Persistent organic pollutants and mercury in the Himalaya and Tibetan Plateau

by

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A Thesis submitted to the Faculty of Graduate Studies of

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DOCTOR OF PHILOSOPHY

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To Marissa

Abstract

Persistent organic pollutants and mercury are important contaminants due to their persistence in the environment and potential toxic effects on ecosystems and humans. Concerns related to these contaminants are particularly pertinent in Asia where the use of pesticides and mercury emissions have been increasing dramatically due to changing agricultural practices and rapidly expanding industrialization. Based on studies in European and North American mountain regions, evidence is increasing that alpine regions function as regional convergence zones for selected organic pollutants due to an effect called orographic cold trapping. It is hypothesized that such an effect may be particularly pronounced in the Himalaya because of dramatic elevational temperature and precipitation gradients relative to contaminant source regions in its immediate vicinity, and because of the regional monsoon system that has been shown to deliver particles and inorganic air pollutants to higher altitudes. We report here evidence for the movement of select environmentally relevant chlorinated organic pesticides into the Central Himalaya with strong seasonal differences due to the Indian monsoon. Atmospheric concentrations of these chemicals are positively correlated with altitude in summer up to an elevation of 5000m a.s.l and then decrease at higher elevation. In winter the atmospheric concentrations are negatively correlated with altitude indicating that during this season remote sites are above the boundary layer. Soil concentrations appear to follow the gradient of forestation, with maximum concentrations at 2600m a.s.l. and then declining above that altitude. Mercury in three Tibetan snow pits, well above the boundary layer shows the likelihood of particulate deposition in winter when particulate concentrations are highest. Strong dust storm activity is the largest source of mercury deposition on the

plateau, though it is unsure if the mercury is transported on dust long distances or if mercury is partitioning onto particulates nearby to the deposition site. Both these deposition mechanisms are likely occurring. The highest elevations of the Himalaya and Tibetan plateau are protected by the upper level westerlies above the boundary layer and are likely only affected by chemicals that have long atmospheric lifetimes such as hexachlorobenzene and mercury.

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1   Introduction

Mountains are revered for their natural beauty. They are mystical places, difficult to access, and have a special effect on the spirit. It is no wonder that in the Himalaya, mountains carry the names of gods and saints travel across a continent to meditate in their midst. One range in the Himalaya is called Annapurna; goddess of the Harvest. This is a particularly appropriate name for a mountain range, like others all over the world, which are massive storage containers of water releasing moisture slowly through the dry season. Even here in the Canadian Prairies we often forget that some of our great rivers start at the foot of the Rocky Mountain glaciers. Hence, the health of these rivers is in some part determined by the health and well being of our mountains. Of any high altitude region in the world, the Himalaya and Tibetan Plateau are the source of rivers that feed more people than any others. The health of this ecological region is very important to our global well being and survival.

The question of this thesis is how atmospherically transported chemical contaminants behave in the Himalayan mountain system and the Tibetan plateau. Organic chemical contaminants are of particular importance with respect to alpine regions. They are cold regions often surrounded by agriculture and human habitation. Recently mountains have been found to contain unexpectedly high concentrations of pesticides, which are often associated with agriculture, due to their physical character interacting with the unique alpine environment (1,2). The semi-volatile nature of some agricultural chemicals render them ideal candidates for atmospheric transport and preferential deposition in comparatively cooler high altitude ecosystems (1,2). This phenomenon is known as

orographic cold trapping which is the environmental phenomenon that steered us to investigate this unique ecosystem as it appeared to be ideally suited to strong deposition of these toxic contaminants (1,2). As such, the Himalaya and Tibetan plateau warrant further research to verify whether this phenomenon is observed. Previously there had been some published research looking at persistent organic pollutants (POPs) at a high elevation site in the Himalaya, which did appear to support this hypothesis (3). However due to the difficulty of working in this region, this environmental phenomenon remains understudied when compared to other mountainous regions of the world.

Other than locally occurring emissions of mercury from geological sources, mercury observed in these high altitude locations is atmospheric in origin. Gaseous elemental mercury, due to its similarity in chemical properties when compared to POPs, may also follow similar patterns of deposition in the environment, though this has not been fully documented.

2   Format of Thesis

This thesis is formatted in a "sandwich style", meaning it is a collection of published and submitted papers related to this thesis. Four papers in varying stages of publication were compiled and are found at the end of this thesis.

Paper I is entitled *"Persistent organic pollutants (POPs) and mercury in the Himalaya"* (4). It is a literature review on the current state of research related to these chemicals in mountain regions, most notably the Himalayan region. There is a reasonable amount of

information on the behavior of POPs in mountains and very little on mercury. Furthermore there is very little literature on chemicals in Asian mountains. In the paper we try to make a case for the Himalaya as an understudied environmental region and offer some novel techniques to study chemical fate in the highest mountains in the world.

This is followed by paper II (5), entitled "*Altitudinal transect of atmospheric and aqueous fluorinated organic compounds (FOCs) in Western Canada*". In this paper, apart from work on FOCs (which is not related to this thesis directly), we did some modeling of how passive air samplers work in a mountain environment and how chemicals behave with respect to the sampling resin and different mechanisms of chemical deposition, most notably snow which is a foundation of chemical deposition in mountains.

In paper III (in review) we undertook a study entitled *Seasonal and altitudinal trends of chlorinated pesticides in the central Himalayan atmosphere* to observe seasonal trends of atmospheric chlorinated pesticides commonly used in the Indian Subcontinent over a very large altitudinal transect (178-5605m a.s.l.). We observed large seasonal differences in air concentrations (higher during the monsoon) due to changes in air mass direction caused by the Indian monsoon. We also observed enrichment of some chemicals? with altitude during the monsoon season. While the levels of contaminants in the remote high elevation samples were not higher than most other mountain sites globally, sites at low elevation did have some particularly high levels of p,p'-DDT and endosulfan. This is likely due to their current use for agriculture and malaria control in the region. One

wonders what might be the human health impact of exposure to these high concentrations in the agricultural areas. Although the levels of chemicals at high altitude do not appear to be of grave concern, they do offer a novel way to study the atmospheric dynamics of the monsoon and of the region.

Mercury, another chemical of environmental concern, while sharing the nature of volatility with the organic chemicals, its deposition in mountain region appears to be driven by a different mechanism. This is described in paper IV, entitled *"Atmospheric transport of mercury to the Tibetan Plateau"* (*6*). Mercury has the interesting characteristic of being environmentally relevant even when it has reacted with species in the air or water but by doing so changes its chemical physical properties. In the atmosphere Hg is typically very stable though it is subject to oxidation. It is believed that bromine chemistry plays a major role in Hg oxidation especially in the upper troposphere and in polar regions. Once oxidized, Hg vapour pressure decreases dramatically and will deposit on the earths surface rapidly. Our studies showed that Hg in seasonally dated snow packs from glaciers on the Tibetan Plateau was associated with winter deposition and also with particulates.

The observed trends in these experiments are unique in the literature and offer some of the first observations of these environmentally significant compounds in remote areas of Asia.

3　General Methods

As the source of contamination in alpine regions is atmospheric, it is sensible to study the concentration of POPs and mercury in the atmospheric compartment of the alpine environment. For POPs, a technology know as passive air sampling (PAS) was utilized due to its ability to give a reasonable estimate of atmospheric concentrations without the need for electrical power (7).

Figure 1: Passive sampler deployed near Mt. Everest.

For mercury, snow deposited in high elevation snow pits was studied as a proxy for direct monitoring of the air. Since precipitation at very high elevations (above 5800m a.s.l.) in this region falls as snow only, we find a very good record of seasonal mercury deposition. In order to assume that snow is a good proxy for atmospheric concentrations we need to assume that the mechanism of deposition is the same season to season. This appears not

to be the case, and in fact the concentrations found in the snow pits likely vary as a result of mechanistic changes rather than atmospheric concentration changes, though this is not clear as concurrent atmospheric measurements would need to be taken.

3.1   Passive air sampling

Passive air sampling is a novel technique of monitoring air concentrations of various chemicals. Detailed information on passive sampling can be found in Papers I and II. In brief, a porous polystyrene resin (XAD-2 mesh size 20/60) is pre-cleaned with sequential extraction with acetone and dichloromethane. It is placed in a stainless steel tube and then placed in a galvanized steel enclosure. The XAD-2 based sampler that we used in our experiments is based a design that relies on a large capacity for organic chemicals and chemical concentrations on the sampler surface never approach equilibrium with the atmospheric concentrations. As such the sampler uptake rate is linear and driven by molecular diffusion and the design of the sampler (see Paper II and reference *4*).

In retrospect passive air sampling was an ideal monitoring technique for studying air mass movements on timescales relating to the length of the monsoon and continental westerly influences in the Himalayan region. The sampling rate of $0.52m^3$/day was adequate for monitoring concentrations of chlorinated pesticides found in the region at all altitudes well above the detection limit. However, for industrial contaminants which are found in lesser concentration in the region, higher flow rates would have improved detection limits for these novel compounds. Furthermore problems associated with uncertainties in uptake rate due to wind speed effects and diffusion rate differences

caused by changes in temperature and pressure over the altitudinal transect gave some uncertainty to atmospheric concentrations of POPs (see Paper II). An uncertainty in uptake rate of the PAS is disconcerting and an alternative design should be used when further investigating atmospheric chemical concentrations over an altitudinal transect.

Use of another type of sampler, as described by Schoieb and Harner, may have rectified this problem (8). It is designed to have less capacity and hence will not operate in the linear uptake phase of the sampler. Mass labeled compounds are pre-spiked onto the polyurethane foam (PUF) disc before deployment in the field and their depuration is monitored in the laboratory as loss from the PUF. By knowing the level of depuration of chemicals from the PUF we can better understand the uptake rate which varies according to the K_{OA} of each chemical.

4   Contribution of the Author

This project took shape from my experiences traveling in the Himalaya through the 1990s and my experience in the field of POPs in remote regions. My hypothesis stemmed from observations made by Blais et al. (1). Much of the analytical work for this paper was done at the Freshwater Institute where I worked on my Master in Science degree in the early 1990s. I thought that the southerly flow of the Indian monsoon would move pesticides which are in heavy usage in the Indian subcontinent into the Himalaya. In 2002 I approached Dr. Derek Muir from Environment Canada about working on a PhD relating to POPs in the Himalaya. Although no funding materialized initially, I managed to convince Dr. Gregg Tomy and Dr. Feiyue Wang at the Freshwater Institute and

University of Manitoba, respectively, to take me on as a graduate student. As such I also picked up on the mercury side of the project. As mercury does elicit some of the same environmental fate characteristics as POPs we hypothesized that mercury may show some of the same concentrations gradients in mountains.

A major breakthrough in moving this project forward was the relationship formed with Kathmandu University most notably with Dr. Subodh Sharma. Dr. Sharma is a very dedicated scientist and has had many international collaborators. I started my PhD in September 2003 and with a small amount of funding from Drs. Tomy's and Wang's grants, I made my way to Nepal in December 2003 with some sampling equipment for both mercury and POPs. I met with Dr. Sharma and on his authority I set up PAS and collected water samples on a transect on the Mt. Everest trek in Solo Khumbu. This site was chosen because of the facilities in the region that are set up for tourists going to see the world's largest mountain. It allowed me to deploy the world's largest altitudinal transect using PAS. This work could not have taken place without the hard work of three porters I hired in Lukla.

I also attended at the time the first environmental conference on the Great Himalaya where I presented a paper on my hypothesis. Italian researchers had worked on this hypothesis in the 1990's but no conclusive evidence was found (See Paper I). It was during the conference when I was asked by one of the conference organizers to write a paper for as special Himalayan issue for the Aquatic Ecosystem and Health Management

Society. It was a review article on the state of knowledge of contaminants in the Himalaya and is the first article in my thesis (Paper I).

I returned to this sampling transect 3 more times, in October 2004, April 2005 and November 2005 to get samples coinciding with the seasonal air mass movement in the region. I added samples in the Asi Khola watershed near Kathmandu University and also in Chitwan National park in the Inner Terai at low elevation near to India. Sampling logistics during this time were complicated by the Nepal civil war which had been going on now for 10 years but had started affecting the Kathmandu Valley during the course of the project. The latest news is that the King of Nepal will now permanently step down after elections in the spring of 2008. I do sincerely hope that Nepal will come to a time of lasting peace and security. This work is the subject of Paper III.

In January of 2005, Dr. Wang started a sabbatical research leave in China. During this time he came to know of an expedition to Mt. Qomolangma (also known as Mt. Everest) for scientific sampling led by Dr. Shichang Kang from the Institute for Tibetan Plateau Research of the Chinese Academy of Sciences. Miraculously Dr. Kang managed to get me on the expedition as the only foreign scientist. This involved dodging a road blockade from Kathmandu to the border town of Kodari on the Chinese border with boxes of sampling equipment. I was picked up by PhD student and friend Zhiyuan Cong and driver Mr. Lee, who took us to Mt. Qomolangma base camp. After a bout with high altitude pulmonary edema at base camp and recovery, we made our way over the span of 3 weeks to a site at the glacier accumulation zone of East Rongbu glacier over 6500m

a.s.l. where a snow pit was dug and samples retrieved. Subsequently samples were retrieved at Mt. Nyainqetanghla and Mt. Geladaingdong by PhD student and friend, Qianggong Zhang in a similar fashion. These samples helped support a paper which is the subject of Paper IV.

Although much of the field preparation was done by me, most of the analysis was conducted by Ms. Debbie Armstrong (mercury, UCTEL) and Mr. Colin Fuchs (POPs, Freshwater Institute). I am in deep gratitude to these two friends and this work could not have been carried out without their good works.

Paper II is the result of some preliminary work using PAS to monitor perfluorinated alkyl substances (PFAS). This paper has now been accepted and is in press by the journal, Environmental Science and Technology. It is related to this thesis, in that an in depth critique of the PAS performance over altitude is carried out. Although it was my intent to look at the fate of PFAS in air and water over an altitudinal transect in Western Canada, it was the idea of Dr. Frank Wania to incorporate this critique and in doing so made a valuable contribution to the thesis. He also assisted with manuscript development for Papers I, II and III.

In short, I was the first author for all the papers in this thesis. I was responsible for or led the study design, field work, data interpretation and writing the manuscripts. Other co-authors on the papers assisted, to various degrees, in the field work, laboratory analysis,

and data interpretation. I have contacted all the co-authors and they all support me to include these papers in my thesis

5   Future Direction

With any luck I will be heading back to the Himalayan, Tibetan Plateau region in the spring of 2008. At that time I will retrieve PAS deployed on an east-west transect just north of the Himalaya range in the Tibetan Plateau. I further intend to start a Trans Himalayan transect using PAS in the Solo Khumbu region as well as the Tibetan Plateau during the monsoon. A Trans-Himalayan transect would finally conclude the way in which the Indian subcontinent and Tibetan Plateau are linked atmospherically with respect to movement of contaminants when the air mass originates from the Indian subcontinent. Larger numbers of samplers surrounding the 5000m a.s.l elevation coupled with humidity measurements would allow for greater certainty of the boundary layer effect hypothesized in this thesis. Further study of high altitude forested regions of the Himalaya, especially those coinciding with heavier monsoon precipitation such as the eastern Himalaya and eastern Tibet may be useful from a human health perspective. Soil concentrations in high altitude forests appear to be higher than expected. Also investigation of orographic uplifting of the wintertime air mass in the Western Himalaya may prove interesting as this region experiences much snowfall.

Further to mercury investigation, atmospheric monitoring for gaseous elemental mercury (GEM), reactive gaseous mercury (RGM) and atmospheric particulate mercury at the Nam Co station in Tibet would be beneficial to understand how these 3 species of

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mercury are interlinked in this environment above the boundary layer. Further, looking at the role and source of oxidizing radicals in the atmospheric environment would be very interesting in understanding the global fate of mercury. Study of the effect of the marine boundary layer and potential for higher atmospheric halogen concentrations during the monsoon on mercury deposition in the Indian subcontinent may further show why such low concentrations of mercury were found at high elevation during the summer.

6   Conclusion

These studies offer some of the first insights into chemical fate in the Himalaya and Tibetan Plateau. The results are interesting and not entirely surprising. It proves that the study of environmental processes and mechanisms of chemical transport and fate are very worthy areas of study. By understanding environmental processes we can gain insight into regions of potential contaminant enrichment.

The very highest mountains in the Himalaya above the boundary layer appear to be protected from chemical contamination by semi-volatile organic chemicals. Chemicals with very long atmospheric lifetimes such as mercury and HCB do move into the upper troposphere and may have some impact at higher elevation. This should be further studied so as to fully understand the effect of the boundary layer and how it is effecting chemical deposition. Further monitoring the 2000-5000m a.s.l. range is warranted to ascertain the long term trends of atmospheric transport and deposition of semi-volatile chemicals. Other than current use areas, the high altitude forest had the highest concentrations of POPs. The eastern Himalaya region experiences greater precipitation

and a higher elevation of forestation. These factors may be facilitating the deposition of toxic chemicals in this region and as such, should be investigated further. Of course not to be overlooked are the areas that showed extremely high POPs concentrations, agricultural and malaria prone areas. Unfortunately, very little funding is available to study the impacts of heavy chemical usage in developing countries.

As chemical usage in Asia is of a global concern we propose the continuation of this air transect. Governments, academic institutions, farmers and industry in Asia need to work together to try to lessen the usage of pesticides and curb industrial emissions in Asia.

7   Acknowledgements

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I

Persistent organic pollutants and mercury in the Himalaya

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Persistent organic pollutants and mercury are important contaminants due to their persistence in the environment and potential toxic effects on ecosystems and humans. Concerns related to these contaminants are particularly pertinent in Asia where the use of pesticides and mercury emissions have been increasing dramatically due to changing agricultural practices and rapidly expanding industrialization. Based on studies in European and North American mountain regions, evidence is increasing that alpine regions function as regional convergence zones for selected organic pollutants due to an effect called orographic cold trapping. It is hypothesized that such an effect may be particularly pronounced in the Himalaya because of dramatic elevational temperature and precipitation gradients relative to contaminant source regions in its immediate vicinity, and because of the regional monsoon system that has been shown to deliver particles and inorganic air pollutants to higher altitudes. A review of studies of persistent organic pollutants and mercury in the Himalayan ecosystem reveals that measurements of these contaminants are sparse and rarely adhere to strict quality control procedures, making it difficult to judge whether relatively high concentrations reported for these materials are indeed an indication of efficient transfer of toxic contaminants to Himalayan ecosystems. Knowledge gaps are identified and suggestions are made for research that would allow for the testing of the hypothesis that the Himalaya is an important cold trap for semi-volatile organic contaminants and mercury.

Keywords: Nepal, India, China, Asia, precipitation, monsoon

Introduction

The Himalaya is a vast mountain system consisting of a series of parallel and converging ranges that cover an area of roughly 6×10^5 km². It stretches from the Indus River in northern Pakistan eastward across Jammu and Kashmir, down into northern India, across parts of southern Tibet and over most of Nepal (Figure 1). Mount Everest (8848 m above sea level (asl)) represents the highest peak in the Himalayan Mountains and in the world. Mountain regions have traditionally been considered pristine environments. High altitudes above 3000 m in the Himalaya are largely unpopulated by people. The lack of human habitation and agricultural impact above these elevations, except during the summer seasons when high alpine pastures are used for grazing, has given rise to the thought that this mountain region is largely free of pollution. However, volatile and semi-volatile toxic contaminants such as certain pesticides and mercury do not heed the boundaries of human habitation.

