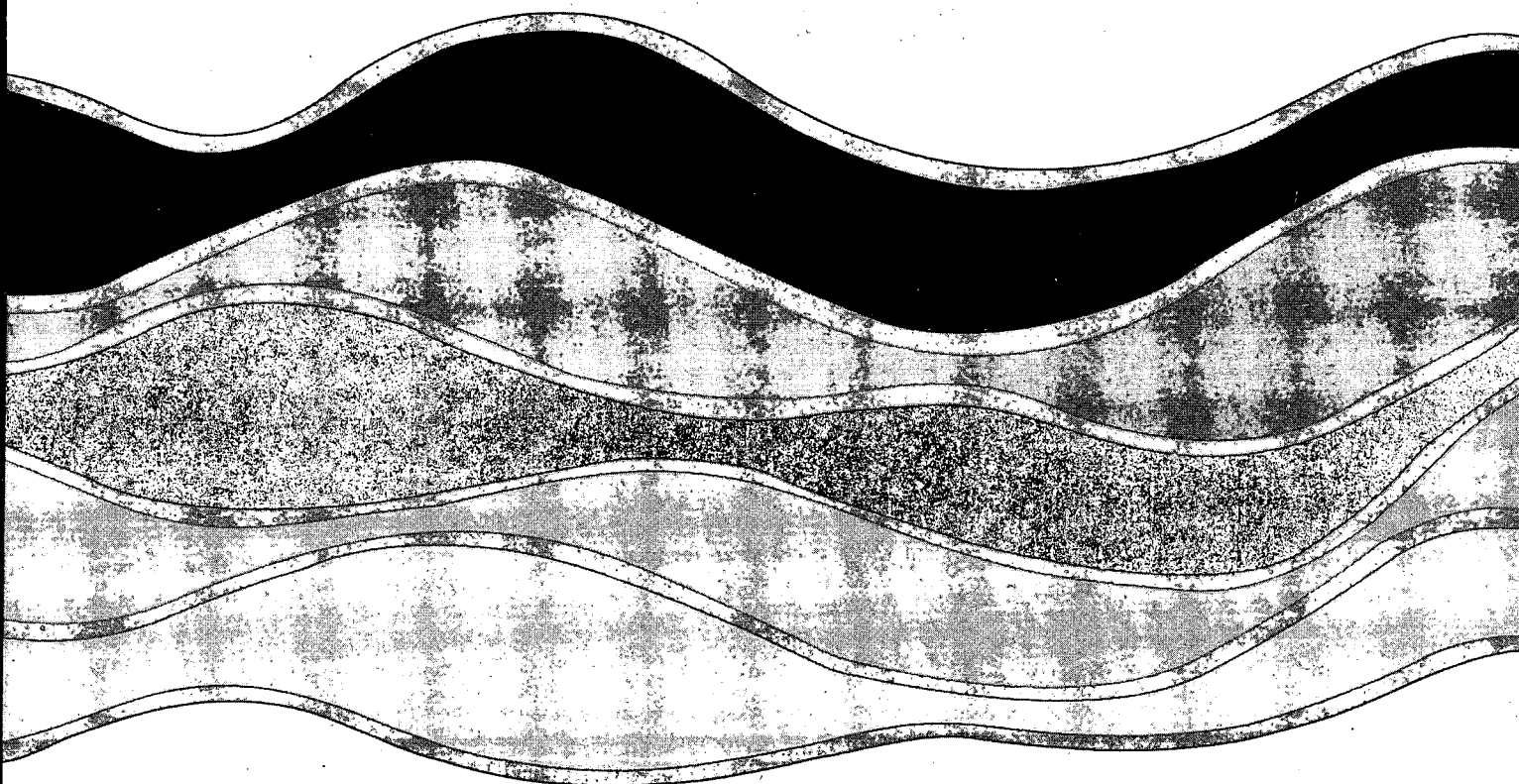
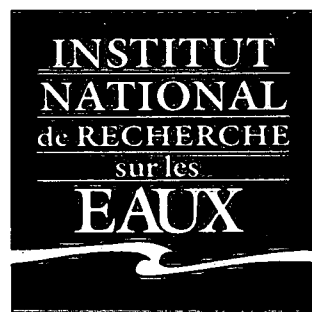


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**ORGANIC MICROPOLLUTANTS IN
SEASONAL SNOWCOVER AND FIRN**

D.J. Gregor

NWRI Contribution No. 91-10

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NWRI Contribution No. 91-10

MANAGEMENT PERSPECTIVE

The Snow Chemistry Working Group of the International Commission on Snow and Ice received support under the Advanced Research Workshop program of the North Atlantic Treaty Organization (NATO) to convene a workshop and publish the proceedings thereof on the subject of "Processes of Chemical Change in Snowpacks". The workshop, restricted to 12 invited speakers and about 20 other observers and reviewers, was held at Maratea, Italy, July 23-27, 1990. This paper was invited by the organizers to review the subject of chemical change of organic micropollutants in snowpacks.

Information on all aspects of organic contaminant deposition and process of chemical change in snowpacks is limited. Flux from the atmosphere to the snow has been measured in both the Arctic and the Antarctic as well as at temperate latitudes. However, only in recent years (since 1986) has any effort been made to understand the processes that control the air/snow/air exchange of these compounds in sub-freezing snow and this has been restricted to Canadian research. Melting snow has received slightly more attention, especially in West Germany and the U.S.S.R..

Although glacial snow and ice has been utilized to measure trends in a variety of pollutants and as a monitor of climate, comparable research concerning organic micropollutants has progressed slowly. Only recently has Environment Canada quantified annual deposition in Arctic Canada as a major component to this environment. In addition it has been observed that the flux is variable due to unsteady meteorologic transport and that glacial snow retains only a small fraction of the semi-volatile organic compounds deposited. This seasonal loss is due to what appears to be revolatilization to the atmosphere during the first summer season.

This review indicates the general paucity of information on this subject while at the same time clearly indicating the lead position which Environment

Canada enjoys with respect to organic contaminant fate in snowfall and snowpacks. A better understanding of not only the quantities of contaminants delivered by snowfall to the aquatic environment and their importance to the ecosystem, especially the arctic ecosystem, will be achieved through a complete understanding of the controlling processes.

PERSPECTIVES DE LA DIRECTION

Le Groupe de travail sur la chimie de la neige de la Commission internationale des neiges et glaces a reçu de l'aide dans le cadre du programme de l'atelier en recherches avancées de l'Organisation du Traité de l'Atlantique Nord (OTAN) afin d'organiser un atelier de travail sur les "Processus de modification chimique dans la neige accumulée" et d'en publier le compte rendu. L'atelier, qui se limitait à 12 conférenciers invités et à environ 20 observateurs et critiques, s'est tenu à Maratea, en Italie, du 23 au 27 juillet 1990. La présente communication portait sur les modifications chimiques des micropolluants organiques dans la neige accumulée.

On possède une information très limitée sur le dépôt de contaminants organiques et sur les modifications chimiques dans la neige accumulée. Le flux provenant de l'atmosphère et atteignant la neige a été mesuré dans l'Arctique et dans l'Antarctique, ainsi qu'aux latitudes tempérées. Cependant, ce n'est que ces dernières années (depuis 1986) qu'on a essayé de comprendre les processus qui commandent l'échange air/neige/air de ces composés dans la neige sous le point de congélation, et ces travaux se limitaient à des recherches canadiennes. La neige fondante a fait l'objet d'études un peu plus poussées, particulièrement en Allemagne de l'Ouest et en URSS.

Bien qu'on ait utilisé la neige glacée et la glace pour mesurer les caractéristiques de divers polluants et surveiller les conditions climatiques, les recherches comparables concernant les micropolluants organiques n'ont progressé que très lentement. Ce n'est que récemment qu'Environnement Canada a quantifié le dépôt annuel dans l'Arctique canadien, en tant que contribution majeure à cet environnement. De plus, on a observé que le flux est variable en raison du transport irrégulier dû aux conditions météo et que la neige glacée ne retient qu'une petite fraction des composés organiques semi-volatils déposés. Cette perte saisonnière est due à ce qui semble être une revolatilisation dans l'atmosphère pendant la première saison estivale.

Cette étude montre l'incertitude générale de l'information sur ce sujet tout en révélant le rôle de leader d'Environnement Canada en matière de devenir des contaminants organiques dans les précipitations de neige et dans la neige accumulée. Mieux on connaîtra l'ensemble des processus de contrôle, mieux on comprendra l'apport quantitatif des contaminants transportés par les précipitations neigeuses jusque dans l'environnement aquatique et leur importance pour l'écosystème, particulièrement l'écosystème arctique.

1 INTRODUCTION

Large areas of many temperate countries receive significant proportions of their total annual precipitation as snowfall and it makes up the primary source of precipitation in polar areas. Importantly, spring snow-melt is commonly the largest annual hydrologic event in temperate and polar areas and as such may be responsible for transporting pollutants rapidly over long distances. Lake sediments have been used to provide a crude temporal record of organic contaminant accumulation in the environment from the atmosphere and elsewhere. However, the chronicle of micropollutant contamination frozen in polar and alpine glaciers has, to date, received only limited attention. This has been the case despite the much improved temporal resolution possible in glaciers over that of most lake sediments, especially in the polar extremes where lake sedimentation rates tend to be very low.

