. A.; Burniston, D. A.; Cussion, S.; Gatz, D. F.; Harlin, K.; Schroeder, W. H. *Atmos. Environ.* **1996**, *30*, 3505.
- (6) Chevreuil, M.; Chesterikoff, A.; Létolle, R.; Granier, L. *Water Air Soil Pollut.* **1989**, *43*, 73.
- (7) Murray, M. W.; Andren, A. W. *Atmos. Environ.* **1992**, *26A*, 883.
- (8) Galassi, S.; Gosso, E.; Tartari, G. *Chemosphere* **1993**, *27*, 2287.
- (9) Chan, C. H.; Bruce, G.; Harrison, B. J. *Great Lakes Res.* **1994**, *20*, 546.
- (10) Poster, D. L.; Baker, J. E. *Environ. Sci. Technol.* **1996**, *30*, 341.
- (11) Tashiro, C.; Clement, R. E.; Lusi, M.; Orr, D.; Reid, N. *Chemosphere* **1989**, *18*, 777.
- (12) Koester, C. J.; Hites, R. A. *Environ. Sci. Technol.* **1992**, *26*, 1375.
- (13) Paasivirta, J.; Knuutila, M.; Paukku, R.; Herve, S. *Chemosphere* **1985**, *14*, 1741.
- (14) Atlas, E.; Giam, C. S. *Science* **1981**, *211*, 163.
- (15) Brun, G. L.; Howell, G. D.; O'Neill, H. J. *Environ. Sci. Technol.* **1991**, *25*, 1249.
- (16) Class, T.; Ballschmiter, K. *Fresenius' Z. Anal. Chem.* **1986**, *325*, 1.
- (17) Jung, W. J.; Fujita, M.; Sohn, D. H. *Jpn. J. Toxicol. Environ. Health* **1992**, *38*, 490.
- (18) Frank, H. *Ambio* **1991**, *20*, 13.
- (19) Frank, H.; Renschen, D.; Klein, A.; Scholl, H. *J. High Resol. Chromatogr.* **1995**, *18*, 83.
- (20) Reimann, S.; Grob, K.; Frank, H. *Environ. Sci. Technol.* **1996**, *30*, 2340.
- (21) Zehavi, D.; Seiber, J. N. *Anal. Chem.* **1996**, *68*, 3450.
- (22) Juuti, S. Ph.D. Dissertation, University of Kuopio, Kuopio, 1997.
- (23) Laniewski, K.; Borén, H.; Grimvall, A.; Jonsson, S.; von Sydow, L. In *Naturally-Produced Organohalogenes*; Grimvall, A., de Leer, E. W. B., Eds.; Kluwer Academic Publishers: Dordrecht, 1995; Environment & Chemistry Vol. 1, pp 113–129.
- (24) Scott, B. F.; Sverko, E.; Maguire, R. J. *Water Qual. Res. J. Can.* **1996**, *31*, 341.
- (25) Laniewski, K.; Borén, H.; Grimvall, A. Accepted for publication in *Chemosphere*.
- (26) Holmlund, P.; Näslund, J.-O.; Richardson, C. *Geogr. Ann.* **1996**, *78A* (2–3), 147.
- (27) Borén, H.; Grimvall, A.; Palmberg, J.; Sävenhed, R.; Wigilius, B. *J. Chromatogr.* **1985**, *348*, 67.
- (28) Thruston, Jr., A. D.; Richardson, S. D.; McGuire, J. M.; Collette, T. W. *J. Am. Soc. Mass Spectrom.* **1991**, *2*, 419.
- (29) Laniewski, K.; Borén, H.; Grimvall, A. *J. Chromatogr.* Accepted for publication.
- (30) Fawell, J. K.; Hunt, S. *Environmental Toxicology: Organic Pollutants*; Ellis Horwood Limited: Chichester, 1988.
- (31) Sassaman, J. F.; Jacobs, M. M.; Kelley, J. M. *Pesticide background statements. Volume 2. Fungicides and fumigants*; Agriculture Handbook-661; United States Department of Agriculture: Washington, DC, 1986; 620 pp.
- (32) Thibaud, H.; De Laat, J.; Dore, M. *Water Supply* **1988**, *6*, 243.
- (33) Williams, D. T.; LeBel, G. L.; Benoit, F. M. *Chemosphere* **1997**, *34*, 299.
- (34) Fazekas, G. B.; Takacs, G. A. *J. Photochem.* **1983**, *21*, 9.
- (35) Carter, W. P. L.; Luo, D.; Malkina, I. L. *Atmos. Environ.* **1997**, *31*, 1425.
- (36) Wilhelm, S. N.; Shepler, K.; Lawrence, L. J.; Lee, H. *ASC Symp. Ser.* **1997**, *652*, 79–93.
- (37) Hutzinger, O.; Sundström, G. *Chemosphere* **1976**, *1*, 3.
- (38) Green, J. J. *Fire Sci.* **1992**, *10*, 470.
- (39) Aston, L. S.; Noda, J.; Seiber, J. N.; Reece, C. A. *Bull. Environ. Contam. Toxicol.* **1996**, *57*, 859.
- (40) Pankow, J. F.; Isabelle, L. M.; Asher, W. E. *Environ. Sci. Technol.* **1984**, *18*, 310.

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