Selected persistent organic pollutants (POPs) and mercury are known to undergo efficient atmospheric transport, often over considerable distances to very
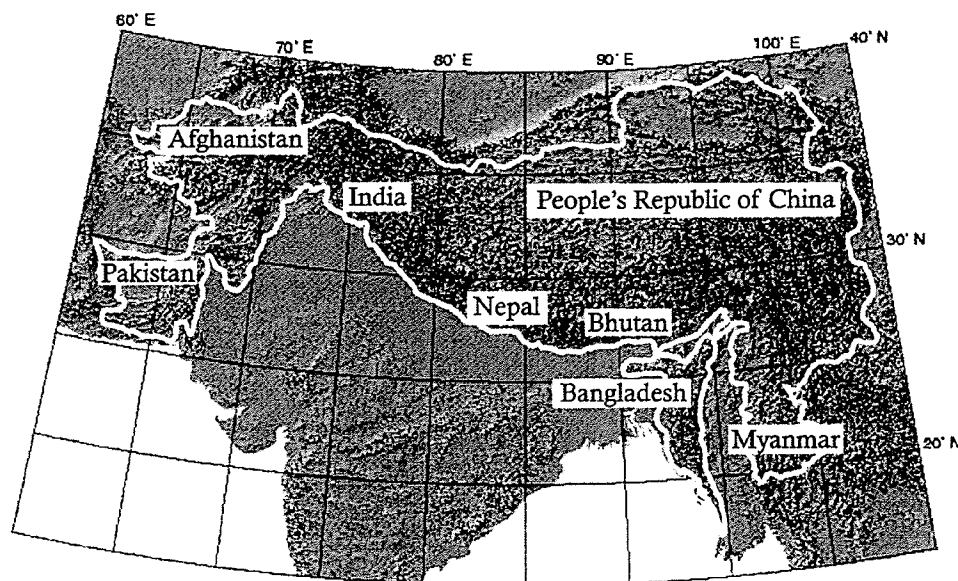
Figure 1. Himalaya, Hindu Kush Mountain Range. Scale: 1:20 million Albers equal-area projection, USGS Digital Elevation model of the world GTOPO30.

remote locations. While contaminants with very low vapour pressures such as highly chlorinated dioxins and furans will not be subject to vapour phase atmospheric transport, highly volatile contaminants such as chlorofluorocarbons typically remain in the atmosphere and do not deposit. For contaminants of intermediate or semi-volatility, vapour pressures are such that they may volatilize in regions of use where it is relatively warmer, become transported in the atmosphere, and deposit in colder climates. In Nepal, over a distance of not more than a few hundred kms one can find a variation in altitude of almost 9000 m, with a corresponding extreme gradient of temperature. Consequently, it is a valid concern to wonder whether the Himalaya may be acting as a cold trap for airborne semi-volatile contaminants. This phenomenon is exacerbated by highly populated and rapidly industrializing countries surrounding the Himalaya, which exhibit high levels of pesticide usage and polluting industries. Melting snow and glaciers in the Himalaya supply the water for perhaps as much as one sixth of the world's population. Although water contamination is of concern, it is typically not the major route of human exposure for these contaminants. Rather, once deposited to aquatic and terrestrial ecosystems, lipophilic POPs and the methylated form of mercury bioaccumulate and biomagnify in food chains contributing to the body burden of contaminants in both animals and humans.

It is imperative that the hypothesis of the Himalaya as a convergence zone of POPs and mercury is tested through field studies. It is the intention of this review to outline briefly the current understanding of contaminant deposition in alpine regions, and specifically to assess the current knowledge and highlight the gaps in knowledge in the Himalayan region. Processes of atmospheric transport and deposition of toxic chemicals are only discussed as they relate to this topic.

Mountains as regional contaminant convergence zones

Persistent organic pollutants

Evidence is emerging that mountain regions sometimes have higher-than-expected concentrations and deposition rates of selected POPs (Wania, 1999). Earliest indications for this phenomenon came from a global survey of contaminants in vegetation, which reported the highest levels of hexachlorobenzene (HCB) in low latitudes in sites at high elevation (Calamari et al., 1991). Elevated levels of organochlorinated compounds were also reported in fish and sediments from the Canadian Rocky Mountains (Donald et al., 1993, 1998). Indeed, toxaphene levels in fish were found to increase with altitude (Donald et al., 1998). Several studies in European mountain regions (Weiss et al., 1998, 2000; Carrera et al., 2001, 2002; Grimalt et al., 2001; Vilanova et al., 2001a,b,c) and in the American Sierra Nevada (Datta et al., 1999) suggest that this is a ubiquitous phenomenon. When measuring along an altitudinal profile in the Austrian Alps, Weiss et al. (1998) found that the site at the highest altitude showed higher

concentrations of nearly all the analyzed substances in spruce needles and in the humus layer compared to the sites at lower altitude. These studies indicate that mountain regions may function as regional convergence zones for POPs (Daly and Wania, 2005).

Specifically, the relative enrichment of POPs in high mountains suggests that a cold condensation effect, similar to that occurring on a global scale (Wania and Mackay, 1993), may also be operating on an altitudinal scale (Grimalt et al., 2001, Davidson et al., 2003). The effect, which refers to the process of POPs being volatilized from warmer source regions, transported through the atmosphere, and 'condensing' in colder regions, is well known on the latitudinal scale (Wania, 1999), resulting in the long-range transport of POPs to polar regions (Muir et al., 1990, 1996). Indeed, the chemical transfer efficiency from valley to mountain may be higher than that from tropical to polar regions, simply because of the closer spatial proximity of mountain regions to source regions. Also, similar to the Arctic and Antarctic, the retentive capacity of the terrestrial systems at high altitudes tends to be low because of sparse soil and vegetation cover, as well as steep slopes - potentially focusing contaminants further into mountain lakes (Blais et al., 2001a,b; Vilanova et al., 2001a,b,c). An additional factor is the high rate of precipitation in many mountain regions, often in the form of snow, which may provide a powerful pump for removing contaminants from the atmosphere to the surface (Blais et al., 1998). Orographic effects often result in precipitation rates at high altitudes that are many times higher than in neighbouring lowlands. Snow is believed to be a very efficient scavenger of both particles and non-polar organic compounds, capable of effectively cleansing the atmosphere (Franz and Eisenreich, 1998, Wania et al., 1999).

Mercury

Like POPs, elemental mercury is semi-volatile (the vapour pressure of the elemental form is 0.167 Pa at 25°C) and is thus expected to exhibit similar patterns of atmospheric transport to alpine regions. Atmospheric mercury is very stable and has a mean global troposphere residence time of about 6 to 8 mo (Schroeder et al., 1998). Therefore, elemental mercury distribution on the planet is governed by regional as well as global air movement patterns. Studies conducted in the Canadian Arctic have reported high levels of mercury in various aquatic species (Lockhart et al., in press). Work in the Wasatch and Teton ranges of the continental United States of America (U.S.) indicated annual

mercury deposition rates increase by a factor of 1.75 with an elevation gain of 1000 m (Susong et al., 1999). Vertical distribution of elemental mercury in the atmosphere above Canada indicates a uniform concentration of between 1.5 and 1.7 ng m^{-3} up to an altitude of 7 km (Banic et al., 2003). This indicates that mercury has the capacity to move into mountain environments up to very high altitudes. Schuster et al. (2002) also described the temporal trends of deposition of total mercury in glaciers of the continental U.S. The results indicated that regional trends in mercury deposition have dramatically increased in the U.S. since the 1950s until its peak in the 1990s, coinciding with accelerated growth in industrialization. Subsequent environmental regulation in the U.S. during the 1980s has resulted in a decline in mercury deposition. This indicates that a similar reduction in atmospheric mercury emissions in Asia will have a positive impact on mercury deposition trends.

While snow deposited Hg(II) can be photoreduced to Hg(0) and reemitted back into the atmosphere (Lalonde et al., 2002), it is largely unknown how precipitation leads to terrestrial and aquatic deposition of the various species of mercury in mountains. Methylmercury, the biologically active and toxic form of mercury can be formed biotically and, to a lesser degree abiotically (Fitzgerald et al., 1991). Of particular concern is the atmospheric deposition of mercury in aquatic ecosystems and its subsequent biotic methylation by certain bacteria (e.g., sulphate reducing bacteria) in typically nutrient and sulphate rich waters (Compeau and Bartha 1985; Gilmour et al., 1992; Benoit et al., 2003).

In brief, the potential convergence effect of POPs and mercury in mountain regions raises serious and timely concerns, among which are their impact on: the local ecosystem, in particular high altitude lakes (Schindler, 1999; Blais et al., 2001a,b); human populations relying on animals grazing at high altitude and consuming fish from high altitude waters, and water supplies derived from snow (Schindler, 1999).

Potential sources of chemical contamination in the Himalaya

Sources for persistent organic pollutants contamination

The Himalaya is wedged in between India and China, the two most populous countries in the world. High population density often results in high usage of

pesticides and high emissions of air pollutants. In the past, the Indian subcontinent and China have experienced heavy use of organochlorine pesticides, such as hexachlorocyclohexanes (HCHs) and DDT, for agricultural purposes. It has been estimated that since its initial formulation, more than 10^8 kg of DDT have been used in India (Sharma, 1993; Santillo et al., 1997). India banned DDT for agricultural purposes in 1989, but continues to use between 5000 and 10,000 kg y^{-1} for malaria control (Santillo et al., 1997). Technical HCH, once the most heavily used pesticide in India with annual consumption exceeding 6×10^7 kg, was banned in 1997, but lindane (γ-HCH) has been used as a replacement since that time (Santillo et al., 1997). From the 1950s until its ban in 1983, China produced and used 4×10^8 kg of DDT as well as 4.9×10^9 kg of technical HCH. Lindane and DDT are still being used in lower amounts to control certain insects (UNEP Regional Report, 2002). Although these extremely persistent chemicals have seen a decrease in usage, they will likely persist in the environment and possibly impact the Himalayan mountain ecosystems for years to come.

People that inhabit the Himalaya and surrounding areas generally rely on snowmelt and glacier fed rivers and streams for potable water. During the melting months, semi-volatile POPs 'trapped' in glaciers and snow are expected to be released into surface waters. In the Canadian Rockies, melting glaciers have been shown to be a major source of semi-volatile POPs to sub-alpine lakes (Blais et al., 2001a,b). Animals grazing on high altitude pastures in the Himalaya are likely exposed to POPs. As the milk and meat from these animals are important food sources, people living at high altitude may be exposed to these contaminants.

Sources for mercury contamination

The magnitude of mercury emissions to both water and atmosphere on the Indian subcontinent and in China are alarming. The mean atmospheric concentration of elemental mercury measured in Okinawa Japan, which is located in the path of the westerly Asian outflow is significantly higher than the global background (Jaffe et al., 2005). Pacyna and Pacyna (2001) estimated that approximately 2.2×10^6 kg y^{-1} of mercury were released globally from anthropogenic sources to the atmosphere in the mid 1990s (for comparison, a similar amount of mercury was released from natural sources), half of which was attributed to Asia. Fossil fuel combustion in stationary sources was the single largest anthropogenic source of mercury, emitting almost 1.5×10^6 kg y^{-1} of mercury globally, 1/3 of

which was attributed to China (4.95×10^5 kg y^{-1}), with another 8% from India (1.17×10^5 kg y^{-1}). The mercury discharge to the atmosphere from these sources in China and India is likely increasing, as coal consumption in China had been increasing at a rate of approximately 5% per year from 1978 to 1995. The second largest global anthropogenic source of mercury to the atmosphere is gold and silver mining (Pacyna and Pacyna, 2001). China appears to be second only to the Brazilian Amazon in terms of mercury emission from amalgamation mining, releasing more than 1.0×10^5 kg y^{-1} of mercury (Lacerda, 1997). Other anthropogenic sources of mercury emissions are chloralkali production, non-ferrous metal production, cement production, waste disposal, and iron and steel industries (Pacyna and Pacyna, 2001) although their contribution to the mercury deposition in the Himalaya is unknown.

Even less understood are the sources of methylmercury in the Himalaya. It is generally thought that the majority of the methylmercury in low altitude environments is not from external sources (such as atmospheric transport of methylmercury); instead it is produced by the in situ methylation of inorganic mercury (Fitzgerald et al., 1991). Whether this is the case in high-altitude areas like the Himalaya remains unknown.

Precipitation and wind direction in the Himalaya

The Himalaya and surrounding lowlands are linked by distinct weather patterns, showing a strong seasonal variability. The transport, fate and effects of POPs and mercury in the Himalaya are expected to be influenced by this unique climatological and meteorological system. There are two distinct tropical monsoon systems that operate in the region: the Southwest or summer monsoon (June–September) and the Northeast or winter monsoon (December–April). Heating over the Indian subcontinent and Tibetan Plateau increases in the early summer months causing a low pressure region to develop over the land. The comparatively cool humid air from the southern hemisphere crosses the equator and is accelerated towards the low-pressure area over the continent. This causes the airmass over India to be driven into the mountain ranges in the northern part of the subcontinent and eventually into the Himalaya which normally results in significant precipitation events. In winter the continent cools off and high surface pressure drives the wind in the opposite direction. While most of southern and eastern Asia is under the influence of this winter monsoon pattern,

Table 1. Orographic increase in precipitation in the Himalaya (mm 100 m^{-1}) (from Bahadur, 1997).

| Region	Annual	Summer (May–Sept)	Winter (Oct–Apr)
Jammu and Kashmir	−37	−30	−7
Punjab and Himachal Pradesh	72	3	69
Himachal Pradesh	−13	−60	47
Uttaranchal	41	35	6
Eastern Nepal	−87	—	—
Sikkim	−33	−32	−1

the Himalaya is dominated by prevailing continental westerlies especially in its more north westerly reaches (Pant and Rupa Kumar, 1997).

The seasonal change in wind direction is often combined with variable precipitation patterns. The southern face of the Himalaya, with multiple mountain ranges, exhibits precipitation variation, which is very complex and at present very poorly monitored. The northern slope of the Himalaya, in the rain shadow of the mountains, receives very little precipitation during the summer. Precipitation in the Himalaya is generally concentrated in the summer months, except in the Western

Himalaya where summer precipitation is low and winter snowfall can be as high as 15 m (Pant and Rupa Kumar, 1997). Table 1 delineates orographic effects on precipitation as well as seasonal and longitudinal trends based on precipitation data collected at Indian and Nepalese weather stations (Figure 2). For instance, in Eastern Nepal there is a dramatic decrease in precipitation at high elevation as most of the precipitation 'rains out' in the more southerly lower altitude ranges where the Siwalik Hills, the Mahabarat Range and Middle Mountain ranges in effect cause a rain shadow on the Eastern Himalaya. Conversely, there are orographic increases in precipitation in Uttaranchal during the summer and even stronger trends in orographic precipitation in the form of snow further west in India during the winter (Bahadur, 1997). The distinct seasonal differences in the wind direction as well as regional and orographic trends in precipitation likely play a major role in atmospheric pollutant transport and deposition.

Effect of seasonal weather patterns on deposition of chemicals in Asia

The effect of the monsoon on air pollution in the Himalaya has been documented for aerosols and inorganic
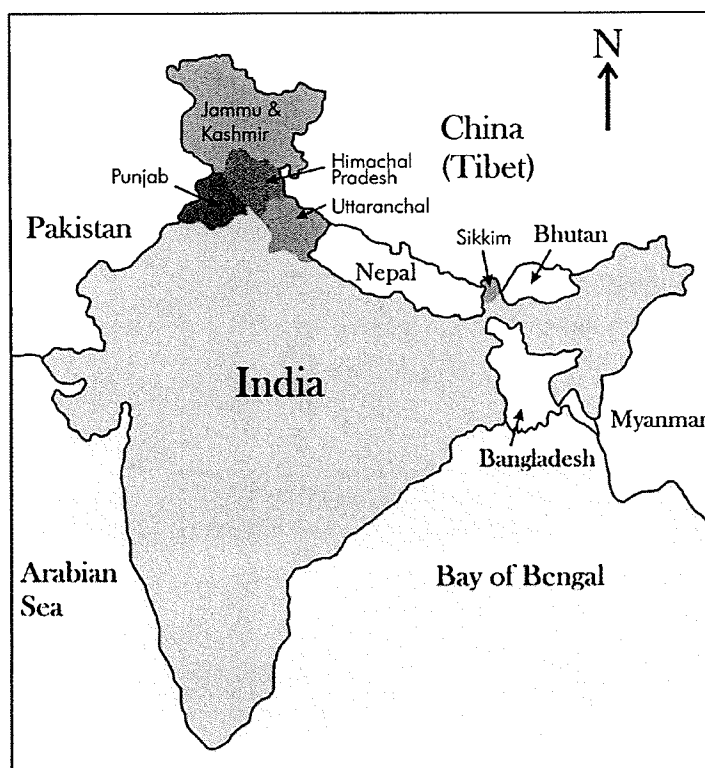
Figure 2. Political map of India.

contaminants (Valsecchi et al., 1999; Shrestha et al., 2000, 2002; Shichang et al., 2000; Hindman and Upadhyay, 2002). In a recent study of sulphur deposition in Asia, India was considered responsible for 60% of the atmospheric deposition of sulphur compounds in Nepal primarily occurring during the wet summer monsoon months (Arndt et al., 1998). Studies in the Arabian Sea indicate the potential of the monsoon to influence the transport of POPs in the region. The Arabian Sea is influenced by air mass transport from the Indian subcontinent during the NE monsoon and air flow from Arabia and Western Africa during the SW monsoon. Such influence of different air masses is evidenced by the occurrence of higher concentrations of DDT, polychlorinated biphenyls (PCBs), and pyrolytic polyaromatic hydrocarbons (PAHs) during the NE monsoon and of fossil hydrocarbons during the SW monsoon (Dachs et al., 1999). Because less volatile PAHs are often bound to particulate matter, the increasing concentration of airborne particulate material in Asia (Asian Brown Cloud) may further contribute to the transport of these chemicals (Ramanathan et al., 2001).

Field studies of persistent organic pollutants in the Himalaya

Northern Slope, Tibetan Plateau

In May and June 2002, Zhu et al. (2004) from Peking University recovered air samples at Dingri (28.655°N, 87.115°E 4340 m asl) and Rongbu Valley (28.193°N, 86.827°E 5050 m asl) near Mt. Everest in Tibet using an active polyurethane foam (PUF) medium with an Anderson active air sampler. After Soxhlet extraction of PUF and fractionation, the organochlorine pesticides in the extracts were analyzed with large volume injection and ion-trap MS-MS analytical technique. Results indicated that concentrations of DDT and its metabolites were three to five times higher than those found in the Canadian Arctic atmosphere while HCH congeners were found to be ten to sixty times lower. The latter result is somewhat surprising considering that the Himalaya is much closer to the major HCH source regions in Asia than the Canadian North. At the time of sampling, air trajectories originated predominantly from India and Nepal. When the air mass originated in North Africa, atmospheric concentrations of these chemicals were reduced. Preliminary analysis of ice cores also sampled in that region indicated strong seasonal variation, with maximum concentrations of DDT

found in snow deposited in the summers from 1978 to 1983. This may indicate that the Indian Subcontinent is the most important source region for airborne DDT to the high Himalaya. The lower deposition of POPs during winter when air masses originate in the north and west questions the contribution of China as a major source of atmospherically deposited POPs in this region of the Himalaya. This should be further investigated by assessing atmospheric concentrations of POPs in various regions of the Himalaya throughout the year coupled with back trajectory analysis of the related air mass.