In this context, it is surprising that research concerned with organic micropollutants in snow has been limited in geographic extent and sporadic in time. The purpose of this chapter is to review existing information on the role of snow in scavenging organic contaminants from the atmosphere, in temporarily storing contaminants and through snow-melt, in introducing these contaminants to the aquatic environment. In order to focus the content, only organochlorine pesticides, polychlorinated biphenyls and polycyclic aromatic hydrocarbons are considered. These classes of compounds are important environmentally as they tend to be long lived in the environment, may bioaccumulate and are frequently toxic and/or carcinogenic at elevated concentrations. Additionally, information regarding temporal trends of the levels of these compounds revealed from glacial studies and the apparent problems in utilizing these data will be considered. At the outset, the chapter will summarily review the physicochemical properties of typical organic micropollutants and the processes controlling their emission to and transport in the atmosphere from which they become incorporated into the falling snow.

2 CHARACTERISTICS OF TRACE ORGANIC MICROPOLLUTANTS

2.1 Potential Sources

Two classes of chemicals, here called chlorinated industrial organics and pesticides (OCs) and polycyclic aromatic hydrocarbons (PAHs) are considered. These groups have distinct characteristics and sources and will be dealt with individually.

2.1.1 Chlorinated industrial organics and pesticides

Relevant OCs are those persistent compounds produced in large quantities and released in part to the environment where they are widely dispersed. These include polychlorinated biphenyls (PCBs), hexachlorocyclohexanes (HCHs), chlordane, dichlorodiphenyl-trichloroethane (DDT), dieldrin, heptachlor and heptachlor epoxide, endosulfan, methoxychlor, hexachlorobenzene (HCB) and polychlorinated camphenes (PCCs) or toxaphene. Production and use statistics for the OCs are difficult to acquire but a recent summary of available production estimates for some of the compounds is provided in Barrie *et al.* (in press) using information from a variety of sources. Current use regulations regarding these compounds have also been summarized for selected countries by these authors while more detailed information is maintained by the International Registry of Potentially Toxic Chemicals (IRPTC) of the United Nations Environmental Programme (UNEP).

PCBs are a concern as most of the 209 congeners, especially those with 5 or more chlorines, are biomagnified (Jensen *et al.*, 1969; Reijnders, 1980; Muir *et al.*, 1988). PCBs have been used world-wide for a variety of purposes with as much

as 370 tonnes (t) estimated to have been released into the environment (Tanabe, 1988).

Organochlorine pesticides are a concern because of their long half lives and tendency to bioaccumulate in aquatic and terrestrial food chains. Because pesticides are applied intentionally over large areas of land, their sources and pathways may differ from PCBs, other industrial organics and PAHs.

HCH can theoretically exist as eight different stereo isomers of which only five are found in the technical product. The approximate abundance of the dominant isomers in technical HCH are α -HCH at 70% and lindane at 13% of the total (Deo *et al.*, 1980). The insecticidal isomer lindane is currently used in pure form in North America and western Europe (Voldner and Ellenton, 1987; IRPTC, 1988). In contrast, technical HCH is widely used in southern Asia and China with estimated annual use in the late 1970's of about 6×10^4 t (Tanabe *et al.*, 1982; Agarwal *et al.*, 1987; Rapaport and Eisenreich, 1988).

Technical chlordane, a multi component product, was used as an insecticide but has more recently been used only for subterranean use in Canada and the US (Canadian Council of Resource and Environment Ministers [CCREM], 1987). Large quantities of chlordane have been used in the US (approximately 25×10^4 t) (von Rumker *et al.*, 1974). Within the last decade, agricultural use in the US and many other countries has been curtailed. Since heptachlor is more insecticidal than chlordane, efforts have been made to purify the technical product to more than 70% heptachlor. Heptachlor is mainly used as a soil insecticide and for seed dressing and has been reported to bioaccumulate. Heptachlor epoxide, a metabolite, has not been used as a pesticide but is commonly identified in the aquatic environment at concentrations greater than heptachlor. Heptachlor epoxide is reported to be more resistant to chemical and biological changes in the aquatic environment than heptachlor and has a predicted half life of several years (CCREM, 1987).

Dichlorodiphenyl-trichlorethane (DDT) has been banned or restricted in Canada, US and western Europe since the early 1970's; however, it continues to be manufactured and used in southern Asia, Africa and in Central and South America (Voldner and Ellenton, 1987). Global production is estimated at about 15×10^5 t (Rapaport and Eisenreich, 1986). Although presently restricted in many countries, world-wide use of DDT remains extensive.

Dieldrin is considered to be persistent, volatile, and bioaccumulative (CCREM, 1987). This product has also been restricted in Canada and the US since the mid 1970's although it is still produced and used in a number of western European countries (IRPTC, 1988). Endrin has properties similar to dieldrin and has been applied widely to cotton and rice (Buchel, 1983). Its use is presently restricted or it is banned in many developed countries (IRPTC, 1988).

Endosulfan, consisting primarily of the α - isomer (70%) photolyzes in the gaseous state and although it is taken up by biota, it appears to be rapidly broken down in the organism or is eliminated and there is little danger of bio-accumulation (CCREM, 1987; Buchel, 1983). It is widely used on cotton and orchards, the latter because it is not toxic toward bees (CCREM, 1987).

Methoxychlor is not stored in fatty tissues of higher organisms (CCREM, 1987; Buchel, 1983) and is still approved for agricultural use in Canada, particularly for the control of blackfly larvae. Use has decreased considerably since the 1970's. It is also approved for use in the US, USSR and many European countries (CCREM, 1987; IRPTC, 1988).

Toxaphene was the most heavily used insecticide in the US during the 1960's and 1970's with over 5×10^5 t produced. There it was used mainly for controlling weevil on cotton (Rapaport and Eisenreich, 1986; Voldner and Ellenton, 1987) while it has been used only in a very restricted way in Canada (CCREM,

1987). Use in Mexico was estimated to be about 2.2×10^3 t in 1978 and projected as 2×10^3 t in 1988 (Voldner and Ellenton, 1987). The USSR produces toxaphene derived from turpentine rather than camphene, for use as an agricultural pesticide (IRPTC, 1983) but production and use figures are not available.

2.1.2 Polycyclic aromatic hydrocarbons (PAHs)

PAHs, a number of which are carcinogenic, occur naturally in the environment as a result of forest and prairie grass fires. However, the quantity of PAHs in the environment due to incomplete combustion has increased as a result of the increased use of fossil fuels (CCREM, 1987). Studies of PAHs in sediments of lakes in the Adirondacks of the eastern US show that atmospheric emissions there peaked in the 1950's corresponding to the decline in the use of coal and the increased use of oil for space heating (Heit *et al.*, 1981). Since the combustion of fossil fuels for space heating increases during the winter, it is to be expected that PAHs will be present in snowfall, especially in the vicinity of human settlements.

2.2 Emission and Atmospheric Exchange

The sources of organic micropollutants are potentially global in nature and may be emitted to the atmosphere either directly through use (e.g., agricultural pesticides) or indirectly and unintentionally as part of industrial, combustion and other processes (e.g., PCBs and PAHs). Once introduced into the atmosphere, these compounds may circulate in the atmosphere and hydrosphere for long periods of time prior to going to permanent sink or being broken down or bound up such that they are effectively removed from the system. Snow, therefore may contain "fresh" compounds recently emitted to the atmosphere and "aged" compounds which have evaded permanent deposition to a sink.

A semi-volatile organic compound that is chemically and biologically stable with respect to, for example, photo-degradation, biodegradation and/or chemical transformation, will tend to migrate over long distances through repeated deposition and volatilization. Many organic compounds are likely to be transported in this way (Bidleman, 1988). The vapor pressure, organic content and the concentration, size and surface area of total suspended particles control the distribution or partitioning between vapor and particles. Vapor-particle partitioning, in turn, will influence the distance travelled by these contaminants by means of determining whether the compound is scavenged by rain and snow scavenging of particles and vapors, by dry particle deposition or by direct vapor exchange across the air-water interface. Overviews of these atmospheric processes are available (Slinn *et al.*, 1978; Eisenreich *et al.*, 1981; Murphy, 1984; Bidleman, 1988). It is sufficient here to note that compounds with saturation vapor pressures greater than 1.3×10^{-2} Pa should exist almost entirely in the vapor phase while those having vapor pressures less than 1.3×10^{-6} Pa should exist almost entirely in the particulate phase (Eisenreich *et al.*, 1981). Most high molecular weight organics have vapor pressures between these extremes, as shown in Table 1, and their atmospheric lifetimes depend on the nature and concentration of particles in the air mass.

PCBs have been shown to be between 80 and 100% in the vapor phase in urban atmospheres and in the area of the Laurentian Great Lakes (Murphy and Rzeszutko, 1977; Doskey and Andren, 1981; Eisenreich *et al.*, 1981). Duinker and Bouchertall (1989) investigated the partitioning of several PCB congeners and concluded that while only a very small fraction of total PCB was found in aerosols, this compartment accounted for more than 99% of the PCBs in rain. More highly chlorinated congeners were particle-associated while the lower chlorinated congeners remained essentially in the vapor phase. Thus the method of deposition and form of precipitation can affect the toxicity of the PCBs and can influence how readily they can be revolatilized from the depositional medium.

Particle deposition processes in polar regions have been reviewed by Barrie (1986). They depend mainly on physical factors including particle size distribution, surface roughness and wind speed. Vapor phase exchange with the surface - which may be water (fresh or saline), snow or soil - depends on the physicochemical properties of the compound, many of which are temperature dependent (Patton *et al.*, 1989).