Southern Slope, Mt. Everest Region, Solo Khumbu Nepal and Uttarnachal, India

There are a few field studies reporting on PCBs, DDT, and HCHs on the Southern slope of the Himalaya (Galassi et al., 1997; Dua et al., 1998; Sarkar et al., 2003). Surprisingly, all of them chose to sample and analyse water samples, although it is known that this is very difficult, and very large sample volumes, possibly several hundred litres, are required for reliable quantification of these sparingly soluble compounds in remote waters. Unfortunately, quality control procedures were not performed in any of these studies; in some cases, the analytical methods themselves are not known. Therefore, the reported results must be treated with extreme caution. Some results are clearly suspect, and in others the authors cannot explain the high levels without considering the possibility of illegal DDT usage. As some of the reported concentrations are remarkably high, it would be worthwhile to check whether they are the result of sample contamination in the laboratory or if indeed they indicate significant contamination. Such studies would be required to adhere to strict quality control guidelines.

A more promising approach, however, is to avoid the analysis of water samples altogether and focus initially on the analysis of samples that are easier to analyse, namely organisms and sediments. In Solo Khumbu, a lake at 5067 m asl (Galassi et al., 1997) shows trends that favourably reflect cold trapping effects. Both lake sediment and zooplankton PCB profiles indicate enrichment of lower chlorinated congeners with sediment samples showing increasing total PCB trends with time. Another study analyzing DDT and HCH in water and fish from rivers and streams in Uttaranchal indicated significant contamination and require further study using certified laboratory techniques (Sarkar et al., 2003).

Field studies of trace metals in the Himalaya

Studies of altitudinal transects of trace elements in the Himalaya are very limited. Lichens were employed as passive monitors for a variety of trace elements in Solo Khumbu in Nepal (Bergamaschi et al., 2002). The general trend showed decreases in concentration from 1350 m asl to 3800 m asl followed by an increase up to 5090 m asl. As many of these trace elements may be associated with very fine aerosols, it is believed that they may be transported long distances and may settle in high altitude regions, although it is not clear as to why they may become enriched at the highest altitudes.

A recent study (Subramanian et al., 2003) showed that the mercury concentration in suspended particulate matter (SPM) from the headwaters of the Yamuna River in the Himalaya can be as high as 25.2 mg kg^{-1} (mean, 1.82 mg kg^{-1}), potentially due to the industrial midstream and agricultural downstream terrain near its confluence with the Ganges. Of particular concern is that the mercury in sediments at these highly contaminated sites is bound predominately to 'mobile phases' (e.g., exchangeable Hg and those bound to carbonates, iron oxides, and organic fractions) instead of in the 'residual phase,' suggesting their high mobility in the environment. Sediment core analysis further demonstrated that the peaks of mercury in the sediments are in direct proportion to the increase in various types of human activities such as thermal power plants, land use changes in the midstream region and intensive fertiliser application in lower reaches of this vast river basin. A similar type of trend might also exist in other aquatic systems in the Himalaya region. It should be noted that Subramanian et al. (2003) did not appear to have used clean techniques for collecting water and SPM. As is always the case with ultra-trace analysis, and in particular for mercury, cross contamination of the samples cannot be ruled out unless samples are collected following clean sampling techniques and the sample preparation and analysis are performed in a certified clean room.

Suggestions for studying atmospheric transport and deposition of persistent organic pollutants in the Himalaya

Air concentration measurements

Delivery of POPs to upland terrestrial and aquatic ecosystems, where they may bioaccumulate and pose risks to humans and other top predators, occurs usually through the atmosphere. It is thus of considerable importance to understand the spatial variability of atmospheric POP concentrations along elevational gradients. Nevertheless, even the most extensive atmospheric monitoring campaigns for POPs tend to be restricted to a fairly small number of sites and the real spatial variability of POP concentrations in the atmosphere remains largely elusive. This is due to the complexity and expense of sampling trace amounts of POPs from the atmosphere using high volume pumps, which currently constitute the state of the art of measuring POPs in the atmosphere. The logistical complexity and cost is magnified when working at high altitudes, although Zhu et al. (2004) have shown the feasibility of performing traditional high volume air sampling under extreme conditions. Plant foliage and tree bark have been used for the monitoring of POPs in the atmosphere (Muir et al., 1993; Kylin et al., 1994). Leaves and needles have a relatively large surface area and their waxy cuticle has a high affinity for many organic pollutants. However, uptake capacity and kinetics vary with species, location, age and season, greatly limiting their potential applications.

Passive air sampling may provide a simple and inexpensive alternative to recording air concentrations of POPs in mountain environments. A passive air sampler (PAS) is a device that collects chemicals from the atmosphere without the help of a pump. In contrast to plants, man-made PAS first have to be deployed, but uniform construction facilitates comparability between different locations and time periods. Whereas such samplers have been routinely employed for the assessment of the workplace exposure of individuals and for the ambient monitoring of a variety of trace gases, PASs are only recently being employed for the ambient monitoring of POPs (Ockenden et al., 1998a,b, 2001; Lohmann et al., 2001; Shoeib and Harner, 2002; Wennrich et al., 2002; Shen et al., 2004; Wilford et al., 2004). Neither electricity nor highly qualified personnel are required for routine operation, making PAS the method of choice in remote locations such as mountains which are only accessible with difficulty and high expense and which may lack a power supply. They thus seem to be ideal for monitoring POPs in developing countries and in remote inaccessible regions such as mountains (Wania et al., 2003). Using an appropriate passive sampler design will minimize uptake rate changes due to differences in wind speed which may be significant over large elevation differences. As temperature differences may be vast, temperature

monitoring at each site would aid in assessing the diffusion rate of chemicals onto the sampler.

Soil inventories

Soil has been shown to contain the bulk of the PCB inventory in terrestrial ecosystems (Harrad et al., 1994). Since atmospheric deposition is the only plausible source of POPs in most regions, the inventory in soil is a measure of the historical atmospheric deposition. For the less volatile and highly persistent compounds, the soil inventory is a good absolute measure, whereas for the more volatile POPs it is only a relative measure of deposition since these compounds are also subject to revolatilization (Mamontov et al., 2000). A recent survey by the authors south of Mt. Everest found reasonable soil cover up to 5400 m asl with a carbon content of 3.5% and up to 10.2% at an elevation of 3800 m asl. A similar survey throughout the southern face of the Himalaya by the authors indicated the frequent presence of relatively flat alpine meadows with reasonable soil cover albeit at somewhat lower elevations into Pakistan. Sampling of soil for the assessment of POP deposition should thus be possible, even at fairly high elevations.

However, as much of the Himalaya is covered by steep bedrock poor in organic matter, much of the POPs may rather be found in high altitude lakes and rivers. A survey of POP concentrations in water and sediment from alpine lakes and rivers may also be necessary to fully discern the environmental fate of deposited POPs.

Butter, milk and animal fat

POPs are lipophilic compounds and tend to accumulate in lipid rich materials. Since levels in the fat tissue or milk of grazing animals from remote areas are largely governed by atmospheric deposition and feed consumption, contaminant concentrations in locally produced butter should reflect the extent of atmospheric contaminant deposition (Kalantzi et al., 2001). A study of the global distribution of several POPs using butter has shown that while PCBs occurred at lower concentration in Indian butter compared to that from industrialized regions, DDT and HCH-related substances exhibited the highest concentrations in the world. The concentration of the sum of DDT and its metabolites in Indian butter was 248 ng g^{-1} while that of the HCH isomers was 222 ng g^{-1} (Kalantzi et al., 2001). While these Indian butter samples were likely from agricultural regions with current or recent pesticide usage, a study of POP concentrations in butter, milk or animal fat pro-

duced locally at different elevations on the southern slope of the Himalaya, would give useful information on the extent of contaminant transfer to higher altitudes. In addition to being an indicator of atmospheric deposition, such samples would also allow a first assessment of human exposure, which is often dominated by the uptake of animal lipids.

Suggestions for studying atmospheric transport and deposition of mercury in the Himalaya

Air and water concentration measurements

Since mercury is largely transported in the atmosphere as the elemental species and deposited as the ionic water soluble species, air and water are the two environmental compartments which are likely candidates for determination of atmospheric transport and deposition. Using the appropriate ultra clean sampling techniques and laboratory facilities, water concentrations may be evaluated using cold vapour fluorescence spectroscopy. Concurrent assessment of elemental atmospheric mercury concentrations may be accomplished by drawing air through a quartz tube filled with gold coated sand. This will yield information about atmospheric mercury concentrations at a given time. As mercury concentrations will fluctuate it is important to continue monitoring using this active air sampling technique or use a costly automated atmospheric mercury monitor. At present no calibrated long term passive mercury air samplers have been developed. This technology would certainly assist in monitoring average atmospheric mercury concentrations.

Conclusions

Despite the paucity of data, there is some evidence of long-range transport and deposition of POPs and mercury in the Himalaya. The historic and current high usage of pesticides and emission of mercury may be having effects on the Himalayan ecosystem. The relationship between contaminant deposition with altitude, season, amounts of precipitation, proximity to oceans and sources of contaminants should be explored in depth. Some work on this issue has recently begun; POPs in high altitude lakes and the atmospheric transport and deposition of selected metals are being studied in Nepal (Italian National Research Council/ Royal Nepal Academy of Science and Technology) and

airborne POPs are being investigated in high elevation regions of Tibet (Peking University). Further studies on organic contamination should include reference to certified reference materials, surrogate recoveries and minimum detection limits to validate the laboratory results. Mercury measurements should be conducted in clean room facilities and reference should be made regarding sample handling techniques. Ideally these lab facilities should be made available in the Himalayan region. The increasing levels of contamination as a result of rapid industrialization in Asia should be taken very seriously.

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II

ALTITUDINAL TRANSECT OF ATMOSPHERIC AND AQUEOUS FLUORINATED ORGANIC COMPOUNDS IN WESTERN CANADA

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Abstract. Neutral perfluorinated alkyl substances (PFASs), which are thought to be volatile precursors of environmentally ubiquitous perfluorocarboxylates (PFCAs) and perfluorooctane-sulfonate (PFOS), were quantified in XAD-2 resin based passive air samples deployed along an altitudinal transect from 800 to 2740 m.a.s.l. in Western Canada (based at N51°20' W117°00') over the spring and summer seasons of 2004. The amounts of fluorotelomer alcohols (FTOHs) and perfluorinated sulfonamido alcohols (FOSEs) sequestered in the samplers increased with altitude, being lowest at an elevation of 1300 m.a.s.l. and highest at either the 2340 m.a.s.l. or 2740 m.a.s.l. site. A variety of potential reasons for these gradients are discussed, including changes in sampler uptake kinetics and phase capacity caused by changes in atmospheric pressure, temperature and wind speed. Vapor phase concentrations were estimated to range from 3.7 to 19 $pg \cdot m^{-3}$ for perfluorinated sulfonamides (FOSAs) and from below detection limits (25 $pg \cdot m^{-3}$) to 88 $pg \cdot m^{-3}$ for FOSEs. Over a similar altitudinal range (800 to 2350 m.a.s.l.), 9L lake water samples were collected in stainless steel cans, extracted with solid phase extraction

columns, and analyzed for PFCAs and PFOS. Aqueous concentrations in lake water, ranging from 0.07 to 1.0 ng·L^{-1} for single PFCAs and from 0.04 to 0.1 ng·L^{-1} for PFOS, were more constant with altitude and were not correlated with the amount of the precursor compounds in the atmosphere. The relative abundance of FTOHs in air and PFCAs in water supports atmospheric FTOH degradation as the source of PFCAs in the mountain lakes.

Introduction

Perfluorinated alkyl substances constitute a diverse class of compounds used in a variety of consumer and industrial applications (*1,2*). The surfactants perfluorooctane sulfonate (PFOS, $C_8F_{17}SO_3^-$) and perfluorooctanoate (PFOA, $C_7F_{15}COO^-$) have received the most attention due to their ubiquitous presence in humans and the environment. PFOS and PFOA have been detected in human serum (*3,4*), freshwater and marine biota (*5,6*), surface water (*6,7*), and rainwater (*8,9*). The stability of PFOS and perfluorinated carboxylic acids (PFCAs) precludes any degradation or metabolism, which contributes to their global dispersion and persistence, and to their bioaccumulation. High water solubility and low Henry's law constant render PFOS and PFCAs susceptible to wet deposition, making it unlikely that they are atmospherically transported long distances in the vapor phase. It has been hypothesized that these chemicals are atmospherically transported as volatile precursors to remote areas where their degradation products are then deposited (*4*). Alternatively, long-range transport of PFCAs and PFOS to remote areas by ocean currents has also been has been hypothesized (*10*).

The estimated global production of fluorotelomer alcohols (FTOHs) is 12·10^6 kg·yr^{-1} 40% of which occurred in North America (*11*). In 2000 the total production volume of perfluorinated sulfonamido alcohols (FOSEs) together with perfluorinated sulfonamides (FOSAs) was 3·10^6 kg

(*12*). FTOHs, FOSAs, and FOSEs are intermediates in the production of polymers used primarily in water resistant coatings (*13*). It is believed that a certain proportion of these intermediates does not undergo polymerization and therefore remains as unwanted residuals in household coatings. Relatively high volatility likely allows the release of intermediates from the coated products and into the environment (*14*). This is supported by higher concentrations of volatile PFASs in urban areas compared to remote locations (*15-17*) and much higher concentrations in indoor air compared to outdoor air (*18-20*).

Snow pack depth in Western Canadian mountains increases with altitude and the flux of contaminants deposited with snow is expected to increase with altitude (*21*). Concentrations of several semivolatile pesticides, such as the hexachlorocyclohexanes (HCHs), in atmospheric and biological samples have been observed to increase with elevation due to orographic cold trapping (*22*). This study was motivated by the concern that neutral PFASs, by virtue of comparable volatility, may behave similarly to such pesticides in the environment. FTOHs are believed to be atmospherically degraded to corresponding PFCAs in the atmosphere (*23*) which may then be deposited to the alpine environment. While FTOHs are more volatile than the HCHs, FOSAs and FOSEs have similar vapor pressures. Both FOSAs and FOSEs have been shown to degrade to form PFOS which may also be a source of PFOS in the alpine environment (*24-25*). In order to gain a better understanding of how PFASs behave over gradients of temperature and precipitation, atmospheric concentrations of 8:2 and 10:2 FTOHs, which are volatile precursors of PFCAs, as well as N-ethylperfluorooctane sulfonamide (N-EtFOSA), perfluorooctane-sulfonamide (PFOSA), N-methylperfluorooctanesulfonamidoethanol (N-MeFOSE) and N-ethylperfluooctanesulfonamidoethanol (N-EtFOSE), which are volatile precursors of PFOS, were measured over an altitudinal transect using passive air samplers. Endosulfan-I and II as well as

α- and γ-HCH were concurrently quantified in those air samples to allow for a direct comparison with substances whose environmental behavior is better understood (*26*). We also examined whether the observed trends in volatile precursor compounds are correlated with water concentrations of PFCAs and PFOS in lakes over a similar altitudinal transect. To our knowledge this is the first study of atmospheric concentrations of volatile PFASs and water concentrations of PFCAs or PFOS over an altitudinal transect.

Material and Methods

Chemicals. Native 2-Perfluorooctyl ethanol (8:2 FTOH) and 2-Perfluorodecyl ethanol (10:2 FTOH), Perfluorooctanoic acid (PFOA), Perfluorodecanoic acid (PFDA) Perfluorooctanesulfonic acid (PFOS), Perfluoro-1-octanesulfanamide (PFOSA), N-ethylperfluoro-1-octanesulfonamide (N-EtFOSA), 2-(N-methylperfluoro-1-octanesulfonamido) ethanol (N-MeFOSE), 2-(N-ethylperfluoro-1-octanesulfonamido) ethanol (N-EtFOSE), were provided by Wellington Laboratories (Guelph, ON, Canada). Mass labelled (1,1 ^{2}H$_2$, 1,2 ^{13}C$_2$) 8:2 and 10:2 FTOH, as well as N-ethyl-^{2}H$_5$-perfluoro-1-octanesulfonamide (d5-N-EtFOSA) were provided by Wellington Laboratories (Guelph, ON, Canada). Mass labeled ^{2}H$_4$-endosulfan I (d4-endosulfan) and ^{2}H$_6$-α-Hexachlorcyclhexane (d6-α-HCH) were purchased from CDN Isotopes Inc. (Port Clair, PQ, Canada). Native α and γ-HCH, endosulfan I and II were purchased from Accustandard (New Haven, CT, USA). Tetrahydroperfluorosulfonate (THPFOS) and perfluorodimethyloctanoic acid, also known as β-perfluorodecanoic acid (β-PFDA) were purchased from Synquest Labs (Alauchua, FL, USA). Pesticide grade dichloromethane (DCM) was purchased from Caledon (Georgetown, ON, Canada) and Optima grade methanol (MeOH) and ethylacetate from Fisher Scientific (Ottawa, ON, Canada). XAD-2 resin was purchased from Supelco (Bellefonte, PA, USA).

Preparation of Passive Air Samplers. XAD-2 resin was precleaned using a Dionex (Sunnyvale, CA) accelerated solvent extraction system with two successive washes each of MeOH, ethylacetate, and DCM at 75 °C and 1500 psi. Sixty mL of this cleaned resin in a MeOH slurry was added to stainless steel mesh tubes and sandwiched between glass wool plugs. After filling and sealing the ends with crimp style caps the prepared XAD-2 filled tubes were immersed overnight in DCM followed by an overnight soak in MeOH. After decanting the MeOH, the tubes were allowed to dry overnight under ultra high purity nitrogen (UHP, 99.999% pure Praxair, Winnipeg, Canada). Tubes were wrapped in baked aluminum foil and then double packed in sealable plastic bags.

Deployment of Passive Air Samplers. Duplicate air sampler tubes were deployed at five sampling sites in galvanized steel sampler housings on an altitudinal transect from 800 m.a.s.l. to 2740 m.a.s.l. in the Canadian Rocky and Purcell mountains for a period of five months between March 27th 2004 and August 27th 2004 (*see* Figure 1) (*27*). The transect's lowest elevation was near the town of Golden, British Columbia, Canada in the Rocky Mountain Trench at an elevation of 821 m.a.s.l. The north east facing transect continued up the mountain within the conifer forest up to the ridgeline at an elevation of 2430 m.a.s.l. (Samples A-D). All samples on this transect were on the same mountain within 10 km of each other. The last sampler was located in Banff National Park close to the Sunshine Village ski centre, on a ridge 100 km south east at an altitude of 2740 m.a.s.l. above the tree line (Sample E). Snow cover averages approximately 7 months in the region with snow coverage during the air sampling period ranging from one month for the lowest elevation to 4 months for the highest elevation site. Samplers were fastened to wooden posts 2-3 meters above the ground. Retrieved sampler tubes were

wrapped in baked aluminum foil and double wrapped in sealable plastic bags, transported to the

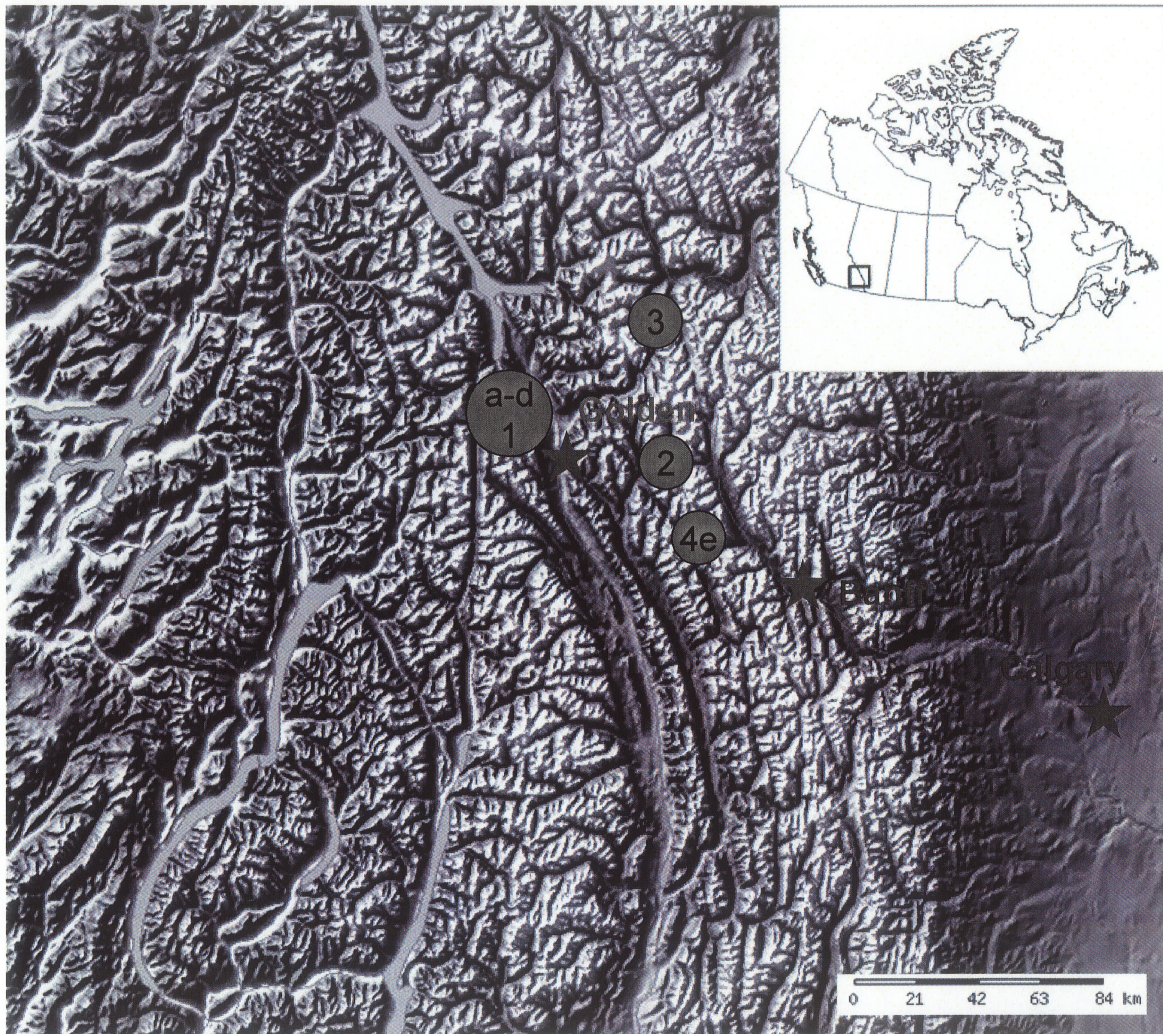Freshwater Institute (FWI) laboratory and frozen until extraction.

Figure 1: Map of Sampling Area. Sites denoted with a letter are air sampling sites, while numbers denote lake water sampling sites.

Collection of Water Samples. At the end of the air sampling period in September 2004 water

was sampled from lakes located at different altitudes near the air sampling transect (*see* Figure

S1). Eighteen litre lake water samples were retrieved from near the shoreline at Cedar Lake (#1, 800m.a.s.l.), a small lake near the town of Golden, Emerald Lake (#2, 1300m.a.s.l.) in Yoho National Park, Bow Lake (#3, 1850 m.a.s.l.) in Banff National Park, and a small unnamed lake near air sampling site E (#4, 2350 m.a.s.l.) in Banff National Park. They were collected in by submersing MeOH pre-cleaned stainless steel cans just below the water surface, spiked with β-PFDA and THPFOS, and shipped to the FWI for extraction and analysis. Samples were split in the laboratory and analyzed as duplicate 9 L samples. At the time of this study no authentically labeled surrogate compounds were available.

Extraction of Passive Air Samples. XAD resin samples were spiked with 50 ng of mass labeled 8:2 and 10:2 FTOH, N-EtFOSA, endosulfan I and α-HCH and added to a 100 mL stainless steel tube filled with ethylacetate. This was allowed to soak for 15 minutes and then eluted with a further 200 mL of ethylacetate. Samples were dried with pre-baked (6 hours, 600°C) diatomaceous earth (Hydromatrix, Varian, Missisauga, Canada), evaporated at 40 °C to 1 mL on rotary evaporator (Heidolph, Brinkmann, Missisauga, Canada) with restricted vacuum control using an external pump, then transferred to polypropylene tubes, evaporated to 200 μL under UHP nitrogen and stored in glass vials.

Extraction of Water Samples. Lake water samples were forced through a MeOH pre-cleaned 1 g Waters Hydrophilic-Lipophilic Balance (HLB) column (Waters, Missisauga, Canada) at 50 mL·min^{-1}. The column was washed with 10 mL of 30% MeOH in water and the eluant discarded. Ten mL of MeOH was used to elute the compounds of interest and was nitrogen evaporated to 1mL.

Gas Chromatography/Mass Spectrometry (GC/MS) Analysis of Air Samples. Two μL of sample was injected on a Hewlett Packard GC/MS (Agilent Technologies, Missisauga, Canada)

equipped with a Varian Factor Four 40 m VX-5 column (0.15mm ID 0.15μm film thickness, Varian, Canada, Missisauga, Canada). The split/splitless injection port temperature was 200 °C while the MS source and quadrupole temperature were maintained at 210 and 150 °C, respectively. Positive chemical ionization (PCI) using UHP methane (Praxair, Winnipeg, Canada) was used for analysis of FTOHs, N-EtFOSA and PFOSA while negative chemical ionization (NCI) was used for FOSE and pesticides. Monitored ions can be found in table 1.

Table 1: Ions Monitored for Gas Chromatography/Mass Spectrometry (GC/MS) Analysis of Air Samples.

Compound	Quantification Ion (m/z)	Confirmation Ion (m/z)
8:2 FTOH	427	465
mass labeled 8:2 FTOH	431	469
10:2 FTOH	527	565
mass labeled 10:2 FTOH	531	569
N-EtFOSA	528	NA
mass labeled N-EtFOSA	533	NA
PFOSA	500	NA
N-MeFOSE	483	494
N-EtFOSE	483	508
mass labeled N-EtFOSA	483	531
α- and γ -HCH	253	259
mass labeled α-HCH	255	261
endosulfan I and II	404	406
mass labeled endosulfan I	408	410

Liquid Chromatography/Mass Spectrometry (LC/MS) Analysis of Water Samples.
Separations were performed on a Genesis C_{18} analytical column (5.0 cm × 2.1 mm i.d., 4 μm particle size, Fisher Scientific, Nepean, Canada). An Agilent 1100 Series HPLC system (Agilent

Technologies, Palo Alto, CA, USA) equipped with a vacuum degasser, binary pump and autosampler was used for all analyses. The mobile phase flow rate was 300 $\mu L \cdot min^{-1}$, and sample injection volume was 3 μL. The mobile phase gradient started at 20% MeOH in water, increased to 95% MeOH in 9.5 minutes, and was held for another 2 minutes. A Sciex API 2000 triple quadrupole MS (Applied Biosystems, Foster City, CA, USA) was used in the electrospray (ES) negative ion mode. Monitored ions can be found in table 2 .

Table 2: Ions monitored during Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS) Analysis of Water Samples.

Compound	Quatitfication Ion Transition	Confirmation Ion Transistion
PFOA	413-369	413-169
PFNA	463-419	463-169
PFDA	513-469	513-269
PFUA	563-519	563-169
PFOS	499-99	499-80
THPFOS	427-407	427-81

Quality Assurance. All neutral compounds were recovery corrected using the corresponding mass-labeled surrogate responses. PFOSA, N-MeFOSE and N-EtFOSE were normalized to deuterated N-EtFOSA and γ-HCH normalized to deuterated α-HCH. Three sampler tubes were brought to the field, unwrapped from their aluminum foil packaging briefly, repackaged and returned to the freezer in the laboratory. These field blanks were analyzed concurrently with the samples. Method detection limits (MDLs), defined as an average of blank values plus 3σ in $ng \cdot sampler^{-1}$, were as follows: 8:2 FTOH (0.65); 10:2 FTOH (0.064); N-EtFOSA (0.39); PFOSA (0.18); NMeFOSE (3.89); NEtFOSE (2.33); endosulfan I and II (5.40 and 0.34). Neither α- nor γ-HCH were detected in blanks. The MDLs for α- and γ-HCH were 2 and 1 $ng \cdot sampler^{-1}$ as

defined as 3 times the absolute detection limit (S/N=3). Average internal standard recoveries of mass labeled compounds were as follows: 8:2 FTOH 53.7%, 10:2 FTOH 68.9%, N-EtFOSA 64.9%, α-HCH 50.1% and endosulfan 52.3%.

All PFCAs were recovery corrected using β-PFDA. PFOS was normalized to THPFOS. MDLs (average of blank value plus 3σ in ng·L^{-1}) were: PFOA (0.21); PFNA (0.18); PFDA (0.04); PFUA (0.05); PFOS (0.04). Recovery of THPFOS averaged 73.2%, while that of β-PFDA averaged 65.0%.

Results and Discussion

Pesticides in Air. The amounts of the HCHs and endosulfans sequestered in the air samplers increased with altitude (*see* Figure 2), which agrees with what had been found in earlier studies in Western Canadian mountains (*26,28*). Consistent with previous observations over a similar transect in the same region the sequestered amounts of all pesticides at least doubled along the range of the transect (*see* Figure 2) (*26,28*). When corrected for the shorter sampling period of 5 months, the amounts sequestered per sampler were very similar to those reported from a 12 month deployment in the previous study.

Perfluorinated Alkyl Substances The amount of FTOHs in air samplers increases with increasing altitude (*see* Figure 2) at confidence levels of 95 % using a two parameter exponential curve. R values were 0.91 for both 8:2 and 10:2 FTOH, respectively. Higher levels at higher altitudes were also observed for N-MeFOSE and N-EtFOSE. Due to high MDLs for these compounds the sampled amounts at the sites at 800 and 1318 m.a.s.l. were below the detection limit. However both compounds were above their MDLs above 1840 m.a.s.l. Confidence intervals at 95% using a two parameter exponential curve show an r value of 0.63 and 0.81 for
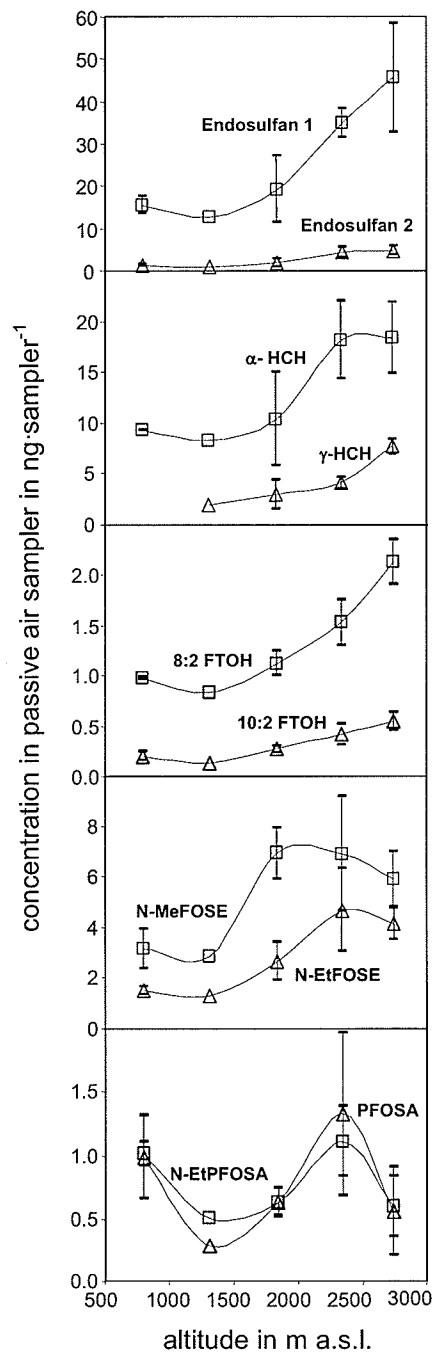
Figure 2 Concentrations of Hexachlorocyclohexanes, Endosulfans, FTOHs, FOSAs and

FOSEs in Passive Air Samplers as a Function of Altitude. Bars indicated ranges of duplicates.

N-MeFOSE and N-EtFOSE, respectively. The sequestered amounts of PFOSA and N-EtFOSA showed no clear trend with elevation (*see* Figure 2).

Perfluorinated Alkyl Substances Lake water concentrations of PFOA along the elevation transect were below 1 ng/L and slightly higher than those of PFNA. PFDA and PFUA had much lower concentrations below 0.2 ng/L. The concentrations of PFOA were similar to those reported in remote freshwater lakes and rivers in Japan (*29*). No clear trend in the concentrations of PFCAs with altitude is apparent (*see* Figure 3). PFOS concentrations were very low, ranging from 0.04 to 0.1 ng/L. These are some of the lowest recorded levels in water samples, and on the order of concentrations found in open ocean samples (*30*). PFOS exhibited highest concentrations in Cedar Lake, the low altitude lake close to Golden (*see* Figure 3). This lake may be influenced by local sources, whereas the high elevation samples are dominated by atmospheric input.

Interpreting Differences in Chemical Amounts Sequestered by Passive Air Samplers Deployed At Different Altitudes. Two passive air samplers that are exposed to identical gas phase concentrations of an organic chemical could sequester different amounts of that chemical, if (1) the kinetics of uptake is different, i.e. if one sampler experiences a higher sampling rate than another, or (2) if the chemical approaches equilibrium between atmospheric gas phase and sampling resin, and one sampler has a higher capacity than the other, e.g. as a result of lower air temperatures. Elevational gradients are often also gradients of atmospheric pressure, temperature and wind speed. Prior to an extended interpretation of the passive air sampling data presented above, it is necessary to assess whether sequestered amounts of a chemical that increase with altitude are indeed reflective of increasing volumetric air concentrations. Specifically, we need to

assess the potential impact of gradients in pressure, temperature and wind speed on the uptake kinetics and uptake capacity of the XAD-based passive samplers used in this study.
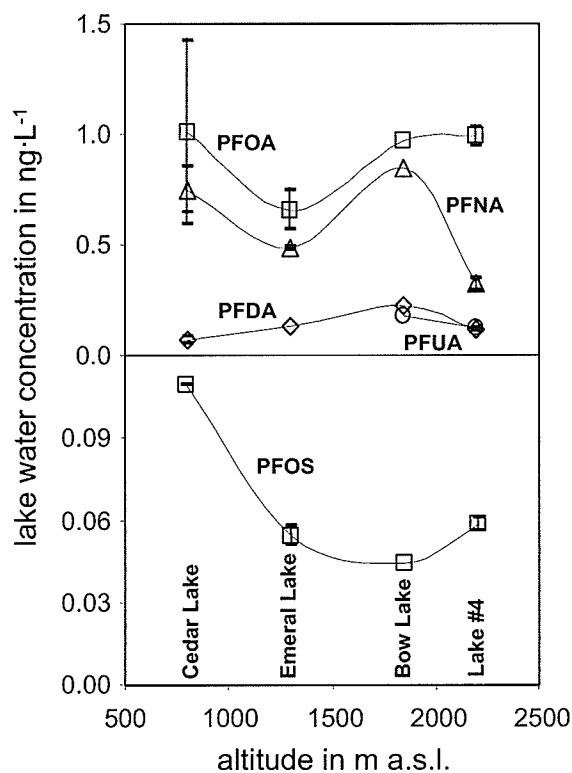

Figure 3   Concentrations of PFCAs and PFOS in Rocky Mountain Lake Water as a Function of Altitude. Bars Indicate Ranges of Duplicates.

Effect of Wind Speed on Sampling Rate. Wind speed often increases with elevation in mountain regions, and sites above the tree line in particular, may experience much higher average wind speeds than those in forested areas. The uptake rate of the XAD-based passive samplers used here was shown to be independent of wind speed up to 15 $m \cdot s^{-1}$ (*27*). However, those experiments were conducted with horizontal wind blowing perpendicular to an upright sampler, a situation for which flow simulations indicated that no wind is entering the sampler

housing (*27*). In a mountain setting, where samplers are often deployed on sloping terrain, upslope winds that develop during day time may not necessarily blow perpendicular to the sampler housing and thus may have a higher chance of blowing directly onto the sampling resin potentially making wind speed a variable in the sampling rate.

Effect of Air Pressure and Temperature on Sampling Rate. The rate of uptake of a chemical in the sampling resin of a passive air sampler is believed to be controlled by molecular diffusion across a stagnant layer of air surrounding the resin. If wind is prevented from flowing over the resin, the thickness of that layer is independent of wind speed, and the sampling rate R (in m^3 air per units of time) is proportional to the molecular diffusivity in air D_{Air}. Diffusion increases with increasing temperature ($D_{Air} \propto T^{1.5}$) and decreases with increasing pressure ($D_{Air} \propto 1/p$). To estimate how strongly elevational gradients in temperature and pressure may impact on diffusivity and therefore sampling rate R in our study, we estimated differences in D_{Air} between 800 and 2750 m. While we do not have a record of the temperature or pressure at the sampling locations, they can be estimated. Starting from an average temperature at the lowest sampling site (Golden, 800 m a.s.l.) during the sampling time of 13.1 °C, a linear lapse rate of 6.5 $K \cdot km^{-1}$ was applied to estimate temperatures at higher elevations. Air pressure P (in Pa) was assumed to decrease logarithmically with respect to altitude according to:

$$P = P_0 \cdot exp(-M \cdot g / (R \cdot T)) \tag{1}$$

where P_0 is the pressure at sea level (101,325 Pa), M is the molecular mass of air (0.029 kg/mol), g is the gravitational force (9.8 $m \cdot s^{-2}$), R is the ideal gas constant (8.314 $J \cdot K \cdot mol^{-1}$), and T is temperature in K. Table 3 shows that the pressure and temperature have opposing effects on diffusivity as a function of elevation and partially cancel each other out. The diffusivity at 2750 m is only about 7 % slower than at 800 m, because of the lower temperatures. It is also estimated

to be 28 % faster because of the lower atmospheric pressure. Overall, we estimate a 20 % higher molecular diffusivity, and therefore higher sampling rate R, between the lowest and highest sampler deployment location. This difference is considerably smaller than the differences in the sequestered amounts of pesticides and PFASs. We note, however, that over much larger elevational gradients, high altitude sampling stations may experience diffusivities and sampling rates that are almost twice those at sea level.

Table 3: Estimate of the relative change in molecular diffusivity in air D_{Air} as a result of changes in temperature T and atmospheric pressure P along an elevation gradient.