Exchange processes and rates between water or soil and the atmosphere have been researched but not at sub-freezing temperatures (Doskey and Andren, 1981; Atlas *et al.*, 1982; Larsson, 1983; Larsson and Okla, 1987; Baker and Eisenreich, 1990). Only recently, have exchange processes between surface snow and the arctic atmosphere been considered for semi-volatile organic compounds. Results of replicate sampling of the 1985/86 snow layer on the Agassiz Ice Cap, Ellesmere Island, Canada (80° 40'N 73° 30'W) in May of both 1986 and 1987 are presented in Table 2. Except for PCBs, the concentration of the OCs measured in this layer in 1986 was an order of magnitude greater than the concentration measured in the same layer in the following year. Similarity between the two years of sampling for firn layers in which sampling was repeated in the two years indicated that this was not an analytical artifact. Comparison of the snow accumulation layer for the winter of 1986/87, represented only by a single sample in May of 1987 and again in May of 1989, shows residual concentrations of OC pesticides of about 1% in the glacier relative to the depositional concentration measured in 1987 (Gregor, unpublished data). In contrast to the 1985/86 situation, the PCBs also disappeared from the 1986/87 snow layer. Since the 1986/87 layer was characterized by only a single sample, as compared to the multiple samples for 1985/86, it is possible that this loss in 1986/87 is an analytical artifact and only future investigation of this phenomenon will confirm the fate of contaminants in the glacial snow during the first summer season.

Since melting on the glacier was limited and the snow layers below showed consistent low concentrations (i.e. no downward transport of contaminants with the percolation of meltwater through the annual layer) it must be concluded that large portions of the OCs, with the possible exception of PCBs, revolatilized to the atmosphere during the summer season as the air and snow temperatures rose. It is conceivable, because of the range of water solubilities and vapor pressures that characterize PCBs (Mackay and Wolkoff, 1973; Shiu and Mackay, 1986) and the different gas/particle partitioning coefficients of PCB congeners (Duinker and Bouchertall, 1989) that some portion of PCB will remain in the firn as was the case in 1986. This hypothesis needs to be confirmed. Thus, utilization of the glacial residues for temporal trend determinations must be approached cautiously until this re-volatilization phenomenon is better understood and quantified.

Supporting evidence for revolatilization from the snow in the Arctic comes from Hargrave *et al.* (1988) who detected HCB in snow collected in May-June, 1986 (33 pg L^{-1}) but not in snow from the same area in August-September. HCB has the highest vapor pressures and one of the lowest water solubilities of the compounds listed in Table 1 and thus it is readily revolatilized from the snow. At 0°C , more than 99% of HCB was found in the vapor phase in air by Bidleman *et al.* (1987). Similarly, chlordane was found at 91 pg L^{-1} in the snow sampled in May-June while it was undetectable ($<1 \text{ pg L}^{-1}$) in August (Hargrave *et al.*, 1988). The quantity of DDT and lindane in surface runoff waters in agricultural river systems and plots in the Soviet Union were less than 1 % of the quantity present or seeded to the snowpack (Bobovnikova *et al.*, 1978). Although it was not considered in the original work, volatilization from the snow may have been an important loss term.

Since the combustion of fossil fuels in the northern hemisphere increases during the winter season, it is to be expected that the products of combustion would be common in snow of even remote regions. The Arctic can be affected by this increase in fossil fuel combustion as a result of long range atmospheric transport. In winter, driven by the Siberian High pressure zone, air flows mainly from the Eurasian continent into the Arctic and then out over the North American continent

In winter, driven by the Siberian High pressure zone, air flows mainly from the Eurasian continent into the Arctic and then out over the North American continent or into major cyclonic regions in the Aleutians and off southern Greenland. Eastern North American and European emissions commonly reach the Arctic only in late winter and spring Barrie et al., 1981).

The sampling and analysis of PAHs is considerably more difficult than for OCs especially in the Arctic where local conditions and the equipment associated with sampling (e.g., aircraft) can indeed be sources. Edwards (1983) notes that the extraction and recovery of PAHs is problematic, resulting in underestimates and considerable sample variability.

Tuominen et al. (1988) demonstrated that the largest proportion of PAHs in the atmosphere in Finland was associated with particulate matter and that precipitation, specifically snowfall, was an efficient scavenger of particulate associated PAH. Czuczwa et al. (1988) identified naphthalene in precipitation in Switzerland with higher concentrations in snow and winter rain than rain events of other seasons. Concentrations of the higher molecular weight PAHs (phenanthrene, pyrene and benzo(a)pyrene) were higher in snow than in winter rain which in turn had higher concentrations than spring and summer rain. The distribution of odd and even numbered n-alkanes in precipitation in Switzerland indicate that fuel combustion sources are dominant in the winter while natural biogenic sources are dominant in the summer (Leuenberger et al., 1988). These authors also noted that snow samples contained five times as much PAH in the particulate phase as winter rain samples. This difference was thought to be explained by the higher particle scavenging efficiencies of snow compared to rain.

Leuenberger et al. (1988) indicate that gas scavenging of PAHs is temperature dependent and decreases by a factor of approximately 2 for every 10°C increase in temperature. This explains the relatively lower gas scavenging ratios of

summer rain compared to winter rain but temperature dependency of snow scavenging has apparently not been investigated. At polar and sub-polar latitudes, the development of ice fog could be an important deposition mechanism of PAHs generated locally as well as those transported over long distances in the atmosphere. Bidleman (1988) argued that the proportion of aerosol bound PAHs increased inversely with temperature and thus both wet and dry deposition were likely to be important at ambient northern temperatures. The air/snow/air exchange of PAHs, as discussed above for OCs, has apparently not been addressed in the published literature.

Fresh snow in temperate and polar regions is evidently a scavenger of large quantities of organic micropollutants from the atmosphere. However, it appears that relatively little is known about the factors controlling scavenging efficiency and the fate of these compounds upon deposition.

2.3 Fate During Snow-Melt

There has been little study of the fate of organic micropollutants during snow-melt, probably in part a result of the few measurements in snow accumulations. The only laboratory investigation of the dynamics of trace organics during snow-melt found by this author in the published literature is that of Schondorf and Herrmann (1987). These authors considered the preferential elution of compounds with a range of physico-chemical properties using metamorphosed snow from Bavaria. Theoretically, the metamorphosis of snow will change and reduce the surface of snow flakes resulting in the transfer of pollutants in either the dissolved or particulate phase to the surface. Subsequently, the first melt is able to carry off most of the dissolved pollutants. Organic compounds with high water solubility will readily be taken with the meltwater front whereas those that are adsorbed stay behind in the

snowpack. Although solubility increases with temperature, the temperature range of meltwater will be small and this effect should be minor.

Schondorf and Herrmann (1987) confirmed that high concentrations of HCH isomers, with relatively high water solubilities (see Table 1), occurred in the first and final meltwater fractions. The melt water in between the first and final fractions contained nearly no HCH. More than 90 % of the mass of PAH compounds remained in the snow column and was only released with the final melt water, suggesting particle adsorption. The cumulative elution of ions and organic micropollutants is illustrated in Figure 1.

Schondorf and Herrmann (1987) also observed that a deeper snowpack shows a greater difference in concentrations with meltwater fractions, especially when the melt is rain induced. Polar snowpacks are likely comparable to the deeper, high altitude snowpack considered by these authors with frequent freeze and thaw cycles but this apparently has not been studied.

Simmleit and Herrmann (1987) considered empirically the transport of organic micropollutants in melting snow in karst water systems in Bavaria. During February, the 24 cm snowpack that had accumulated in January began to melt. Measurements included bulk snow samples on a daily basis, precipitation at weekly intervals and water samples from the karst springs. Typically for karst systems, the spring water was particulate free, except for a few hours during peak flows. This increase of particulate matter coincided with a sudden increase in benzo(a)pyrene and benzo(ghi)perylene concentrations. The major water soluble compounds such as HCH and fluoranthene responded more directly to discharge during the first melt fraction and were concluded to be transported in a dissolved state.

The work of Simmleit and Herrmann (1987) also showed that 88 to 96% of the PAHs and HCHs were retained in the karst system. These calculations were

based on complete retention of the compounds in the meltwater and conceivably, a portion of the high vapour pressure HCH compounds were revolatilized (see above) as opposed to being lost in the karst system. The interaction of the melting and revolatilization of at least high vapour pressure compounds in snow, especially in regions where sublimation may also be an important term in snow wasting, is a subject that needs careful investigation.

3 MEASUREMENTS IN SNOW

3.1 Temperate and Polar Regions

3.1.1 Chlorinated industrial organics and pesticides

Pioneering work was undertaken in the Antarctic by George and Frear (1966) on snow samples collected at the South Pole and at Byrd Station (80°S 120°W) during November and December, 1964 and January, 1965. DDT was not detected in any of the 1 L water equivalent surface rime frost and snow samples with a detection limit of $1.0 \mu\text{g L}^{-1}$. The British Antarctic Survey (Peel, 1975) reported DDT residues of the order of 100 to 2,000 pg L^{-1} in antarctic snow for samples representing the period of snowfall between 1965 and 1969. These results questioned those of Peterle (1969) which were considerably higher. Although twenty years have past, this work has apparently not been pursued in the Antarctic until very recently.

The earliest known reported work on organochlorine compounds in the Canadian Arctic was undertaken in 1970 as part of the Ice Field Ranges Research Project (IRRP) in the Yukon Territory (Stengle *et al.*, 1973). Sampling for subsequent analyses of DDT was undertaken at an elevation of 5,364 m on Mount Logan. Nineteen samples were taken in snow at depths of 1 to 15 m with DDT not detected in any of these samples at a detection limit of 5 ng L^{-1} .

The earliest atmospheric deposition measurements for OCs in northern Sweden were conducted in 1972 and 1973 using a silicone oil impregnated nylon mesh (Larsson and Okla, 1989). These data (see Table 3) were compared to measured depositions from a similar study conducted in 1984-1985 and it was concluded that the overall fallout of Σ DDT (p,p'-DDT plus p,p'-DDE) decreased during the intervening period. The ratios of DDT to DDE were found to have decreased from 4.10 (n=17) in 1972-1973 to 2.64 (n=52) in the more recent study. Since DDT degrades to DDE in ultraviolet light in the atmosphere and by the metabolism of organisms, it was concluded that the restrictions on DDT use in Sweden in 1971 had been effective and that the DDT reaching Sweden presently has "aged" during long range transport from distant source regions. The trend of PCB concentrations over this time period was more complicated having decreased slightly in the northern part of Sweden. Other research in Scandinavia includes that of Lunde *et al.*, (1977) and Haglund *et al.* (1987).

Concentrations in snow in temperate regions (not including Norway and Sweden) are limited. Probably best known of this work is that conducted on pesticides and PAHs in Bavaria (Schrumpf *et al.*, 1979; Herrmann, 1981; Simmleit and Herrmann, 1987 and Schondorf and Herrmann, 1987). Some of these studies have been discussed above.

Strachan and Huneault (1979) collected accumulated snow from 17 remote sites throughout the Canadian Laurentian Great Lakes drainage basin in February, 1976. With the exception of PCBs and methoxychlor, all of the substances examined were at lower concentrations than in rainfall, collected as part of the same study as event samples between May and November. These concentrations are compared to Canadian arctic snow chemistry data in Table 7. The most noticeable differences between the results of these two studies are the much higher concentrations of PCBs and DDT in the snow of the Great Lakes region.

Alpha-endosulfan and dieldrin, while present in the Arctic, were not detected by Strachan and Huneault (1979) although this is likely an artifact of detection limits.

An investigation of organic micropollutants at 28 sites in the Great Lakes region of Canada (International Environmental Consultants Ltd. [IECL], 1979) revealed only a limited number of samples with concentrations of PCBs and OC pesticides greater than detection limit (10 ng L^{-1} and 1 ng L^{-1} , respectively). Murphy and Schinsky (1983) have considered PCBs in snow at selected sites in the US portion of the Great Lakes basin. Trace organic pollutants in snowfall have also been studied in southern California and Oahu, Hawaii by Kawamura and Kaplan (1986) and Bevenue *et al.* (1972). Pesticide concentrations in the snow from Mauna Kea Summit (about 4,200 m) were 15, 2 and 3 ng L^{-1} for p,p'-DDT, dieldrin and lindane, respectively (Bevenue *et al.*, 1972).

Although still limited, recent work involving snow has focussed on the Canadian Arctic. The Finnish Huure Expedition to the North Pole in 1984 collected a series of snow samples of 1 litre of water equivalent for analyses of a broad range of chlorinated pesticides and chlorophenols (Paasivirta and Pauku, 1987). None of the target compounds, which included OC pesticides, were quantified above the detection limit of 0.5 ng L^{-1} in these snow samples.

In 1979, McNeely and Gummer (1984) undertook snow sampling in the area of east-central Ellesmere Island. Sampling included snowpack at 5 sites, fresh snow at 3 sites and rime frost from 2 sites between May 24 and June 19, 1979, yielding 19 samples with replicates and repeat analyses for a total of 28 analyses. The results for organochlorine pesticides are summarized and compared to selected data from the much more extensive studies of Gregor and Gummer (1989) and Gregor *et al.* (in press) in Table 4. The two stations selected for comparison were Alexandra Fiord sampled in 1986, the only station overlapping between the two studies, and the surface snow for both 1986 and 1987 from the Agassiz Ice Cap,

approximately 175 km to the north. Although the results for Alexandra Fiord for 1986 were below the level of detection available to McNeely and Gummer, the concentrations observed at the Agassiz Ice Cap support concentrations of the magnitude found in the earlier study, at least for HCHs.

Concurrent with the 1986 and 1987 snow chemistry survey of Gregor and Gummer, Arctic Laboratories Limited (1988) undertook work at the Canadian Ice Island during 1986 and 1987. Good agreement was found between the results of these two studies (Table 5) given the very low concentrations of these samples.

HCH data for 1987 Ice Island snow samples are compared for three different laboratories using three different sampling methods in Table 6. The University of South Carolina (USC) results are relatively high. The dominance of lindane in the USC results also does not agree with the other analyses and is not supported by HCH ratios observed in the arctic atmosphere (Patton *et al.*, 1989). The very low concentrations in the snow, and the inevitable desire or need to compare spatially and temporally among different studies underlie the obvious need for more extensive inter-laboratory evaluations as part of future research.

Toxaphene measurements in the arctic snowpack are restricted to four samples. Two of these were 1985/86 snowpack accumulations collected from the Canadian Ice Island in May 1986 and two others were collected from the Devon Ice Cap on Devon Island (75° 6'N, 82° 45'W) and from the vicinity of Resolute Bay on Cornwallis Island (74° 42'N, 94° 54'W) in May, 1987. Concentrations for the two Ice Island samples were 85 and 307 pg L⁻¹ while the Resolute Bay and Devon Ice Cap samples were 600 and 1700 pg L⁻¹, respectively (Bidleman *et al.*, 1989). The wide range in concentration between the three stations was not surprising given the distance between these stations, the difference in elevation (the Ice Island and Resolute Bay locations are essentially at sea level while the Devon Ice Cap site is nearly 1,700 m above sea level) and the different snow accumulation rates.

The results of precipitation samples collected in the Moscow region of the USSR from January 1978 to September 1979 have been reported by Bobovnikova and Dibtseva (1980) for each month. Although the authors have not indicated specifically which monthly samples were snow, it was reasonable to assume for this latitude that samples from December through March were primarily snowfall. Based on these four months, it can be estimated that Σ DDT ranged from 76 to 110 ng L⁻¹; α -HCH ranged from "trace" to 25 ng L⁻¹; and lindane ranged from "trace" to 30 ng L⁻¹. Σ DDT was taken here as the sum of p,p'-DDT, o,p'-DDT, p,p'-DDD and p,p'-DDE as reported by Bobovnikova and Dibtseva (1980) of which p,p'-DDT and p,p'-DDE were the dominant compounds. The detection limit for any of these analyses was not stated. The concentrations of α -HCH were similar to those noted for the Canadian Arctic (Gregor and Gummer, 1989) while lindane tends to be somewhat higher, likely reflecting relative proximity to sources. Σ DDT was two orders of magnitude higher in the Moscow snow samples than the arctic snow samples (Gregor and Gummer, 1989).

Lindane, in daylight, can be transformed to the α -HCH isomer with a half life, dependent upon temperature and other conditions, of the order of one year (Oehme and Ottar, 1984). Although degradation rates are likely substantially different in a polar climate than a temperate one, this ratio may be informative with respect to possible age or length of time of HCH transport. Also, chemical formulations differ. North America and western Europe use pure lindane. Aerosol ratios are reported at 1:7 (α -HCH:lindane) in the Great Lakes region (Eisenreich et al., 1981) while European ratios tend to be 1:3-4 (Oehme and Mano, 1984).

HCH ratios (α -HCH:lindane) in the air at the Ice Island, which appear to be indicative of the Canadian North, were 6:1 and 15:1 in the spring and summer, respectively, of 1986 (Hargrave et al., 1988). Based on Table 2, the ratio for surface snow from the Agassiz Ice Cap was 2:1 in 1986 and 4:1 in 1987. The average ratio for all surface snow samples reported by Gregor and colleagues (Gregor and

Gummer, 1989; Gregor, 1990) in 1986 and 1987 was 2.5:1. These low ratios in the snow relative to the atmosphere, are thought to be related to the higher vapor pressure of α -HCH relative to lindane. Lindane, having a higher vapor pressure, will be more likely to be particle associated and thus will be preferentially scavenged by snowfall. Also, α -HCH may be preferentially revolatilized from the snowpack resulting in a lower isomeric ratio than observed in fresh snow and the atmosphere.

3.2.2 Polycyclic aromatic hydrocarbons

Rural, mountainous area snow samples from California collected in 1982 showed that of the total organic substances identified, more than 80% originated from natural plant waxes of biogenic origin. Accordingly, anthropogenic organic compounds were minor constituents of the rural snow samples (Kawamura and Kaplan, 1986).