Altitude (m)	T (K)	T/T_{ref}	$D_{Air}/D_{Air\text{-}ref}$ (due to T)	P (Pa)	P/P_{ref}	$D_{Air}/D_{Air\text{-}ref}$ (due to P)	$D_{Air}/D_{Air\text{-}ref}$ (due to P and T)
800	286.1	1.00	1.00	92088	1.00	1.00	1.00
1300	282.9	0.99	0.98	86593	0.94	1.06	1.05
1800	279.6	0.98	0.97	81310	0.88	1.13	1.09
2340	276.1	0.97	0.95	75839	0.82	1.21	1.15
2750	273.4	0.96	0.93	71846	0.78	1.28	1.20

Effect of Temperature on Sampler Uptake Capacity. Since the influence of changes in diffusivity on sampling rates is relatively minor, increasing sampler concentrations with altitude should be due to increasing volumetric air concentrations in the vicinity of the sampler, as long as the passive air samplers operate in the linear uptake phase and uptake rates are independent of wind speed. However, if the XAD-resin in the sampler should approach equilibrium with a compound's atmospheric vapor phase during the deployment period, sampler concentrations that increase with altitude could be related to the increased uptake capacity of the resin at lower temperatures. As samplers at higher altitude are exposed to lower temperatures, the equilibrium

concentrations in the high altitude samplers would be higher than those of low altitude samplers if exposed to the same gas phase concentrations. Whether a compound approaches equilibrium depends on the compounds volatility, the temperature during, and the length of, the deployment period. Volatility is characterized by vapor pressure or, more specifically, by the adsorption coefficient onto the XAD-2 resin.

To compare the relative sorptive capacity of XAD-2 resin for PFASs and HCHs, their retention volumes V_g were estimated using a linear free energy relationships (*31*):

$$\log(V_g \text{ at } 20°C \text{ / } L·g^{-1}) = 0.54·A + 0.85·B - 0.70·E + 1.21·\log L^{16} - 1.92 \tag{2}$$

Equation 2 relates a compound's V_g to a number of solute descriptors, including the solute's hexadecane/air partitioning coefficient L and molar refraction E, as well as the parameters A and B describing its electron donating and accepting character (*31*). These solute descriptors are available for 8:2 FTOH and 10:2 FTOH from Goss et al. (*32*) for α- and γ-HCH from Abraham et al. (*33*), and for hexachlorobenzene from Shen et al. (*34*) and are listed in Table S4. Also given are the estimated retention volume on XAD-2 V_g, the adsorption coefficient onto XAD-2 K_{ads} estimated from V_g as described in ref. (*34*) and liquid phase vapor pressures P_L reported in the literature (*35-37*). Furthermore, K_{ads} at the average temperatures of the sampling sites at 800 and 2750 m, were estimated using a heat of adsorption, which itself had been estimated using an empirical relationship with K_{ads} at 20 °C (*38*).

Compounds as volatile as HCHs and HCB are not believed to approach equilibrium in XAD-based sampler during a one year deployment under typical temperate conditions (*28*). Although the vapor pressures of FTOHs are only slightly higher than those of the HCHs (Table S4), V_g and K for the FTOHs are estimated to be lower than those for the HCHs and HCB by more than two orders of magnitude (Table 4) (*35*). We can thus not be sure that the capacity of the XAD-2 resin

in the sampler is large enough to prevent equilibration of FTOHs during the 5 month deployment. The adsorption coefficient for 8:2 and 10:2 FTOH at 0.3 °C is estimated to be 2 and 2.4 times higher than at 13 °C (Table 4), which would imply that at equilibrium the sampler deployed at 2750 m would be able to sequester about twice as much FTOHs as the sampler at 800 m. This is actually close to the observed differences in sequestered amounts (Figure 1) and supports the assumption that the FTOHs may have approached equilibrium during the five month deployment. Previous studies have shown the efficacy of XAD-2 resin for atmospheric sampling of FTOHs with excellent retention characteristics (16). Cao and Hewitt proposed that a sorbent is satisfactory for passive air sampling if its V_g is greater than 100 L/g sorbent. The V_g estimated for the FTOHs on XAD-2 at 20 °C listed in Table S4 are more than an order of magnitude above this threshold (39). Also, ambient temperatures at the sampling sites were generally below 20 °C. However, not all of the XAD-2 resin in the sampler will be equally accessible for uptake, and so it is conceivable that the capacity of the XAD in the samplers is insufficient to prevent equilibration for substances such as the FTOHs.

Solute descriptors are not available for FOSEs and FOSAs, preventing an estimate of their V_g and K_{ads}. Liquid phase vapor pressures for N-MeFOSE of 0.002 Pa and N-EtFOSE of 0.0086 Pa have been reported by Shoeib et al. suggesting that they are considerably less volatile than the FTOHs (18). FOSAs are expected to have volatility in between that of the FTOHs and FOSEs (40). The samplers are thus likely adequate to sample FOSEs and FOSAs in the linear uptake regime.

Table 4: Compound properties used in the interpretation of the data. L^{16}, A, B and E are solute descriptors used in linear free energy relationships, V_g and K_{ads} are the retention volume and adsorption coefficient on XAD-2, respectively, P_L is the liquid phase vapor pressure and $K_{snow/air}$ is the sorption coefficient into snow.

Compound	$\log L^{16a}$	A^a	B^a	E^a	$\log(V_g/\text{L·g}^{-1})^b$	$\log(K_{ads}/\text{mol·m}^{-2}\text{·Pa}^{-1})$			$K_{ads}/K_{ads\text{-}ref}$	P_L/Pa^e	$\log(K_{snow/air}/\text{m})^f$
Temperature					20°C	20°C^c	13°C^d	0.3°C^d	0.3°C/13°C	25 °C	-6.8 °C
8:2 FTOH	3.47	0.55	0.25	-1.56	3.88	-5.05	-4.89	-4.58	2.0	4	-1.85
10:2 FTOH	3.9	0.55	0.25	-1.87	4.62	-4.31	-4.12	-3.74	2.4	0.2	-1.57
α-HCH	7.317	0	0.71	1.45	6.52	-2.41	-2.13	-1.58	3.5	0.245	0.23
γ-HCH	7.467	0	0.68	1.45	6.68	-2.25	-1.96	-1.40	3.6	0.076	0.22
HCB	7.89	0	0.07	1.466	6.66	-2.27	-1.98	-1.42	3.6	0.094	-1.57

[a] LSER solute descriptors from ref. [32,33,34]; [b] estimated using equation by Poole and Poole[31]; [c] estimated from V_g as described in ref. [34]; [d] estimated from value of K at 20 °C using heat of adsorption estimated with an equation from ref. [38]; [e] taken from ref. [35,36,37]; [f] estimated using equation by Roth et al.[42].

Potential Reasons for Air Concentrations that Increase with Altitude. As snow fall and snowpack depth is strongly correlated with altitude in this Western Canadian mountain region, atmospheric deposition of snow-scavenged organic chemicals per unit area is larger at higher altitude (*21*). Some of the scavenged chemical will evaporate during winter due to a metamorphosis-driven decrease in snow surface area. Also during and after snowmelt, the chemicals are expected to re-evaporate effectively because of increasing temperatures and a low capacity of high altitude environments to retain them (lack of dense vegetation cover, shallow soils low in organic matter). So while the deposition of contaminants increases with altitude, the capacity to retain them decreases (*41*). This highly dynamic behavior of contaminants at high altitudes has been hypothesized to explain annually averaged air concentrations of HCHs and other organo-chlorine pesticides that increase with elevation (*22*). This increase would presumably be localized to air near the surface. Since the 5 month deployment of this study comprised the period of snow melt and snow-free summer, when re-evaporation is believed to occur, it is not entirely unexpected that higher atmospheric pesticide concentrations are observed at higher elevations. However, we can not assume that the concentration profiles of the PFASs measured in the passive air samples are necessarily due to the same mechanism.

In order to assess whether PFASs are subject to equally efficient snow scavenging as the pesticides, sorption coefficients $K_{Snow/Air}$ to the snow surface were estimated using a linear free energy relationship by Roth et al.(*42*):

$$\log (K_{Snow/Air} \text{ at } 6.8 \text{ °C/m}) = 3.53 \cdot A + 3.38 \cdot B + 0.639 \cdot \log L^{16} - 6.85$$

(1)

The $K_{Snow/Air}$ sorption coefficients estimated for the FTOHs (Table S4) are much smaller than for the HCHs and so small, that snow scavenging is not expected to be a major deposition process (*43*). Evaporation of snow-scavenged material can thus not explain sequestered amounts of FTOHs that increase with altitude. The lack of solute descriptors for FOSEs and FOSAs again prevents the estimation of their $K_{Snow/Air}$, but their vapor pressure is lower than that of the FTOHs, which suggest the possibility of efficient snow scavenging, at least at lower temperatures. Reports of particulate bound FOSAs, FOSEs and FTOHs which would also be efficiently scavenged by snowfall is another potential mechanism of deposition (*17,19*). Overall, it appears plausible that the distribution behavior of the FOSEs and FOSAs in the mountains is similar to that of the HCHs.

Estimation of Volumetric Air Concentrations. Assuming an uptake rate of 0.52 m^3 per day and sampler (*27*), approximately 78 m^3 of air was sampled during the sampling period. Based on this air volume, and correcting for surrogate recoveries, air concentrations in units of pg·m^{-3} were estimated to range from 3.7 to 19 pg·m^{-3} for perfluorinated sulfonamides (FOSAs), and from below detection limits (25 pg·m^{-3}) to 88 pg·m^{-3} for perfluorinated sulfonamido alcohols (FOSEs). These concentrations do not account for potential influences of changes in pressure, temperature or sampling resin capacity on uptake rates. Air concentrations above the MDL were considered acceptable. The air concentrations of FOSAs and FOSEs are similar to those observed at a "remote" location by Stock et al (*15*). They are also similar to those observed at Long Point, Ontario, a rural area on Lake Erie (*16*) and in the North Atlantic and Arctic atmosphere (*17*). No volumetric concentrations were estimated for fluorotelomer alcohols (FTOHs) due to the potential for these compounds to have exceeded the capacity of the sampler.

We can only state that FTOH concentrations were at least 0.8 to 27 $pg \cdot m^{-3}$. High volume

air sampling would be required to obtain reliable volumetric air concentrations for

FTOHs, but this was not possible due to access to power.

Altitudinal Gradients in Lake Water Concentration. In contrast to the airborne

precursors in the atmosphere, concentrations of perfluorinated acids in lake water do not

increase with altitude. Two processes may contribute to the presence of PFOS and

PFCAs in lake water: the atmospheric deposition of the acid themselves, and the

atmospheric deposition and subsequent degradation of their volatile precursors. These

two routes are likely to display opposing trends along gradients from source to remote

regions. Direct deposition of the acids is likely to decrease with increasing distance from

sources due to fast deposition rates of these types of compounds. Conversely, the

transport behavior of the volatile precursors may result in their enrichment in cold remote

environments, and thus the formation of more acids further removed from sources. The

contribution of both these processes may explain why we did not observe obvious trends

in the concentration of fluorinated acids in lake water taken along an elevation gradient.

Relative Abundance of PFASs of Different Chain Length in Air and Water. Whereas

direct emission of PFCAs and PFOS can explain their presence in some areas, the

presence in the mountains of Western Canada is most likely due to the oxidative

degradation of volatile precursor compounds. 8:2 FTOH degrades to the PFOA and

PFNA via intermediates in roughly equal quantities (23). Similarly 10:2 FTOH degrades

to PFDA and PFUA. We would then predict that not only would we find equal amounts

of the corresponding acids, but that PFOA and PFDA would be found in a similar ratio to

the corresponding FTOHs. This is indeed what is observed. The water concentrations of

PFOA and PFNA and those of PFDA and PFUA are very similar, except for lake #4 where PFNA is less abundant than PFOA (Figure 3).

Also, 8:2 FTOH averages 3.5 times more abundant in air than 10:2 FTOH, which is slightly lower than the average relative abundance of PFOA and PFNA relative to PFDA and PFUA in lake water with a mean value of 5.9. Further enrichment of PFOA and PFNA compared to PFDA and PFUA may be due to particulate transport of the acids themselves which would favour PFOA and PFNA.

Acknowledgements

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III

SEASONAL AND ALTITUDINAL TRENDS OF CHLORINATED PESTICIDES IN THE CENTRAL HIMALAYAN ATMOSPHERE

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Abstract. XAD-resin based passive air samplers were used to measure the concentrations of

hexachlorobenzene (HCB), endosulfan I, α-hexachlorocyclohexane (α-HCH), γ-

hexachlorocyclohexane (γ-HCH), p,p'-DDE and p,p'-DDT over an altitudinal transect from 174

to 5605 m a.s.l in the Central Himalaya (27°34'-27°60'N, 84°29'-86°50'E). While there is no

known usage of these chemicals in the high altitude range of the study region, they are used

extensively in the low altitude section of the transect region. Air concentrations of those

pesticides in the Central Himalaya were on the order of tens to hundreds of pg/m^3, similar to

those found in North American mountains, while current use areas in malaria prone agricultural

regions of Nepal concentrations up to several thousand pg/m^3 were observed. Concentration

gradients with altitude displayed large differences between summer (May to October) and winter (November to April). In summer concentrations of all the chemicals in the high altitude region increased with elevation up to a maximum near 5000 m a.s.l and then declined above that elevation. In contrast, winter time concentrations of all the chemicals declined with altitude, except for HCB which had similar elevational trends year-round. This indicates that during the summer monsoon, lower tropospheric air contaminated with pesticides is likely being driven by thermal and mechanical forcing from the Indian subcontinent into the Central Himalaya. During winter high altitude sites are above the boundary layer. For HCB global sources appear to be more important than regional monsoonal transport. Carbon normalized soil concentrations tend to decline above 2600m a.s.l. following the gradient of forestation.

Introduction

Evidence is emerging that mountain regions sometimes experience relatively high concentrations and deposition rates of selected persistent organic pollutants (POPs) considering their remoteness from sources located mostly at lower elevations. Earliest indications for this phenomenon came from a global survey of contaminants in vegetation, which reported the highest levels of hexachlorobenzene (HCB) in low latitudes at sites with high elevation (2). Elevated levels of organochlorinated compounds were also reported in fish, sediments, snow and air from the Canadian Rocky Mountains (3-6). To date, very little research has been published on POPs in the Himalaya to test if this phenomenon is observed in the highest mountain range in the world (7-9).

The Himalaya is wedged in between India and China, the two most populous countries in the world. High population density often results in increased usage of pesticides and high emissions of air pollutants. In the past, the Indian subcontinent and China had experienced heavy use of

organochlorine pesticides, such as hexachlorocyclohexanes (HCHs) and DDT, for agricultural purposes. It has been estimated that since its initial formulation, more than 10^7 kg of DDT have been used in India (*10*). India banned DDT for agricultural purposes in 1989, but continues to use 1×10^4 kg/y for malaria control (*11*). Technical HCH, once the most heavily used pesticide in India, was banned for agricultural use in 1990 and totally banned in 1997, with estimated usage of 1.1×10^9 kg (*12,13*). Lindane (γ-HCH) has been used as a replacement since that time. From the 1950s until their ban in 1983, China produced and used 4×10^8 kg of DDT as well as 4.5×10^9 kg of technical HCH (*14,15*). Lindane and DDT are still being used in lower amounts to control certain insects. Recent DDT contamination has been attributed to dicofol, a miticide that contains small amounts of DDT and is heavily used in China (*16*). Due to the banning of even more persistent chemicals, endosulfan has become a widely used insecticide in the last two decades. It is now the organochorine insecticide most frequently detected at high concentrations in the global atmosphere (*17*). Hexachlorobenzene is found in the global atmosphere at a reasonably constant concentration due to its resistance to atmospheric degradation and deposition. It is an impurity in many current use pesticides. Recent studies have shown HCB to be elevated in air samples from China in industrial areas (*18*).

The Himalaya and surrounding lowlands are linked by the Southwest or summer monsoon, a distinct climatic system that operates in the region from June to September. The Tibetan Plateau plays a very important role in this phenomenon. With an average altitude of over 4000 m.a.s.l., and at a subtropical latitude, the plateau is strongly heated by the early summer sunshine. As it is fully halfway into the troposphere, it is very easy for the upper atmosphere to become heated. This coupled with the low density of the air at this altitude conspires to form a very deep convective layer. This in effect forms a pump also known as the "Tibetan chimney" which has

been shown to pump air from below the boundary layer up to and even exceeding the tropopause (19-22). Comparatively cooler humid air from the southern hemisphere crosses the equator and is accelerated towards the low-pressure area over the Indian sub-continent and Tibetan plateau. This thermal forcing causes the air mass over India to be driven into the mountain ranges in the northern part of the subcontinent with the orographic lifting of the mountains causing significant precipitation events (23). In winter (October-May), the Himalaya is dominated by prevailing continental westerlies (24). Atmospheric modelling has shown that this westerly flow is split by the Tibetan Plateau rather than going over the plateau (25). As the thermal forcing of the Tibetan plateau is reversed in the winter, cold air is pushed away from the plateau shielding it from the continental westerlies.

Summer precipitation amounts vary widely over Nepal with the majority of the rain falling in the "lower" mountains south of the Great Himalaya (<4000m a.s.l.). As the monsoon activity moves from southeast to northwest from the Bay of Bengal towards the mountains, much of the rain falls in the eastern hills. Due to the high altitude of these "hills" (up to the 3500 m.a.s.l. range) south of the Great Himalaya, much of the precipitation is rained out before reaching the high mountains. For instance, during the monsoon months of July and August 1994, the Italian Research Pyramid (the 5000 m.a.s.l. site in this study) received 269 mm total precipitation compared to the average for Kathmandu (1336 m.a.s.l.) which is 672 mm (26). Precipitation rates increase up to 2000 m.a.s.l. and then decline above that elevation (23).

Precipitation trends are reversed in winter, with snowfall in the western Himalaya being heavy compared to the scant snowfall in the central and eastern mountains. As a result little precipitation occurs at the higher elevation with low elevation agricultural areas receiving heavy summertime precipitation (23,26). The atmospheric transport and fate of pesticides in the

Himalaya is expected to be influenced by this unique meteorological system. In this study we attempt to understand the movement of a variety of persistent chlorinated pesticides in the Central Himalayan atmosphere on a seasonal basis over a wide range of elevations.

Material and Methods

Air. Duplicate XAD-2 resin-based passive air samplers (PAS) prepared as described by Wania et al.(*27*) were deployed in Nepal (Figure 1a and Table S1). One was deployed at 174m a.s.l. in Chitwan National Park near agricultural areas (Region A), two in agricultural locations at 880 m a.s.l. and 1881 m a.s.l. (Asi Khola, Region B), and five at remote locations ranging from 2638 to 5605 m a.s.l. (Solo Khumbu, Region C, Figure 1b). The samplers were deployed during two seasons: May 2004-October 2004 and November 2004-April 2005 in order to coincide with major changes in the air mass movement over the Himalaya. Sampler tubes were packaged for deployment and retrieval in baked aluminium foil and double packaged in sealable plastic bags. At the end of the sampling period, sampler tubes were retrieved and sent to the laboratory of the Freshwater Institute where they were stored frozen until analysis. The XAD-2 resin (Supelco, Bellefonte, PA, USA) inside the PAS tube was spiked with deuterated endosulfan and α-HCH (CDN Isotopes Inc. Port Clair, PQ, Canada) as well as PCB-30 surrogate compounds (Accustandard, New Haven, CT, USA) and allowed to soak in 100 ml dichloromethane (DCM, Caledon, Georgetown, Canada) for 20 min. and then eluted with a further 250 ml of DCM from a stainless steel column. The samples were evaporated with a rotary evaporator (Heidolph, Brinkmann, Missisauga, Canada) taken into 1 ml hexane (Caledon, Georgetown, Canada) and dried with sodium sulphate (Fisher, Ottawa, Canada, baked at 600°C 6 hours), followed by cleaning up and fractionation on 1.2% deactivated Florisil (Fisher, Ottawa, Canada, baked at 600°C 6 hours).

The samples were then taken into isooctane (Caledon, Georgetown, Canada) evaporated to 200μl and spiked with an aldrin performance standard (Accustandard, New Haven, CT, USA). One μl of each sample was injected onto a Varian GC/ECD (Missisauga, Canada) equipped with a 60m J&W DB-5 capillary column (Agilent Technolgies, Missisauga, Canada) and analyzed for several chlorinated pesticides.