PAHs have been measured in fresh snow samples in Bavaria, F.R.G. (Schrumpf *et al.*, 1979; Schrupf, 1980; Herrmann, 1981; Schondorf and Herrmann, 1987 and Simmleit and Herrmann, 1987) and in Switzerland (Giger *et al.*, 1987). In a comparative, seasonal study of snow and rain near an urbanized area of Switzerland, Leuenberger *et al.* (1988) and Czuczwa *et al.* (1988) found that alkylbenzenes were the dominant volatile organic component with snow having higher concentrations (up to $10 \mu\text{g L}^{-1}$) than rain at any time throughout the year. Based on the mean of five snow samples, the rank order of total (dissolved plus particulate) concentrations of the major compounds were - fluoranthene > phenanthrene > pyrene > Σ methylphenanthrene > chrysene > benzo(b+j+k)fluoranthenes. These six compounds comprised more than 80% of the mean total PAHs in the snow. Naphthalene concentrations were higher in winter than other seasons with winter rain concentrations higher than snow concentrations.

Several factors are believed responsible for the higher winter concentrations. First and quite obvious is the higher hydrocarbon emissions due to domestic heating. Second, snow has a scavenging efficiency of particulates an order of magnitude greater than rain. Finally, there are more opportunities for dilution in the atmosphere in the summer time due to the increased atmospheric mixing heights in summer, the increased volatility of the compounds with summer temperatures and the increased photoreactivity or hydrolysis in the summer (Leuenberger *et al.*, 1988; Czuczwa *et al.*, 1988).

Arctic snow samples collected in 1987 have been analyzed by this author (unpublished data) for 17 PAHs by capillary gas chromatography with electron impact, multiple ion monitoring mass spectrometric detection (MIM-GC/MSD). EPAH concentrations were highly variable ranging from non-detectable to 125 ng L⁻¹. The seven PAHs detected consistently were phenanthrene, 1-methylnaphthalene, 2-methylnaphthalene, 1,2,3,4-tetrahydro-naphthalene and indene with generally small quantities of fluorene and/or acenaphthene. All seven of these PAHs are coal tar derivatives, practically insoluble in water (although having higher solubilities than many of the OCs) and of relatively low molecular weights for PAHs (Table 1). These PAHs are mildly toxic with some having a tendency to bioaccumulate, to be slightly carcinogenic and even to be mutagenic. Some, such as acenaphthene and 1,2,3,4-tetrahydro-naphthalene have commercial uses either alone or in conjunction with other products (Windholz, 1983). Compounds commonly associated with internal combustion exhausts (e.g., fluoranthene and pyrene which were dominant in the snow samples from Switzerland [see above]) were either not detected or were detected only occasionally and were believed to be sample contamination. Phenanthrene, also a combustion product, was present in the Arctic. Relative to other PAHs, it appears that it is the lower molecular weight, high vapor pressure, more water soluble PAHs that are being found in the arctic snow, but the long range transport of PAHs to the Arctic requires a great deal more research.

3.3 Contaminant Flux and Trends

The comparison of contaminant concentrations in precipitation is frequently trivial without consideration of the total quantity of precipitation as required in determining flux. Median winter deposition rates for selected organochlorines based on concentrations in Canadian arctic snowpack in the spring of 1986 and 1987 are presented in Table 7. Although these are shown as winter deposition rates, it is reasonable to assume that these represent for all intents and purposes, annual deposition in the Arctic. There are two reasons supporting this assumption. First, approximately 80% of the total precipitation in the high Arctic arrives as snowfall (Woo *et al.*, 1983). Second, the period of snow accumulation at these arctic stations generally ranges from September to May and this encompasses the period during which the arctic aerosol has been shown to be most heavily contaminated with anthropogenic pollutants (Barrie and Hoff, 1985; Barrie *et al.*, 1985; Barrie *et al.*, 1989) due to the tropospheric circulation patterns typical of the winter season.

These flux estimates are limited by the fact that the snowpack samples are commonly collected from remote sites and total annual snowfall at the specific sampling site has to be assumed to be equal to that recorded at the nearest weather station which may be several hundreds of kilometres distant. In addition, total snow storage in a basin generally exceeds weather station records by as much as from 130 to 300% (Woo and Marsh, 1977; Woo *et al.*, 1983). It must also be remembered that deposition to the snowpack does not necessarily mean a direct transfer of this quantity of contaminant to the aquatic system following snow-melt as revolatilization may occur (see section 2.2).

Published data from the USSR appear to be limited to the annual fluxes in rainfall and snowfall provided by Bobovnikova and Dibtseva (1980) for the Moscow area. Fluxes there were estimated to be about $52 \mu\text{g m}^{-2} \text{yr}^{-1}$ for EDDT

(p,p'-DDT + o,p'-DDT + p,p'-DDD + p,p'-DDE) and 14 and 12 $\mu\text{g m}^{-2} \text{yr}^{-1}$ for α -HCH and lindane, respectively, for the 1978 calendar year. The flux of α -HCH is similar to the maximum of the range for the Arctic while lindane is about 6 times greater and Σ DDT is about 10 times greater in the Moscow region than in the Canadian Arctic. As noted in the discussion of concentrations, the Moscow data likely show much closer proximity to source regions. However, the Moscow data precede the arctic data by nearly 10 years and conditions could have changed considerably during this time due to different pesticide formulations, application procedures and quantities used.

Rapaport *et al.* (1985) analysed snow and rain samples collected at Minneapolis, Minnesota, USA from 1981 through 1983 for p,p'-DDT. Concentrations in the snow ranged from 100 to 550 pg L^{-1} in 1981/82; 400 to 1,000 pg L^{-1} in 1982/83 and from 100 to 210 pg L^{-1} in 1983/84. Mean annual fluxes of p,p'-DDT for snow reported by these authors averaged 0.2, 0.4 and 0.13 $\mu\text{g m}^{-2} \text{yr}^{-1}$ for 1981/82, 1982/83 and 1983/84, respectively. The time interval and the variability present in these data preclude any assessment of trends.

To date there has been limited conclusive research regarding trends of trace organic contaminant deposition in the Arctic despite the extensive work conducted on glacial records for other anthropogenic contaminants. Periodic measurements in air and fresh snow have been too restricted temporally to provide any time series information with the exception of the Swedish study of Larsson and Okla (1987) noted in section 3.2. Stengle *et al.* (1973) sampled at depth on Mount Logan but could not quantify DDT. The extensive research on Greenland ice sheets has apparently not been extended to include trace organic contaminants. Thus the only research that has been directly concerned with determining temporal trends of OC deposition is that on the Agassiz Ice Cap on north-central Ellesmere Island.

The Agassiz Ice Cap has been sampled at a remote site at an elevation of approximately 2,000 m above sea level in both 1986 and 1987 to include 17 years of samples between 1969/70 and 1986/87 (Barrie *et al.*, in press; Gregor *et al.*, in press). Intuitively, this cold glacier should provide a credible historical record of anthropogenic pollutant deposition because (i) average summer melt affects only about 3% of the winter snow layer resulting in negligible redistribution of ions between adjacent snow layers (Barrie *et al.*, 1985) and (ii) annual snow accumulation at this latitude and elevation represents, on average, more than 75% of the total annual precipitation (Woo *et al.*, 1983). The seasonal specific conductance record of the firn (Figure 2) is preserved and is consistent with that reported by Barrie *et al.* (1985). As noted by these authors, this profile reflects the trace constituent composition of the atmospheric aerosol which undergoes a strong seasonal variation with maximum ion concentrations and therefore specific conductance during the arctic winter (Hoff and Barrie, 1986; Rahn and Shaw, 1982). In general, it appears that annual inventories of chlorohydrocarbons in the firn at the Agassiz Ice Cap have decreased over the period of record as follows:

- α -HCH	from >300 to 70 ng m ⁻² ;
- lindane	from 90 to <20 ng m ⁻² ;
- heptachlor epoxide	from 20 to 5 ng m ⁻² ;
- dieldrin	from >50 to 20 ng m ⁻² ; and,
- PCB	from >300 to 100 ng m ⁻² .

The consistent decline among all compounds is quite remarkable. Support for a decrease in the supply of chlordane and α -endosulfan to the Agassiz Ice Cap is provided by the less frequent detection of these compounds in recent years.

However, as noted in section 2.2, the firn does not seem to be an effective permanent trap of the semi-volatile trace organic compounds, with the possible exception of PCBs. The residues in the firn therefore are not quantitatively representative of the annual flux of these pesticides to the glacier. Thus the residue

trends seen in the glacier for lindane, α -HCH, heptachlor epoxide and dieldrin are not solely related to a trend in the annual loadings, but rather are being controlled to an unknown degree by meteorological conditions influencing the snow/atmosphere exchange. Notwithstanding the absence of confirmatory data regarding the retention of PCBs in the glacial firn, Gregor *et al.* (in press) conclude that, at the present time, only the trend for PCBs has any relevance to a real trend in annual deposition to the ice cap. Although the residue masses of PCBs in the glacier will be influenced somewhat by the annual variability of summertime losses, it is conceivable that the actual annual deposition is the dominant factor controlling the trend for PCBs, as was the case in 1985/86. Nonetheless, meteorologic conditions that control atmospheric transport to the Arctic and deposition to the snow vary from year to year. Thus, it is necessary to consider this variability and to attempt to adjust for it.

Gregor *et al.* (in press) normalized the PCB trend for annual meteorologic variability with ^{210}Pb flux measurements which were also determined for the glacier. The radioactive isotope ^{210}Pb is derived from the decay of ^{222}Rn which emanates from the earth's surface where it is produced as a member of the ^{238}U decay series. ^{222}Rn decays in the atmosphere to ^{210}Pb with a half life of 3.8 days. The charged daughter ions produced are chemically reactive and soon become irreversibly associated with aerosol particles (Robbins, 1978).

Since the source of ^{210}Pb (i.e., the earth's surface) remains more or less constant with time, it can be hypothesized that the deposition of ^{210}Pb to the glacier would be uniform from year to year if the air mass movements and the complex interaction of factors controlling transport and deposition to the glacier remain constant. Thus, the differences of measured decay corrected ^{210}Pb inventories in the snow layers can be assumed to represent, simplistically, the year to year differences in atmospheric transport and deposition of terrestrially derived anthropogenic pollutants. Under these assumptions, any trends in these adjusted trace organic

substance residue data should represent real changes in the flux of contaminants to the glacier.

The ^{210}Pb normalized PCB inventories in the annual layers of the Agassiz Ice Cap are compared to measured fluxes in Figure 3. It is evident that the years having the greatest measured flux to the snow of PCBs generally coincided with high ^{210}Pb flux resulting in a much smoother normalized or adjusted trend line. These ^{210}Pb corrected inventories imply that after variable meteorological conditions have been considered, the annual normalized inventory of PCBs in the glacial layers have remained essentially constant since 1976/77 through to 1985/86 at a level approximately one half of that which prevailed between 1970/71 and 1975/76.

This decline in ^{210}Pb normalized PCB inventories in the glacier agrees in general with trends in PCB body burdens in ringed seals from the western Arctic between 1972 and 1981 (Addison and Zinck, 1986) and for the Lancaster Sound area between 1975-76 and 1984 (Muir *et al.*, 1988). However, correspondence among these limited data may be merely fortuitous and a great deal more work is required to thoroughly evaluate trends in contaminant deposition in the Arctic.

4 SUMMARY AND CONCLUSIONS

The aquatic environment and the atmosphere have received considerable research over the past several decades for the purpose of measuring the extent of environmental contamination by organic micropollutants. However, one of the major sources of precipitation in temperate and polar regions and a major atmospheric scavenger, snowfall, has to a large extent been ignored. Information on the sources, atmospheric pathways, present deposition rates, deposition trends and processes controlling the fate of organic micropollutants in snow is sparse.

Actual processes of deposition and re-volatilization from snow has received only limited attention. While deposition has been confirmed in a variety of concentration and flux measurements throughout the world, only recently has evidence been put forward that large percentages of the semi-volatile compounds may be revolatilized to the atmosphere from the snow as temperatures rise. These processes warrant more research under temperate and polar conditions.

Despite extensive work utilizing glacial ice cores for monitoring pollutant trends for such concerns as acid deposition and climate change, there has been only limited research on the glacial record of organic micropollutant deposition. The only glacier in the northern hemisphere that has been studied for this purpose, with quantitative results, is the Agassiz Ice Cap on Ellesmere Island. This research, although limited to 17 years of record at this time, indicates first that the glacial organochlorine pesticide residues are not directly related to actual deposition but are largely a function of variable meteorologic conditions. Only the PCB record appears relatively intact and these data, after correction for annual meteorologic differences, suggest that PCB deposition has decreased by a factor of approximately 2 since 1970 and has remained nearly constant over the past decade.

Clearly, more comprehensive research is required to expand the information base for organic micropollutants in snow. This research must seek a broader geographical as well as temporal coverage. Equally important though, is the research directed at understanding the processes and fate of these contaminants in temperate and polar environments and their effect on the cycling and storage of micropollutants. This must come from both laboratory and field based research. Only with this information, combined with ecological effects assessments, will an understanding of the role of snow in transporting and cycling organic contaminants be attained.

ACKNOWLEDGEMENTS

I wish to thank Dr. W. Giger of the Swiss Federal Institute for Water Resources and Water Pollution Control, Dr. M. Tranter of the Department of Oceanography, University of Southampton and Dr. Wm. Strachan of the National Water Research Institute, Environment Canada for their very helpful and knowledgeable comments. I also want to thank NATO for sponsoring this Advanced Research Workshop on Processes of Chemical Change in Snowpacks and congratulate T. Davies, P. Brimblecombe, M. Tranter, G. Jones and all others who were instrumental in making this workshop a success.

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TABLE 1: Physicochemical properties of selected organochlorine compounds and PAHs^a

Compound	Henry's Law Constant ^a Pa(mol m ⁻³)		vapour pressure ^b over liquid (25°C) (KPa)	water solubility ^c ug L ⁻¹) @25°C)
	freshwater (°C)	seawater (-2°C)		
organochlorines				
lindane	0.32 (25)	0.03	6.5x10 ⁻²	2000-12000
α-HCH	0.55 (22-25)	0.10	2.3x10 ⁻¹	1200-2000
toxaphene	0.61 (20)	0.09	1.7x10 ⁻³	300
hexachloro- benzene	83.0 (25)	7.8	1.3x10 ⁻¹	<20
α-endosulfan	1.09 (25)	0.10	6.1x10 ⁻³	150-600
dieldrin	1.12 (20)	0.125	1.0x10 ⁻²	186-200
chlordan	4.92 (25)	0.47	5.1x10 ⁻³	56-1850
DDT	5.3 (25)	0.5	5.1x10 ⁻⁴	< 1-25
DDE			3.3x10 ⁻³	1-140
2,4,5,2', 4',5'-PCB	42.9 (25)	4.1	5.0x10 ⁻⁴	
PAHs				
pyrene	1.2 (25)	0.11	1.4x10 ⁻²	
phenanthrene	4.0 (25)	0.38	1.0x10 ⁻¹	1000-1800 ^d
naphthalene	43 (25)	4.1	3.8x10 ¹	26000 ^d
fluoranthene	220 (25) ^e		6.4x10 ⁻³	≈ 200 ^e

^a modified from Barrie *et al.* (in press)^b Hinkley *et al.*, 1990^c from Arctic Laboratories (1988)^d from CCREM (1987)^e from McKay and Shiu (1981)

TABLE 2: Comparison of 1985/86 season concentrations for selected chlorohydrocarbons in Agassiz Ice Cap as measured in 1986 and again in 1987

Compound	concentration (pg L ⁻¹) (mean \pm standard deviation)		
	<u>1986</u> (n=5)	<u>1987</u> (n=3)	<u>residue</u> (%)
lindane	4080 \pm 909	128 \pm 43	3
α -HCH	6576 \pm 1441	497 \pm 90	8
heptachlor epoxide	358 \pm 55	47 \pm 15	13
chlordane	760 \pm 89	40 \pm 26	5
dieldrin	1346 \pm 238	213 \pm 75	16
α -endosulfan	1094 \pm 156	ND	nil
PCB	972 \pm 344	648 \pm 118	67

TABLE 3: Contaminant deposition data for northern Sweden and Moscow compared with Canadian arctic data ($\mu\text{g m}^{-2} \text{ yr}^{-1}$)

Compound	Moscow ^a		Sweden		Arctic ^d
	1978-79	1972-73 ^b	1974-76 ^c	1984-85 ^b	1986-87
alpha-HCH	14				0.2-9.1
lindane	12				0.01-2.0
DDT	52	$\approx 1.2-13.2$		$\approx 0.1-8.79$	0.01-3.0 ^e
PCB		$\approx 1.2-16.6$	24-60	$\approx 24-154$	0.04-0.6

^a from the Moscow area as reported by Bobobnikova and Dibtseva (1980)

^b estimated from figures published by Larsson and Okla (1989) for stations north of 60°N only. Actual data were reported for a monthly time period and these data have been multiplied by 12 to provide a comparable annual value.

^c from Lunde *et al.* (1977) only for stations north of 60°N

^d from Barrie *et al.* (in press) and determined from annual snowpack samples representing September to May and here assumed to represent the annual deposition

^e includes only 1987 data

TABLE 4: Summary of pesticide snow chemistry data collected in 1979 by McNeely and Gummer (1984) from east-central Ellesmere Island compared with selected data from Gregor and Gummer (1989) for Alexandra Fiord (1986), and the surface snow layers from Agassiz Ice Cap in 1986 and 1987

pesticide	1979 range (ng L ⁻¹)	confirmed detections ^a	unconfirmed detections ^b	Alexandra Fiord ^c (ng L ⁻¹)	Agassiz L-1 ^d (ng L ⁻¹)	Agassiz L+1 ^c (ng L ⁻¹)
α -HCH	<1 - 18	21	5	0.43	6.7	19.1
lindane	<1 - 8	10	5	0.22	4.4	6.8
chlordan	<1 - 4	3	7	0.17	0.74	0.23
DDT	<1 - 6	4	10	0.07	0.01	0.13
α -endo sulfan	<1 - 2	1	2	0.24	1.1	1.1
dieldrin	<2 - 4	5	12	0.83	1.4	1.0

^a Includes both detections above the detection limit and below the detection limit but confirmed by MID-GC/MS

^b Indicate instrument responses below the detection limit but of insufficient concentration to permit confirmation by MID-GC/MS

^c Single sample

^d Represents the mean of 5 samples from this layer

TABLE 5: Comparison of 1987 Ice Island samples for organochlorine residues as reported by Arctic Laboratories (1988) with results from Gregor and Gummer (1989) based on 3 replicates for each laboratory

Compound	concentration (pg L ⁻¹) in melted snow	
	Gregor & Gummer (mean \pm 1SD)	Arctic Laboratories (mean \pm 1SD)
Aroclor (1254) ^a	129 \pm 37	185 \pm 160
hexachlorobenzene	11 \pm 6	12 \pm 3
heptachlor	<3 ^b	6 \pm 3
aldrin	Int	0.5 \pm 0.5
o,p'-DDE	ND	2.8 \pm 2.4
p,p'-DDE	ND	20 \pm 14
Mirex	ND	<4.0
trans-chlordane	8 \pm 1	20 \pm 15
cis-chlordane	<12 ^c	25 \pm 18
p,p'-DDT	23 \pm 19	<47 \pm 26
heptachlor epoxide	30 \pm 11	46 \pm 26
alpha-endosulfan	21 \pm 1	97 \pm 58
dieldrin	54 \pm 5	<140 \pm 55
endrin	spike	27 \pm 11
methoxychlor	55 \pm 35	37 \pm 26

Abbreviations: SD = standard deviation
 Int = interference on chromatograms
 ND = non-detectable

^a For this comparison, the PCB data from Gregor and Gummer are reported as Aroclor 1254 whereas in all other Gregor and Gummer references in this report PCBs are reported as the 1:1:1 mixture of Aroclor 1242, 1254 and 1260.