Method detection limits (MDLs), defined as the average of four field blanks plus 3 times the standard deviation, were 0.22, 0.28, 0.26 and 1.24 pg/m^3 for HCB, α-HCH, γ-HCH and p,p'-DDE, respectively, based on an air sampling rate of 0.52 m^3/day (27). Endosulfan I and p,p'-DDT were not detected in blanks. The concentrations in all the samples were well above their respective MDLs. Surrogate recoveries averaged 78, 72 and 76 percent for PCB-30, deuterated α-HCH and deuterated endosulfan I, respectively. Deuterated surrogates were easily resolved from the native compounds by retention time on the 60 m column. Samples were recovery corrected.

Soil. Three soil samples were pooled at 7 sites between 174m a.s.l to 5400m a.s.l. using a 60 mm ID corer to the bottom of the organic layer. The samples were pooled, double wrapped in sealable plastic bags and sent back to the Freshwater Institute (FWI) and frozen. Ten gram samples were spiked with the same surrogates and accelerated solvent extracted (Dionex, Sunnyvale, CA) with DCM 3 times at 100 °C and 2000 psi. Extracts were rotary evaporated and taken into 1 ml hexane, processed with Florisil and GC analyzed using the above method. Total carbon was measured by combustion. Inorganic carbon was below detection limit so the total was taken as organic. Samples were carbon corrected on a dry weight basis. All samples were well above the detection limit.

Sample site description. Sampling site coordinates are specified in Table 1. Sampling regions were separated into 3 distinct zones (Figure 1a). Region A had one sampler in a National Park in a low elevation area. The region is malaria prone and has agriculture in close proximity. Much precipitation falls in the summer months and is subtropical in climate. Region B had 2 sampling sites, one at 841 m a.s.l. and another at 1881m a.s.l. The low elevation site is typified by intensive agriculture and is also malaria prone. As it is accessible by road and close proximity to Kathmandu, and therefore a large market, pesticide usage is very high. Although the site at 1881m a.s.l is in close proximity to the low elevation site, road access is very limited. Pesticide usage is much less and it is not malaria prone due to the elevation. The low elevation site is subtropical in climate. Slightly higher precipitation rates are observed at the upper site and snow can fall in the winter. Sampling region C, Solo Khumbu is remote. Pest problems above 2600 m.a.s.l. in this high altitude portion of our study site are limited. Access to chemicals is also extremely limited due to long distance to a roadhead (6 days walk for a porter). Precipitation rates decline with altitude in this region (Figure 1b).

Table 1: Sampling site coordinates, PAS deployment times soil sample carbon content and vegetation type

Site Name	North Lat.	East Long.	Altitude (m a.s.l.)	Deploy date	Retrieval/2nd-Deploy date	1st Sampling Duration (days)	2nd Retrieval date	2nd Sampling Duration (days)	Soil carbon content (% ?)	Vegetation
Chitwan Park	27°34.605'	84°29.839'	174	Oct.23/04	May 1/05	190	Nov. 4/05	187		Tropical Forest
Dhaitar	27°42.571'	85°36.375'	841	Oct.21/04	Apr.27/05	188	Nov. 1/05	188	0.7	Agricultural
Tulichour	27°41.568'	85°33.013'	1881	Oct.20/04	Apr.27/05	187	Nov.1/05	188	1.5	Agricultural
Phakding	27°44.466'	86°42.745'	2638	Oct.28/04	May 2/05	186	Nov.8/05	190	2.1	Forested
Namche	27°48.248'	86°42.899'	3571	Oct.30/04	May 4/05	186	Nov.10/05	190	5.1	Forested
Dingboche	27°53.380'	86°49.438'	4360	Nov.1/04	May 5/05	185	Nov.12/05	191	7.2	Alpine
Lobuche	27°57.657'	86°48.789'	5061	Nov.3/04	May 7/05	185	Nov.13/05	190		Alpine
Kala Patthar	27°59.236'	86°49.374'	5450						3.5	Alpine
Kala Patthar	27°59.296'	86°49.336'	5605	Nov.3/04	May 7/05	185	Nov.13/05	190		None
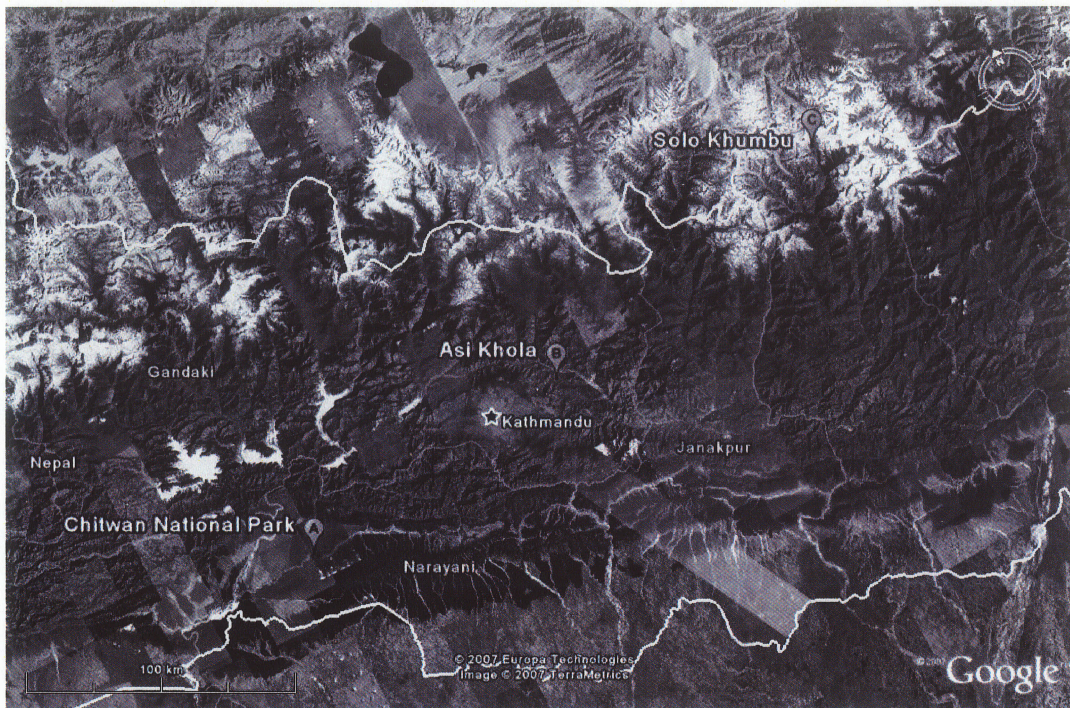
Figure 1a&b: a: Sampling regions in Nepal. b: Remote sampling region in the Central Himalaya. Mt.

Everest is labelled for reference.

Results

The passive air sampler we used has been calibrated by comparison with HiVol-derived air concentrations and tested in wind tunnel experiments to study the effect of wind speed on sampling rate (*27*). The rate of uptake is governed by molecular diffusion across an air boundary layer. Several studies have used an uptake rate of 0.52 m^3/day to derive volumetric air concentrations from the amount sequestered in the XAD-resin over the deployment period. This number is somewhat uncertain, but because it is believed to be relatively independent of wind speed, the uncertainty of the uptake rate has only a minor influence on the ability to make a relative comparison between samplers deployed at different locations.

However, when comparing concentrations derived from PAS deployed at widely different altitudes, it is important to take into consideration factors that may influence chemical diffusivity. Decreasing temperature with increasing altitude has a small effect in decreasing the rate of diffusion while a decrease in atmospheric pressure yields a stronger increase in diffusivity (*28*). We estimate that over the altitude range in this study the effect of temperature and pressure combined yields a sampling rate that is 1.7 times faster at the highest elevation site when compared to the lowest site. The atmospheric concentrations were calculated taking into account the change in sampling rate over the transect. (See Figure 2)
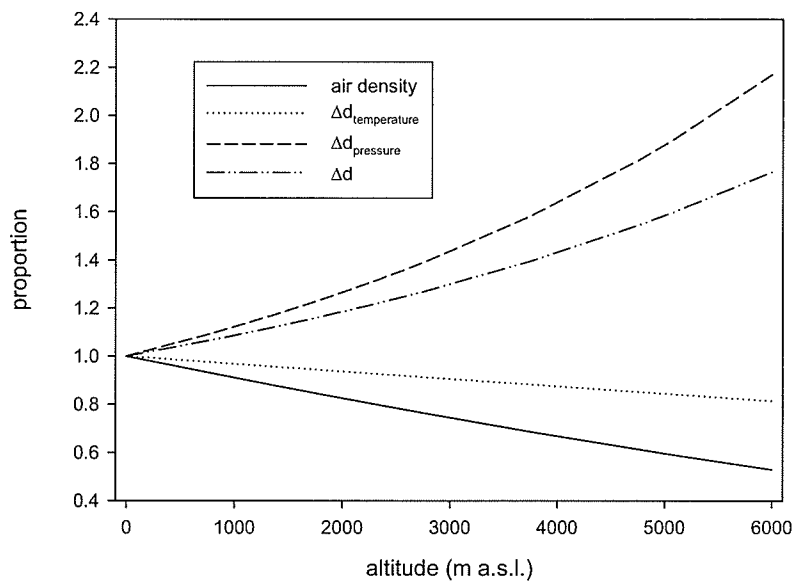
Figure 2: Change in diffusivity due to temperature and pressure. Δd is the sum of these phenomena. Air density is shown for reference.

Air. Figure 3 compares the seasonal and elevational trends in atmospheric concentrations of more volatile POPs including HCB, α-HCH, γ-HCH, while Figure 4 compares the less volatile compounds, endosulfan I,p,p'-DDE and p,p'-DDT in both current use and remote areas. Agricultural low elevation sites shows high concentrations of endosulfan and one site had the highest reported p,p'-DDT levels reported globally with over 3000 pg/m^3 (*17*). The observed concentrations reflect current usage of the chemicals. In remote areas, there is a significant difference between winter and summer concentrations for all chemicals except HCB which was observed to have similar concentrations in either season. All the chemicals behaved similarly over the altitude range in summer with increasing concentrations up to an elevation of 5000 m.a.s.l. followed by a decrease at

5600 m.a.s.l. Not including the site at 5600m a.s.l., the concentration increase over altitude in the remote region was significant ($p < 0.05$) for more volatile chemicals while increases for less volatile compounds was not significant. In winter all the chemicals decreased in concentration with altitude with the exception of HCB which showed an increase over the same elevation range. Summer levels of endosulfan I, α-HCH and γ-HCH in the Central Himalaya are similar to those detected in the Canadian Rocky Mountains during the snowmelt and summer seasons of 2004, while the winter levels in the Central Himalaya are much lower (*28*). HCB levels are slightly higher than those found recently in Europe and lower than those detected in industrial parts of China in 2004 (*18,29*). The atmospheric concentration of p,p'-DDT were found to be higher than p,p'-DDE at all elevations; both chemicals were within the range of concentrations reported recently in Europe (*29*).
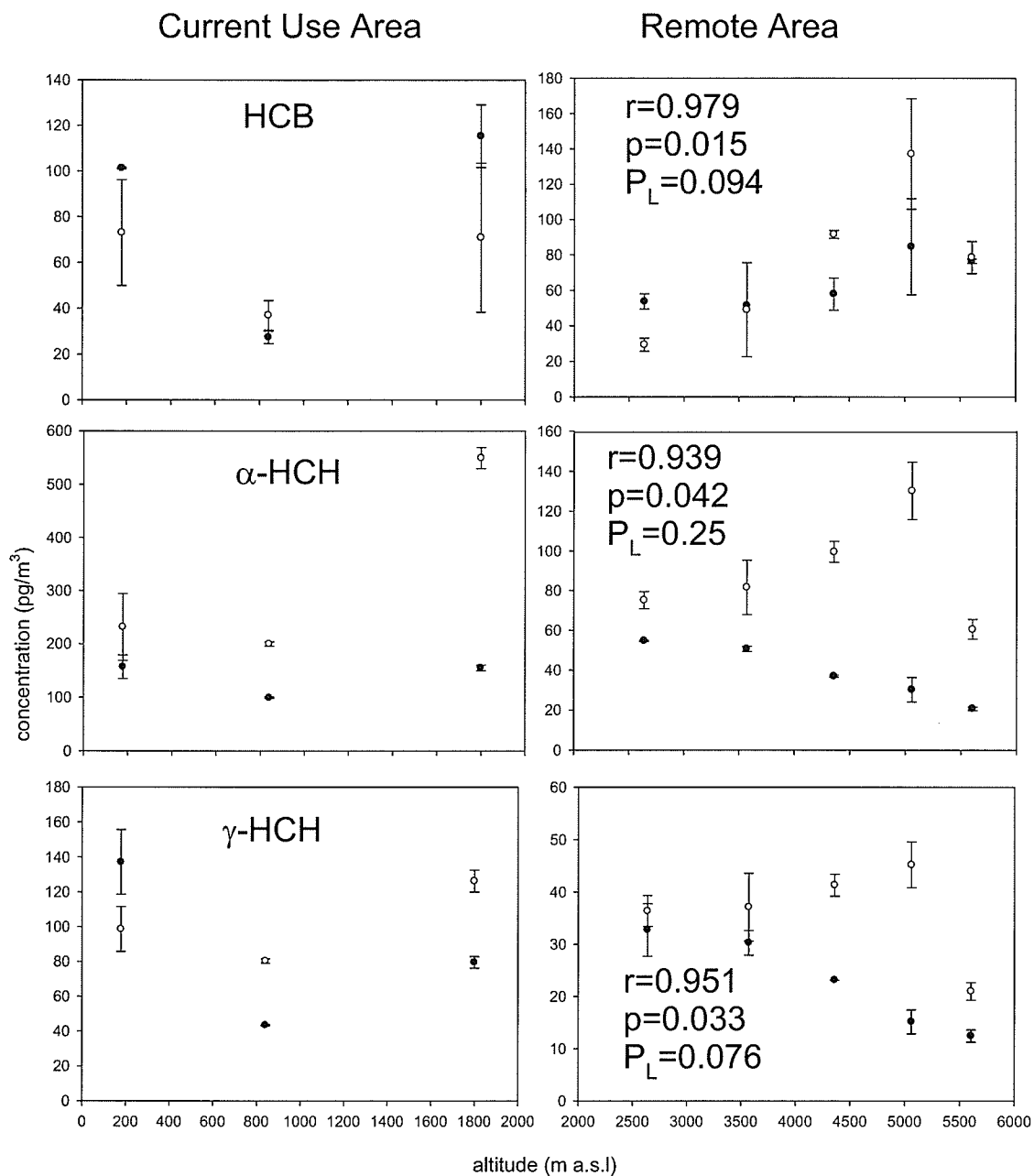
Figure 3: Seasonal and altitudinal atmospheric concentrations of volatile POPs, HCB, α and γ-HCH in current use and remote regions of the central Himalaya. r (correlation coefficient), p (statistical significance) and vapour pressure (P$_L$) are also given for the summer concentrations between 2600 and 5000m a.s.l. Bars indicate ranges of duplicates.
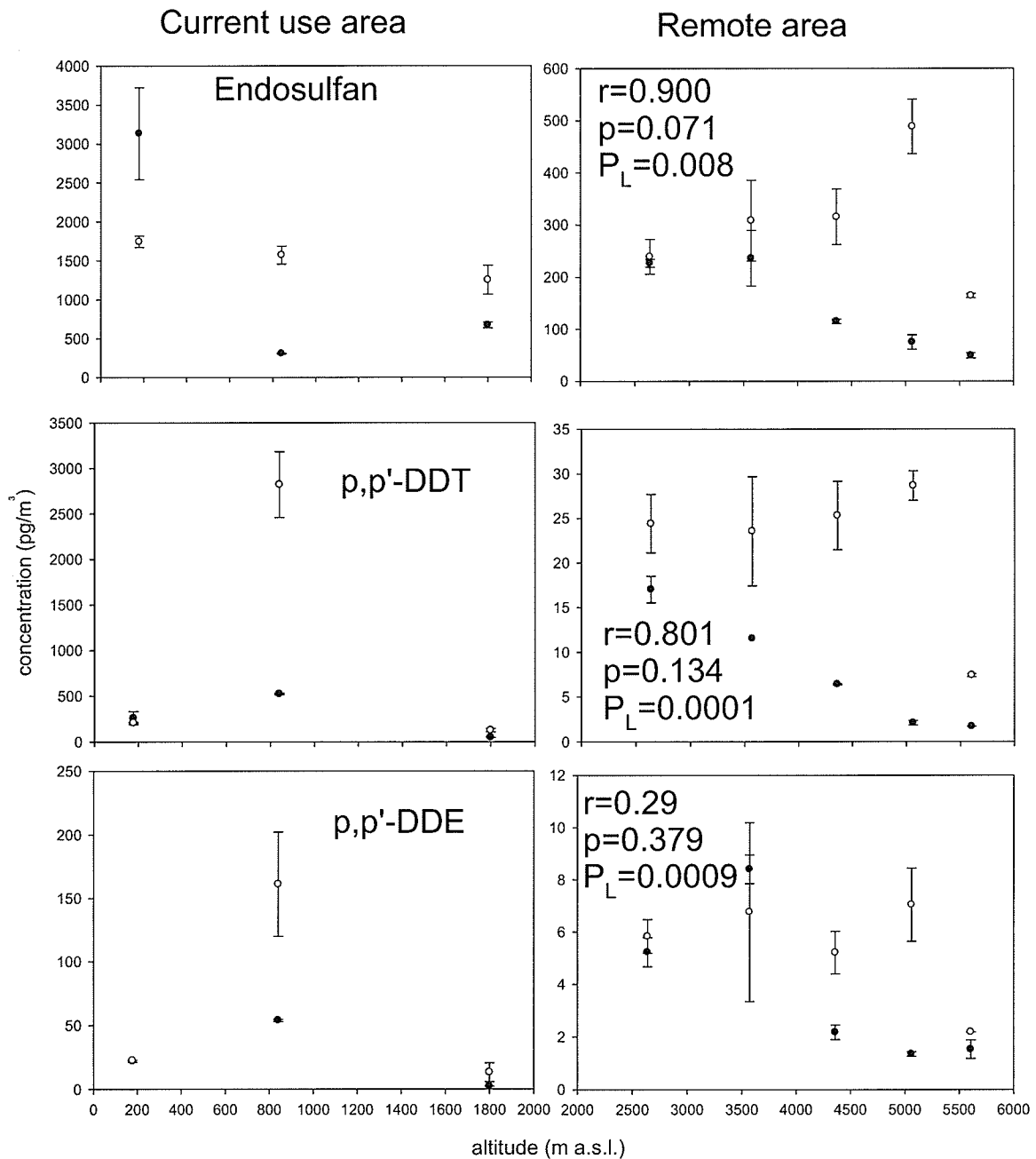
Figure 4: Seasonal and altitudinal atmospheric concentrations of less volatile POPs, endosulfan, p,p'-DDT and DDE in current use and remote regions of the central Himalaya. r (correlation coeffiecit), p (statistical significance) and vapour pressure (P_L) are also given for the summer concentrations between 2600 and 5000m a.s.l. Bars indicate ranges of duplicates.