^b One of the three samples was ND. Therefore the concentration is reported as less than the maximum concentration observed with no standard deviation.

^c Two of the three samples were ND. Therefore the concentration is reported as less than the concentration of the single value with no standard deviation.

TABLE 6: Comparison of 1987 Ice Island snow samples for hexachlorocyclohexane (HCH) residues among Gregor and Gummer (1989), Arctic Laboratories (1988) and University of South Carolina (USC) as reported by Arctic Laboratories

Compound	concentration (pg L ⁻¹) in melted snow		
	Gregor & Gummer ^a (mean ± SD)	Arctic Labs ^b (mean ± SD)	USC ^c (mean ± SD)
α-HCH	143 ± 13	290 ± 130	315 ± 25
lindane	83 ± 9	192 ± 96	365 ± 15

^a Based on 3 samples collected June 6, 1988

^b Based on 3 samples collected June 8,9 and 15, 1988

^c Based on 2 samples collected June 7 and 9, 1988

TABLE 7: Median and range of concentrations and corresponding winter season deposition of trace organic compounds from Canadian arctic snow chemistry surveys in 1986 and 1987 compared with 1976 snow chemistry data from the Laurentian Great Lakes

Compound	1986 (n=12)		1987 (n=15)		Great Lakes snow concentration (pg L ⁻¹)
	concentration (pg L ⁻¹)	winter deposition (ng m ⁻²)	concentration (pg L ⁻¹)	winter deposition (ng m ⁻²)	
PCB	745 (20-1760)	73	907 (257-1773)	95	2900
alpha-HCH	3185 (430-8120)	285	910 (143-42700)	95	100
lindane	1160 (220-4446)	104	700 (83-10500)	73	900
heptachlor epoxide	97 (ND-362)	10	117 (ND-1600)	16	NA
alpha-endosulfan	345 (100-1094)	37	175 (ND-4880)	24	ND
dieldrin	540 (205-1402)	58	400 (ND-4420)	56	ND
HCB	28 (10-70)	3	16 (ND-104)	2	ND
ΣDDT	18 (10-50)	2	93 (ND-1380)	8	100
ΣCBZ	NA	NA	240 (ND-915)	30	NA
ΣPAH	NA	NA	19000 (190-149000)	4246	NA

NA = not available

ND = not detectable

HCB = hexachlorobenzene

ΣDDT = sum of all detected DDT compounds and metabolites

ΣCBZ = sum of all detected chlorobenzene compounds targetted

^a from Strachan and Huneault (1979) reported as a mean of 17 samples

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- Figure 3: PCB inventories in annual layers of teh Agassiz Ice Cap from teh winter of 1970/71 to the winter of 1986/87 compared to the ^{210}Pb normalized inventories which are interpreted as the trend compensated for variable annual delivery resulting from variable meteorologic conditions.

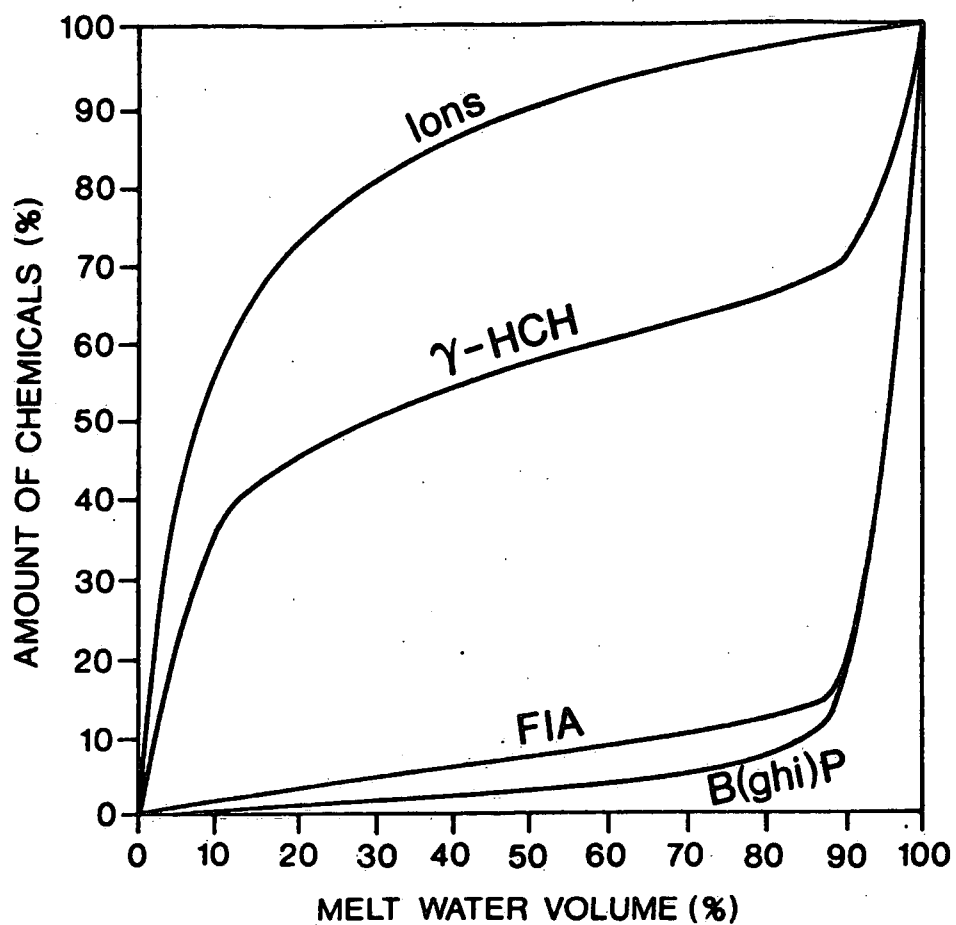


Figure 1 Cumulative elution of ions and organic micropollutants from snow-melt (redrawn from Schondorf and Herrmann, 1987)

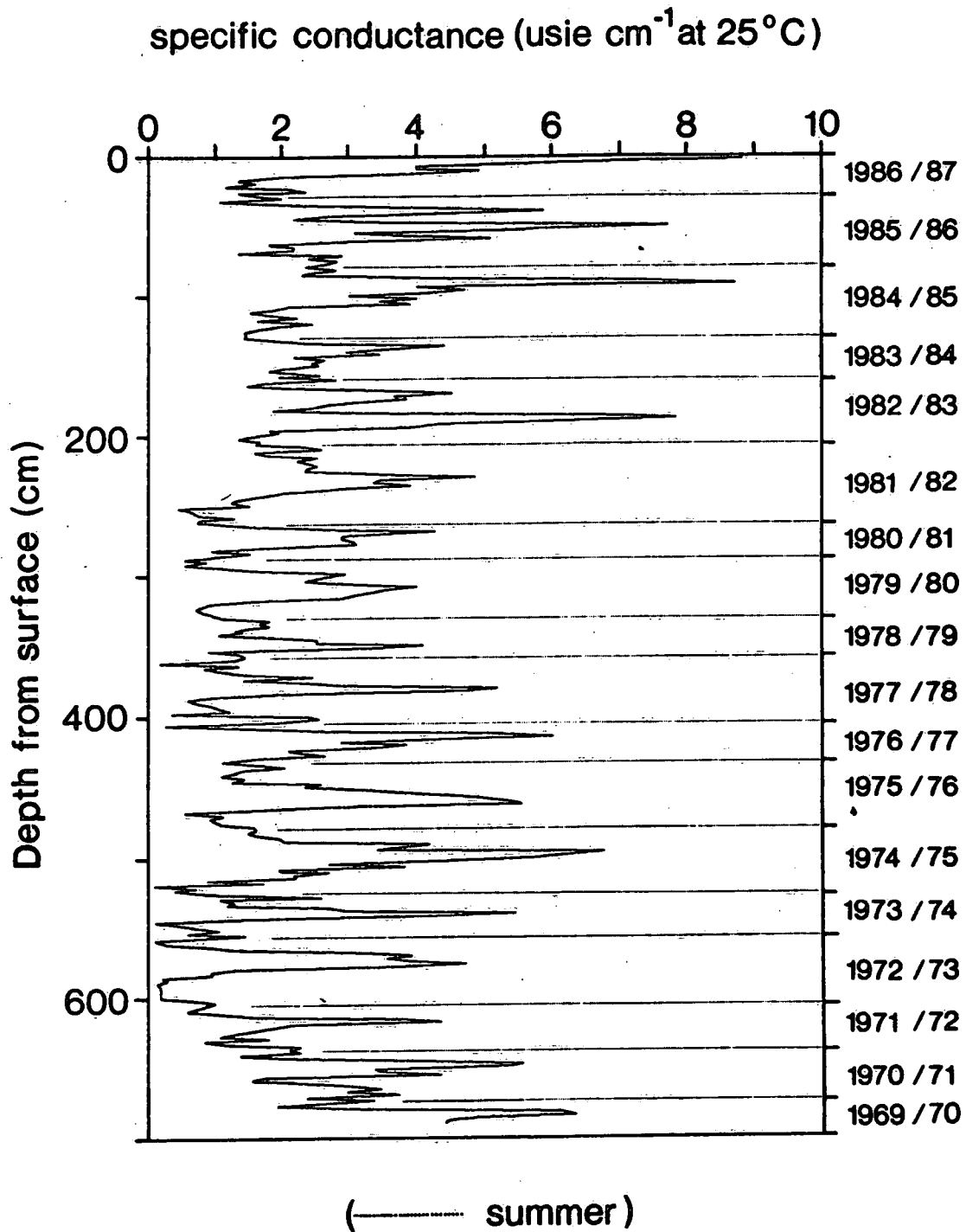


Figure 2 Plot of specific conductance versus depth for the Agassiz Ice Cap from the snow surface in the spring of 1987 to a depth of 6.9 m