Soil. Figure 4 shows soil concentrations normalized for carbon content and moisture. Highest levels of chemicals were found at the forested site at 2360m a.s.l. Levels of DDT and DDE decline from that site to a minimum at 5400m a.s.l.
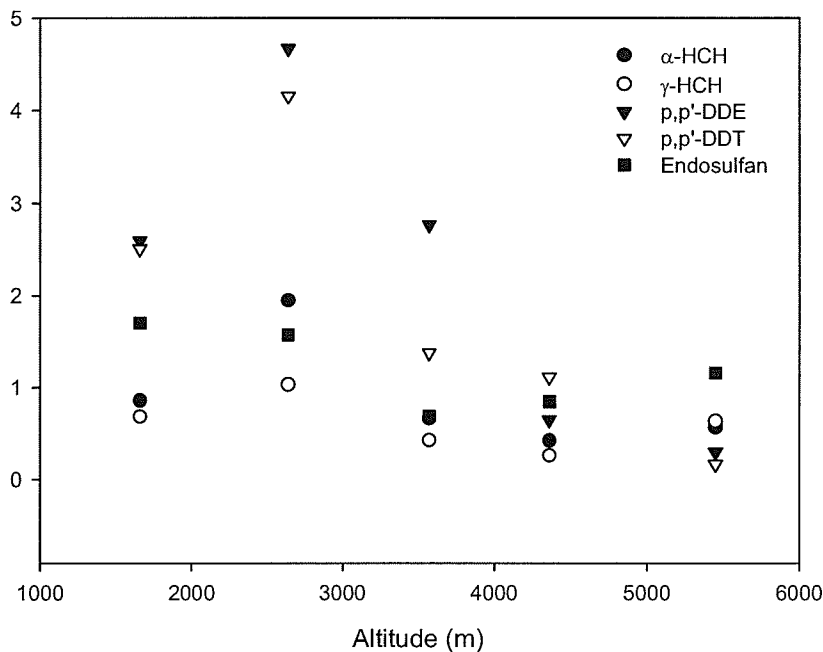
Figure 4: Pesticide concentrations in soil on a ng/g carbon dry weight basis as a function of altitude.

Discussion

Higher summer atmospheric concentrations. Hexachlorobenzene is an excellent chemical marker as it is found in reasonably uniform concentrations in the remote global atmosphere (*17*). The fact that HCB showed similar concentrations during both seasons indicates that the samplers are giving a reasonably accurate reflection of actual atmospheric concentrations of chemicals. During summer in the Indian sub-continent, the atmospheric movement is overwhelmingly from the south due to the thermal forcing of

the monsoon. The significantly higher atmospheric concentrations coincide with the summer deployment time implicating the Indian monsoon as the driving force for chemical movement to the Central Himalaya. The southerly air mass movement strongly links the Indian Subcontinent with atmospheric contaminants up to 5000m a.s.l. Chemicals of lower volatility such as DDT and DDE are also moving into the high alpine regions though their concentration increases over altitude do not appear to be significant (p>0.05) . This is in contrast to results from the Canadian Rocky Mountains where these chemicals are not found to be enriched in the air at high altitude (*30*). Altitudinal enhancement of semi-volatile chemicals in temperate mountains is thought to be driven by orographic enhancement of precipitation and consequent increase in chemical flux. Because this occurs during the winter, differences in chemical volatility will play a larger role as to which chemicals will move atmospherically to high altitude. As the chemical enrichment in the Central Himalaya occurs during the summer, it is not surprising that less volatile compounds will move to higher elevation. Differences observed between subtropical and temperate zone mountains is also likely due to the higher temperatures observed in this region. Interestingly we see that snow deposition is not playing a role in chemical deposition. During snowmelt we would expect chemicals in the snowpack to volatilize enhancing their atmospheric concentration. As the snow deposited and melted completely in the entire transect during the winter deployment season it is surprising that we did not observe any enrichment. This may be due in part to low levels of snowfall in this region of the Himalaya and the direction of the air mass. However a more plausible reason for such strong seasonal differences may be due to the height of the boundary layer in the different seasons.

Boundary Layer. We observed the same upper elevation limits of chemicals regardless of vapor pressure indicating an upper level atmospheric barrier in summer. HCB is once again a valuable marker not only for its uniformity in the atmospheric environment, but also in its ability to move into the upper troposphere due to its resistance to atmospheric degradation and deposition (*31*). We hypothesize that lower tropospheric air is moving to higher than normal altitude in the summer time due to thermal and mechanical forcing (*see* Figure 4). With the influence of the summer Indian Monsoon and enhancement by the "Tibetan Chimney", the atmospheric boundary layer is pushed to higher elevation when the northerly moving airmass impacts the Himalaya and is forced upwards. This is supported by a study which observed carbon monoxide at 150hPa over the Tibetan Plateau during the Indian monsoon (*21*). As these chemicals could not have come from the Tibetan Plateau itself because of extremely low population density, it is believed that these chemicals came from the Indian subcontinent. Conversely in winter, air moves away from the Tibetan Plateau when the airmass moves along the Himalaya the boundary layer moves to a more common elevation for the boundary layer in the 700-800hPa range. This is supported by the observed reduction of chemicals which do not favour the upper troposphere and the consistent HCB concentrations in the atmosphere in both seasons.

In summer the atmospheric boundary layer moves up to 5000m a.s.l. as observed by the increasing concentrations of all chemicals up to that elevation. At the 5600m a.s.l. site we observe a decrease in atmospheric concentrations of all chemicals, but more marked concentration decreases for less volatile compounds such as p,p'-DDT, p,p'-DDE and endosulfan. This observation is supported by studies by Valsecci et al. (*32*) who found a decoupling of the monsoon above 5050m a.s.l. (the same site used in our study) by

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monitoring major ions in precipitation from that altitude to 7000m a.s.l. on Mt. Everest. Valsecci et al. observed that major ion in precipitation above 5050m a.s.l. was due to "local breezes" and free tropospheric air (32). Similarly we observe the typical "grass hopper effect" where more volatile chemicals move more freely into higher elevations when compared to less volatile chemicals. The effect of temperature and pressure on the sampling rate of PAS cannot be used to explain these differences.
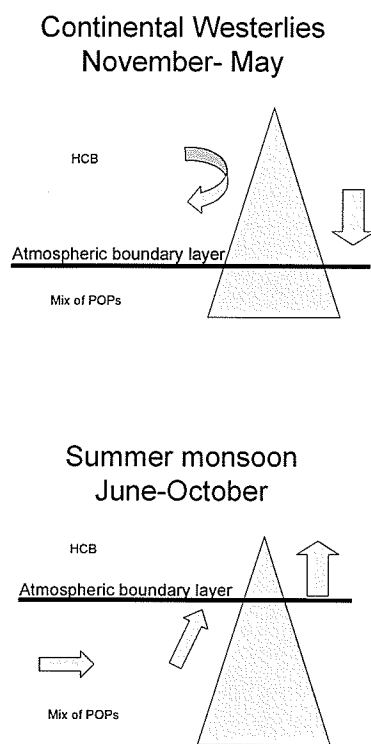

Figure 4: A schematic showing thermal and mechanical forcing resulting in heightened boundary layer during summer in Central Himalaya.

Higher atmospheric concentrations in remote regions during monsoon. An interesting feature of our observations is the altitudinal enhancement of chemicals with

respect to altitude in summer, which is significant for more volatile compounds but insignificant for less volatile compounds. Altitudinal atmospheric enrichment is usually caused by deposition followed by selective revolatalization. Preferential altitudinal deposition is usually caused by orographic precipitation increases and lowered temperatures. In the case of Great Himalaya, precipitation is reduced due to rain out in the southerly ranges that are up to 3500m a.s.l. These data are based on observations from government of Nepal weather stations that are typically situated in mountain valleys (*23*). This may bias the precipitation amounts as ridgelines have been found to give typical orographic increases in precipitation (*33*). Nevertheless, precipitation amounts at the high elevation sites in our study are remarkably low. One would think that a preferential mechanism for deposition does not occur. Recent observations by Daly et al. have noted that precipitation temperature may play a strong role in the deposition mechanism (*34*). Although there is little precipitation in the region, low level cloud and fog are typical occurrences in the high altitude regions during the monsoon (*32,35*). Valsecci observed that during monsoon precipitation collection, condensation was collected rapidly (*32*). It is not inconceivable that cooling as a result of elevation gain could preferentially condense fog onto our passive sampling media altitudinally. Several studies have further concluded that fog can be potentially supersaturated with chemicals when simply modelling using droplet size (*36*). Although fog deposition has not been well studied in this region it is entirely possible that this is an important mechanism for atmospheric deposition of pesticides in high altitude regions of the Himalaya. Further studies to investigate the direct role of fog are warranted.

Soil. Concentrations of p,p'-DDT and DDE at the 841m a.s.l. site were found to be over 6 μg/g carbon normalized. This region is known to be malaria prone and may have received recent application for this purpose. Soil concentrations decrease quickly between 841m a.s.l. and 1880m a.s.l. even though air concentrations of HCH increase between these 2 sites. Highest concentrations of all the chemicals from the 1880m a.s.l. site and upwards were found at 2600m a.s.l. Both p,p'-DDT and DDE were the compounds found in the highest concentration at this altitude and are the ones most likely to be affected by sequestration by the forest due to their high K_{OA} values. From the 2600m a.s.l site upwards, chemical concentrations tend to decline. Chemicals of all volatilities showed close correlation with levels of forestation in the remote regions. Above the tree line (4300 m a.s.l.) only more volatile chemicals show some slight enrichment. Soil carbon content appears to be reasonably consistent across the transect even though the vegetation changes drastically so carbon normalization is not playing a key role in the observed concentrations when compared to level of forestation. In fact, the lowest organic carbon content was found at the lowest elevations most likely due to intensive agriculture. Similar trends have been observed in Western Canada (*34*) where orographic precipitation rates are observed. This lends more evidence to the forest itself as an important sink for contaminants. This has been documented in the literature (*37*).

Source region air and soil. In this region there is less of a trend with respect to altitude as the air and soil concentrations are likely determined by local usage. Local usage of endosulfan appears to be very high with p,p'-DDT being exceptionally high at 841 m a.s.l. Although p,p'-DDT usage has in recent years been in decline in Nepal, it is likely to rise again, as the World Health Organization (WHO) has recently changed its policy

sanctioning further usage of p,p'-DDT for mosquito control in malaria prone regions (*38*). Although the WHO is planning for an indoor spraying program for malaria prophylaxis in order to reduce usage when compared to outdoor spraying, it is almost certain that is being used sparingly. Furthermore, Nepal is expected to begin manufacture of DDT soon. It is imperative that these chemicals be appropriately restricted (not used for agriculture) and people trained in their proper usage. In any case, there is a strong need to monitor the fate and effects of pesticide usage especially in current use areas where chemical use is heavy. The use of extremely persistent chemicals in the environment may possibly impact agricultural areas and the Himalayan mountain ecosystems for years to come.

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IV

Atmospheric Transport of Mercury to the Tibetan Plateau

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The Tibetan Plateau (including the Himalayas) is one of the most remote and cold regions in the world. It has very limited to nonexistent industry but is adjacent to the two most populous and rapidly industrializing countries (China and India) and thus provides a unique location for studying the atmospheric transport of mercury. Here we report the first study on the atmospheric transport of mercury to the Tibetan Plateau. The total mercury profiles in four snowpits from glaciers above 5700 m asl along a southwest-northeast transect across the central Tibetan Plateau were obtained in 2005–2006. In general, the total mercury concentrations in the snow samples ranged from <1 to 9 ng L^{-1}, increasing northeastward from the southernmost site at Mount Everest. Higher total mercury concentrations were found in the snow deposited in the nonmonsoon season, as indicated by seasonal variation of $\delta^{18}O$ values and major ions in the snowpack. The annual atmospheric depositional flux of total Hg was estimated to range from 0.74 to 2.97 μg m^{-2} yr^{-1} in the region, the majority of which occurred via particulate matter deposition.

Introduction

Long-range transport is an important source of mercury (Hg) in many remote regions. Following the discovery of the tropospheric mercury depletion events (MDEs) in the Arctic (*1*) and Antarctic (*2*) regions, the photochemically induced oxidation of long-range transported gaseous elemental mercury (GEM) during polar sunrise is thought to provide an important mechanism of Hg deposition into the frozen surface in the polar regions (*3, 4*). However, much of the deposited Hg may not enter the aquatic or terrestrial environment due to its subsequent photoreduction in snow (*5, 6*). Until now, there has been no report on the long-range transport of Hg to another remote, cold climate region, the Tibetan Plateau of Asia.

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With an average elevation of over 4000 m asl, the Tibetan Plateau is the largest and highest plateau in the world, home to the highest mountain range, the Himalayas, and the highest mountain, Mount Everest (or *Qomolangma* in Tibetan). Unlike the Arctic where Hg transport via other pathways (e.g., rivers, permafrost melting, oceanic circulation) is also important (*7*), atmospheric transport is essentially the only external source of Hg to the Tibetan Plateau because of its high altitude, sparse human population, and minimal to nonexistent industrial activities. Furthermore, the plateau is adjacent to the two most populous and rapidly industrializing countries in the world (China and India), is subject to seasonal changes in air mass, and thus provides a unique opportunity to study the global and regional atmospheric transport of Hg. As snowmelt from the Tibetan Plateau is the source water for some of the largest rivers in the world, the Hg transported to the plateau may also play an important role in the global biogeochemical cycle of Hg, as well as in ecosystem and human health.

South Asia is mainly influenced by continental air masses originating over central Asia, and equatorial-maritime air masses originating in the Pacific and Indian Oceans. The Tibetan Plateau plays a pivotal role in the climatology of this region, acting as a heat sink in winter and heat source in summer causing a complete reversal of weather patterns (*8*). Major meteorological components of the southern and central Tibetan Plateau are the Indian monsoon and the Tibetan anticyclone during summer and subtropical jet stream at other times (*8, 9*). During the winter months, high-pressure drives cold and dry air away from the plateau (winter monsoon) and blocks the midlatitude westerly jet stream, splitting it into two currents that flow south and north of the plateau. In summer, low-pressure caused by heating over the plateau induces a supply of moist air from the Indian and Pacific Oceans to the continent (summer monsoon).

Here we report the first study on the Hg distribution profiles in snowpits from glaciers above the atmospheric boundary layer at sites in excess of 5700 m asl along a southwest-northeast transect across central Tibetan Plateau. At these altitudes both winter and summer precipitation are in the form of snow. Our analysis suggests that the Hg is deposited on the plateau primarily associated with particulate matter.

Experimental Section

Study Area. Four snowpits were sampled along a southwest-northeast transect on the Tibetan Plateau, covering from the south edge of the Plateau to the north boundary of the summer Indian Monsoon (Figure 1). Snowpit ER1 (28°01.190′N, 86°57.779′E, 6536 m asl) was sampled from the East Rongbuk Glacier on the northern slope of Mt. Everest (peak height: 8844 m asl) on April 21, 2005. Snowpit NQ1 (30°28.079′N, 90°39.041′ E, 5800 m asl) was sampled from the Zhadang Glacier on the northeastern slope of Mt. Nyainqentanglha (peak height: 7102 m) on June 17, 2006. This site was visited again on October 16, 2006. Snowpits GL2 (33°36.361′N, 91°10.454′E, 5750 m asl) and GL3 (33°57.227′N, 91°16.985′E, 5823 m asl) were sampled from the Guoqu Glacier in the north of Mt. Geladaindong (peak height: 6621 m) on November 5, 2005.

The East Rongbuk Glacier on Mt. Everest in the Himalayan Range is at the boundary of the Indian monsoon-dominated wet and warm climate in the south and the westerly jet stream-dominated continental climate in the north. Snowfall
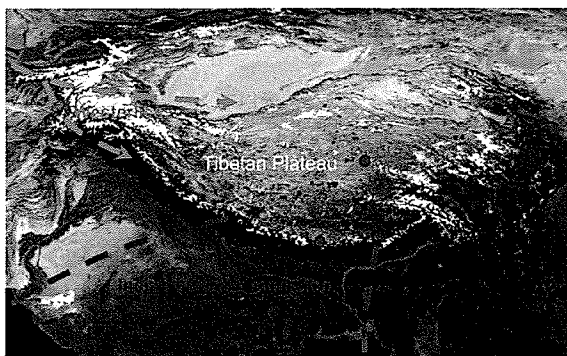
FIGURE 1. Map of the sampling locations. ER: Mt Everest; NQ: Mt. Nyainqentanghla; GL: Mt. Geladaindong.

at the glacier is caused by moisture transported by the Indian monsoon and local moisture from short distance convective air mass in summer (July to September), and by the westerly jet stream during other seasons (9).

Mt. Nyainqentanglha in the Nyainqentanglha Range is approximately 380 km northeast of Mt. Everest, on the south shore of Lake Nam Co (4718 m asl), the second largest lake on the Tibetan Plateau. The climate is in transition between semihumid and semiarid. Most of the snowfall occurs between June and October caused by long-range transported moisture via the India monsoon and local moisture from the nearby Lake Nam Co (10).

Mt. Geladaindong of the Tanglha Range is located in the central region of the Tibetan Plateau, the snowmelt from which is the source water of the Changjiang (Yangtze River), the fourth largest river in the world. It represents the northernmost extent of the summer Indian monsoon (11). Its summertime precipitation is derived from the moisture transported by the Indian monsoon and regional convection, with limited precipitation during the winter due to the occasional influx of westerly disturbances (12).

Snowpit Sampling. At each sampling site, a snowpit was dug into the snowpack and snow samples were collected at a vertical resolution of 5–10 cm using a precleaned plastic scoop. Snowpit ER1 was sampled in duplicate, and NQ1, GL2, and GL3 in quadruplicate. The return trip to NQ1 was sampled in triplicate. Field blanks were also taken during the sampling. The samples were stored in double bagged, precleaned 500-mL amber glass jars with Teflon liners and spiked with 250 μL of CMOS grade HCl (J.T. Baker) or in 50-mL new polypropylene Falcon (VWR) tubes spiked with 100 μL of BV-III grade HCl (Gaoheng, China). Both types of bottles were randomly tested for Hg concentrations before being used in the field; the Hg concentrations in the bottles were always less than the 0.2 ng L^{-1} detection limit. The two-person "clean hands, dirty hands" Hg sampling protocol (13) was followed strictly during the sampling; polypropylene cleanroom suits and nonpowder vinyl cleanroom gloves were worn at all times to minimize potential contamination of samples. The snow samples were shipped in coolers to the laboratories for the analysis of total Hg, δ^{18}O, particulate matter, major ions, among many others. The density of the snow samples was measured on site.

Sample Analysis. The analysis of total Hg concentrations (Hg$_T$) in the snowpit samples was carried out at the metal-free Class 100–1000 Ultra-Clean Trace Elements Laboratory (UCTEL) at the University of Manitoba. The melted snow samples were analyzed by cold vapor atomic fluorescence spectroscopy (CVAFS) on a Tekran 2600 mercury analyzer, following the U.S. EPA Method 1631 (14). The method detection limit was <0.2 ng L^{-1}. Certified reference materials ORMS-2 and ORMS-3 (National Research Council of Canada)

were used for quality control and were within 5% of their certified values. Further QA/QC was conducted as part of the interlaboratory comparison program under the Collaborative Mercury Research Network (COMERN) of Canada. The concentration was reported as ng Hg L^{-1} of melted snow.

δ^{18}O was measured on a MAT-253 Isotope mass spectrometer ($\pm$0.2‰ precision) via the standard CO$_2$ equilibration technique. All data were reported in the standard δ notation vs the Vienna Standard Mean Ocean Water (SMOW). Ca^{2+} was analyzed on a Dionex ISC 2000 ion chromatograph using an IonPac CS12A column, 20 mM MSA (methanesulfonic acid) eluent and CSRS suppresser. SO$_4^{2-}$ and Cl$^-$ were analyzed on a Dionex ISC 2500 ion chromatograph using an IonPac AS11-HC column, 25 mM KOH eluent, and ASRS suppresser. The detection limits were 1 μg L^{-1} for all ions.