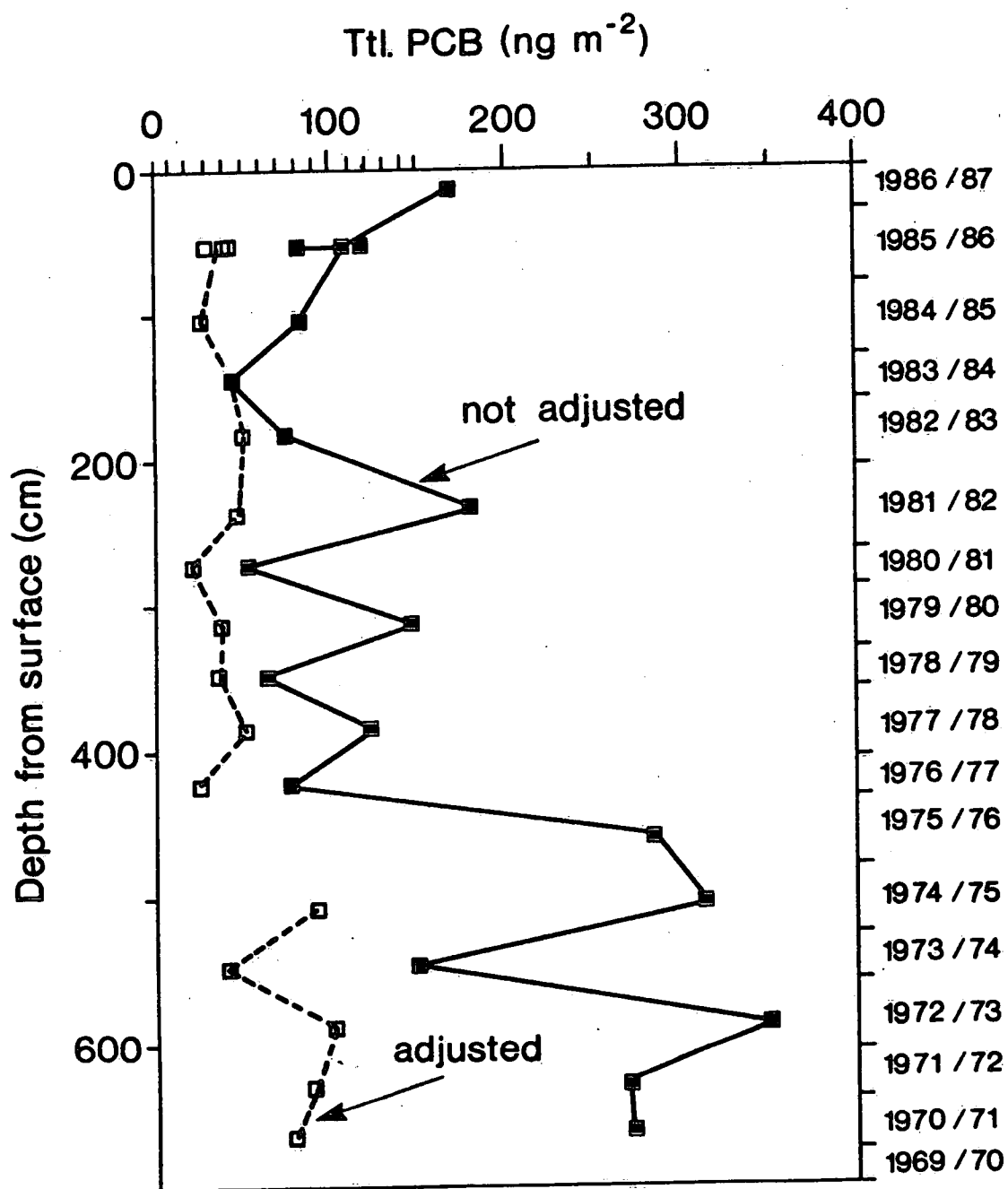
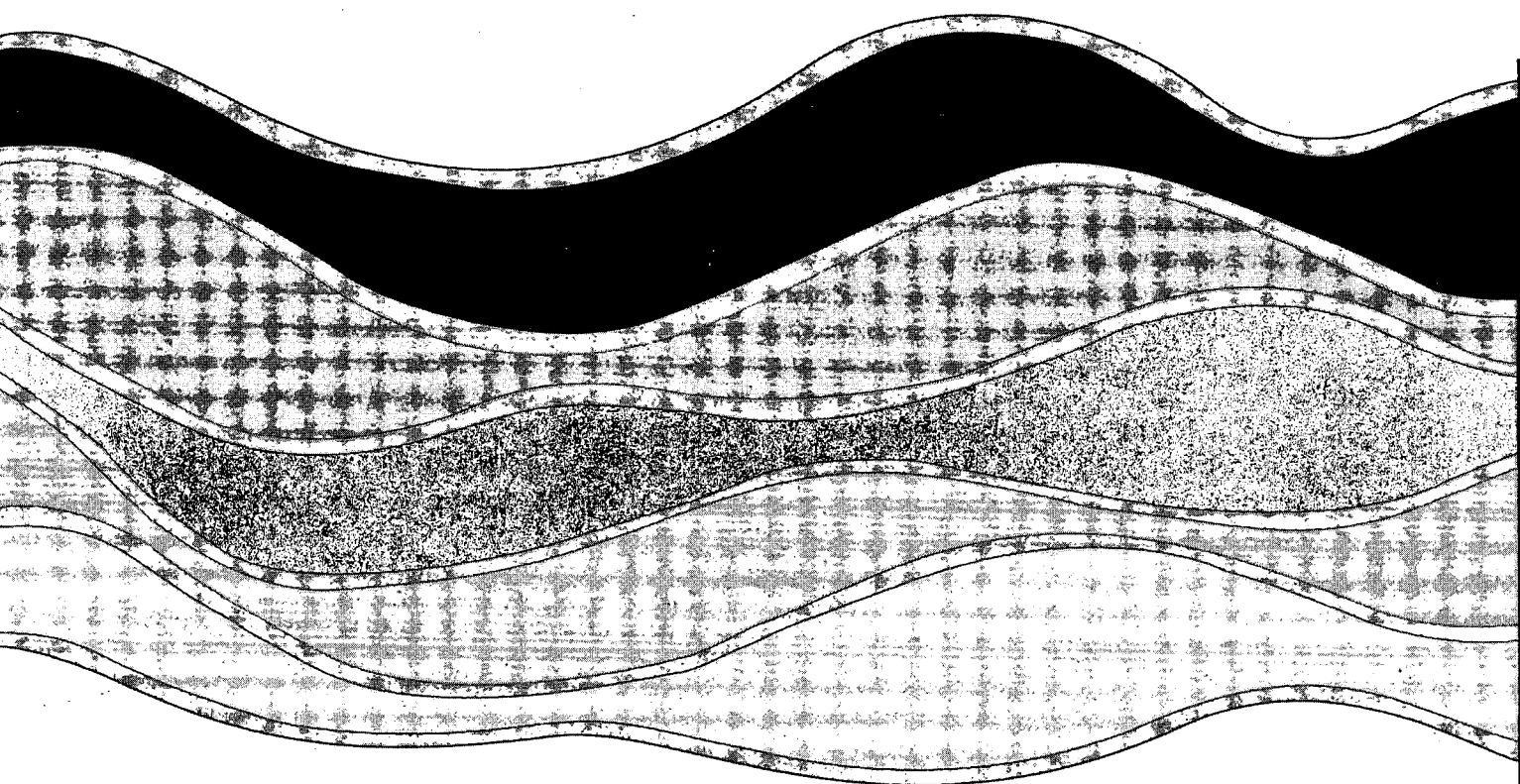


Figure 3 PCB inventories in annual layers of the Agassiz Ice Cap from the winter of 1970/71 to the winter of 1986/87 compared to the ^{210}Pb normalized inventories which are interpreted as the trend compensated for variable annual delivery resulting from variable meteorologic conditions

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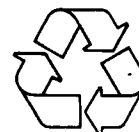
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