Particulate matter in the snow samples was analyzed on a Beckman Multisizer 3 Coulter Counter with a 50-μm diameter aperture, following a procedure similar to that described elsewhere (15). The particles were counted in 300 channels between 1 and 30 μm diameter (i.e., 2% to 60% of the aperture diameter) on a logarithmic size scale. Only particulate matter less than 10-μm diameter (PM$_{10}$) will be reported in this study. Particulate matter of other sizes showed similar distribution profiles.

Wind Trajectory Analysis. Average 500-hPa wind fields in winter and spring (December–May) from 1948 to 2005 over the Tibetan Plateau were mapped using the data from the National Centers for Environmental Prediction/National Center for Atmospheric Research (NCEP/NCAR; NOAA, Camp Springs, MD) reanalysis (16). A 5-day backward 400-hPa wind trajectory analysis was also done to show the movement of the dust storm on January 6, 2006, which was the largest dust storm over the region ever recorded by the satellite monitoring program (17).

Results

The profiles of total mercury (Hg$_T$), along with other chemical measurements, of the four snowpits are shown in Figures 2–4. The two replicate snowpits from Mt. Geladaindong (GL2 and GL3), which were located 1 km away from each other, showed similar chemical profiles (Figure 4).

Seasonal Variations of δ^{18}O Values in the Snowpits. Seasonal differences in δ^{18}O values have been well documented in fresh snow and snowpit samples taken from glaciers in the Tibetan Plateau region (18, 19). In general, more negative δ^{18}O values occur in snow during the summer monsoon season (July–September) due mainly to the "amount effect" (or "precipitation effect"), while less negative δ^{18}O values occur in spring snow (March–May). This trend is clearly demonstrated in snowpits taken from the glaciers in this study. The 1.70-m Snowpit ER1 from Mt. Everest recorded a 2-year snow deposition, with seasonal changes in δ^{18}O values ranging from −20.0‰ during summer monsoon to −10.7‰ in spring. The 0.85-m snowpits GL2 and GL3 from Mt. Geladaindong showed a 1-year snow accumulation, with δ^{18}O values ranging from −24.6‰ during summer monsoon to −8.0‰ in spring. The seasonal variations of δ^{18}O values in Snowpit NQ1 from Mt. Nyainqentanglha showed a similar pattern with lower values in summer than in spring. The δ^{18}O profiles also indicated Mt. Everest received more (in terms of vertical thickness) monsoon-induced snowfall than Mt. Geladaindong, reflecting their distances from the Indian Ocean. In addition to the amount effect, low temperature in winter (December–February) could also result in lower δ^{18}O values in snow; however, very limited snowfall occurs during winter over the Tibetan Plateau.

The seasonality of the snow deposition as revealed from δ^{18}O values agreed very well with the vertical profiles of major ions Ca^{2+}, SO$_4^{2-}$, and Cl$^-$ (Figures 3 and 4), with increasing
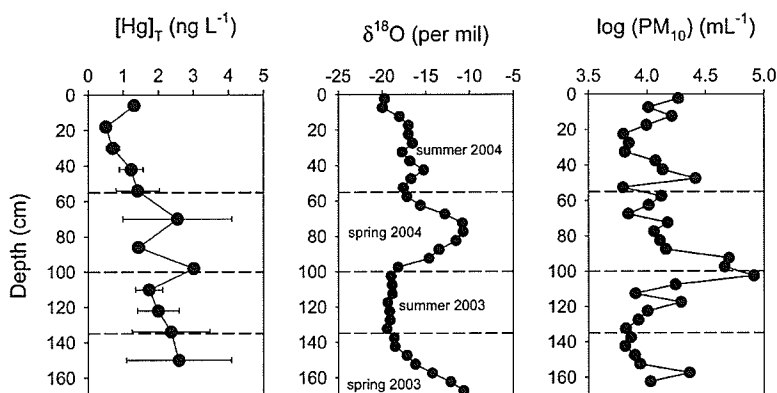
FIGURE 2. Vertical profiles of Hg_T, $\delta^{18}O$, and PM_{10} in Snowpit ER1 from Mt. Everest (March 2005). Spring 2005 snowfall was blown away from the site.
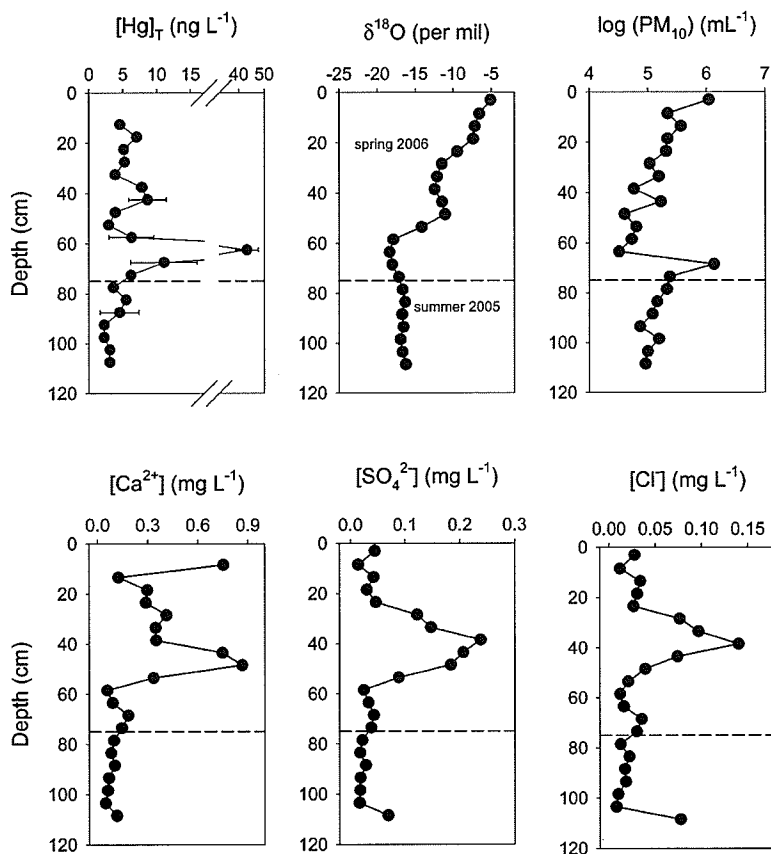

FIGURE 3. Vertical profiles of Hg_T, $\delta^{18}O$, PM_{10}, and some major ions in Snowpit NQ1 from Mt. Nyainqentanglha (June 2006).

concentrations in nonmonsoon snow, consistent with the previous result (18).

Variations of Hg_T Concentrations in the Snowpits. In general, the Hg_T concentrations in the snowpits were very low, ranging from <1 ng L^{-1} to 9 ng L^{-1}, similar to the levels reported for the snowpacks along the Arctic coasts in the absence of MDEs (20). Snowpit ER1 from Mt. Everest had the lowest Hg_T throughout the depth ($<1 - 3$ ng L^{-1}); higher Hg_T concentrations were found in Snowpits NQ1, GL2, and GL3.

In all the four snowpits, the concentration of Hg_T varied greatly with depth, showing a variation pattern similar to that of $\delta^{18}O$ values and PM_{10} concentrations in snow (Figures 2 and 4). In particular, a Hg_T peak of as high as 43.2 ng L^{-1} was observed in Snowpit NQ1 at about 62.5 cm below the surface (Figure 3). As detailed below and shown in Figure 5,

this depth corresponded with a distinctive brown-yellowish dust layer.

Replicate measurements at the same depth of the same snowpit also showed a seasonal trend in the Hg_T variability, as indicated by the error bars ($\pm$ standard deviation) in Figures 2–4. Samples taken at the lowest $\delta^{18}O$ values (corresponding to the summer monsoon season) showed less variability, whereas samples taken at higher $\delta^{18}O$ values showed higher variability.

Discussion

Deposition of Particulate Mercury. Following the discovery of the tropospheric MDEs (1), intensive studies have suggested that the atmospheric Hg deposition in the Arctic occurs mainly via in situ photochemical oxidation of the long-range
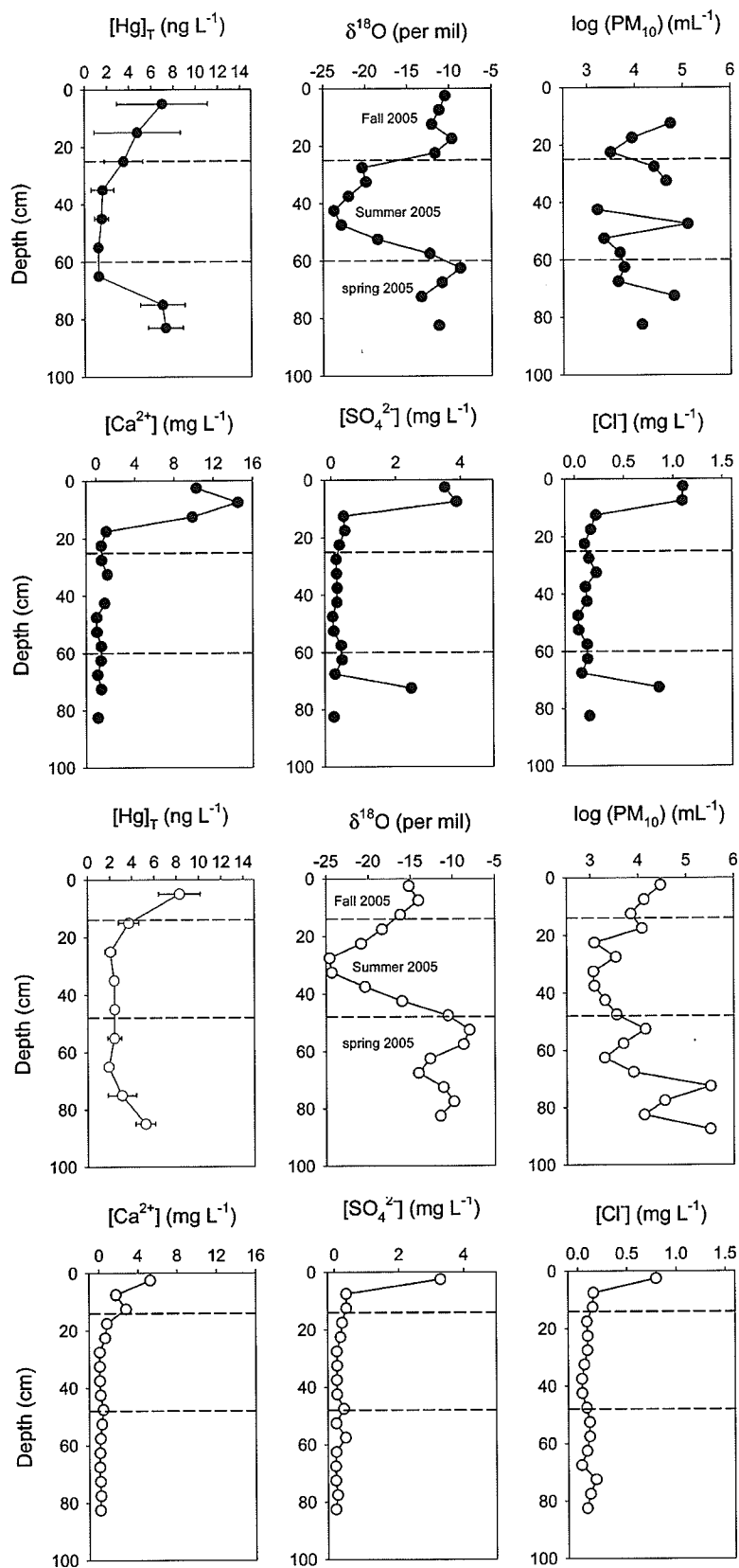
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FIGURE 4. Vertical profiles of Hg$_T$, δ^{18}O, PM$_{10}$, and some major ions in Snowpits (A) GL2 and (B) GL3 from Mt. Geladaindong (November 2005).

transported GEM (4). Our snowpit data from the Tibetan Plateau, however, suggest a different mechanism is occurring on the Tibetan Plateau. Although no information is available at this time on the Hg speciation in the atmosphere over the plateau, we believe that the deposition of Hg is driven primarily by the atmospheric particulate load which exhibits
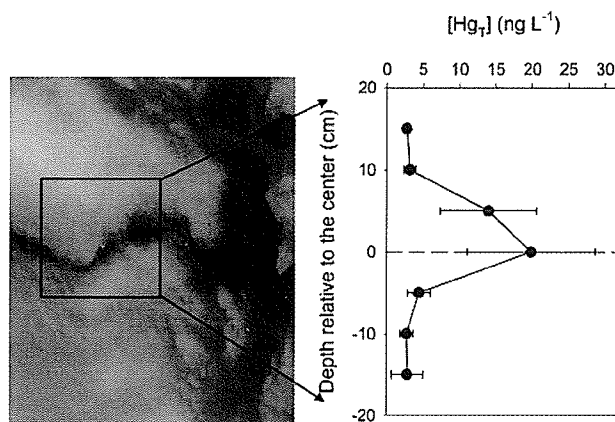
FIGURE 5. (A) A picture showing the dust layer in Snowpit NQ1 from Mt. Nyainqentanglha. (B) Vertical profile of Hg_T across the dust layer (October 2006).

dramatic seasonal differences over the plateau.

As shown in Figures 2—4, the particulate matter load in the atmosphere over the Tibetan Plateau differed by 1—3 orders of magnitude between the summer monsoon season and the nonmonsoon season. During the summer monsoon months, the air mass over the central-southern Tibetan Plateau comes from the Indian Ocean. The increased precipitation during the monsoon effectively removes particulates in the atmosphere, resulting in the low concentrations of particulate matter (Figures 2—4). The particulate matter load in the atmosphere over the Tibetan Plateau usually peaks in the nonmonsoon season (Figures 2—4) due to the dust storms transported from South and central Asia by the westerly jet stream. As a result, major ion composition in fresh snow and snowpack in the Himalaya and Tibetan Plateau region has been shown to be influenced by the Indian monsoon in summer and Asian dust in winter (Figures 3 and 4; also refs 18, 19).

The particulate matter driven Hg deposition is most clearly demonstrated by the sharp Hg_T peak at Snowpit NQ1 from Mt. Nyainqentanglha at a depth where a distinctive, brown-yellowish dust layer was present. To further confirm that the high Hg_P was indeed due to the dust layer, the site was revisited on October 16, 2006, 4 months after the original snowpit sampling. A 30-cm cross-section around the dust layer (Figure 5A) was carefully resampled at a vertical resolution of 5 cm and analyzed for Hg_T. The profile (Figure 5B) showed a convincing trend; the Hg_T concentration was the highest near the center of the dust layer, decreasing both upward and downward.

The particulate matter-driven Hg deposition in the Tibetan Plateau is further supported by the observed increase of Hg_T in the snowpack on Mt. Geladaindong and Mt. Nyainqentanglha during the winter compared to Mt. Everest as a result of their closer proximity to arid regions and higher particulate load (Figure 1). It also explains the increase in variability of Hg_T in the snowpack during the high atmospheric particulate matter season (Figures 2—4), due to the heterogeneous nature of particulate matter deposition.

Sources of Particulate Hg over the Tibetan Plateau. The particulate Hg over the Tibetan Plateau could result from several sources: (1) "in-situ" particulate mercury (Hg_P) produced from the oxidation of GEM and the subsequent scavenging of the reactive gaseous mercury (RGM); (2) "ex-situ" Hg_P associated with Hg-containing particulate matter from South and Central Asia or locally from the Himalayas. Unfortunately because of the logistical limitations of working at high latitude glaciers, no Hg speciation data were collected during the present study. As a result, the relative importance of these two sources of Hg_P over the Tibetan Plateau remains unknown.

The in situ oxidation of tropospheric GEM to RGM by oxidants such as O_3 and $\cdot OH$ radicals is known to be slow (21, 22). The oxidation is promoted in the Arctic and Antarctic during polar sunrise due to the photochemical formation of halogen radicals such as $Br\cdot$ and $BrO\cdot$, resulting in the MDEs (1, 4). While MDEs have not been reported in nonpolar areas, recent studies suggest that higher BrO concentrations might be present in the free troposphere, particularly in the upper troposphere or lowermost stratosphere (21, 23). Over the Tibetan Plateau, particularly above the atmospheric boundary layer of the glaciers sampled in this study, it is plausible that the oxidation of GEM may occur to a greater extent due to the high BrO concentrations, as well as high intensity of solar UV radiation, and high levels of tropospheric ozone (70—80 ppbv (24), compared with ~40 ppbv in the Arctic (1)). Furthermore, halogen salts from widespread saline lakes on the Tibetan Plateau might provide an additional source of bromine radicals in the troposphere.

The ex situ sources of Hg_P include the dust transported by the westerly jet stream, as well as that produced from the local Tibetan crustal particles. The westerly jet stream in winter can transport particulate matter from South and Central Asia and as far as the Sahara Desert and North Africa (25). In addition, since the Tibetan Plateau has its own dust storms during winter and spring (25), some of the particulate Hg may originate locally from the Plateau. The contribution of ground-originated particles in Hg_T in rainwater has been reported by the strong correlation between Hg_T and ^{210}Pb (a particle tracer) in a remote area of Wisconsin (26).

Figure S1 (see the Supporting Information) shows a backward air mass trajectory analysis leading to the dust layer seen at Snowpit NQ1 (Figure 5A). In January 2006, the Tibetan Plateau recorded the largest dust storm since the availability of satellite observations (17). As shown in Figure S2 (see the Supporting Information), the wind during that dust storm can be tracked at least to Iran and Afghanistan and had traveled over thousands km in 5 days before reaching Mount Nyainqentanghla. Snowpit NQ1 was sampled from Mount Nyainqentanghla in June (Figure 3) and October (Figure 5), 2006. Seasonality analysis based on the $\delta^{18}O$ suggested that the dust layer in Figure 5A was indeed from the dust storm in January 2006. A similar trajectory analysis has shown that particulate Hg can be transported some 500—800 km northward from the source areas in Central Europe to Sweden (27).

Atmospheric Depositional Flux. Assuming there was no postdepositional change in the Hg concentration in the snowpit (i.e., deposited snow preserves the same chemistry as fresh snow), the atmospheric depositional fluxes at the three sites could be estimated from the profiles of (Hg_T) and snow density. The estimated annual deposition flux ranged

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TABLE 1. Seasonal and Annual Atmospheric Deposition Fluxes of Mercury at the Three Snowpit Sites

site	year	monsoon season (μg m^{-2})	nonmonsoon season (μg m^{-2})	annual (μg m^{-2} yr^{-1})
ER	2003-2004	0.31	0.43	0.74
NQ	2005-2006	0.52	2.45	2.97
GL	2005	0.14	0.85	0.99

from 0.74 to 2.97 μg m^{-2} yr^{-1} at the three sites (Table 1), which is similar to the lower end of the Hg deposition rate in the Arctic Ocean (28) and close to the global natural atmospheric deposition rate (2−5 μg m^{-2} yr^{-1} (29)). Because of possible postdepositional loss (see below), this estimate is likely conservative. Consistent with the Hg concentration data, the flux data also suggest that the atmosphere deposition of Hg occurs predominately in the nonmonsoon season associated with high particulate loads.

It has been observed in the Arctic that the majority of the Hg(II) deposited in fresh snow during the MDEs may undergo rapid photoreduction and thus release back to the atmosphere in the form of GEM (5, 6). Such rapid photoredution is promoted by the dominance of RGM during the MDEs. In the Tibetan Plateau, the loss due to photoreduction may not be as significant as in the Arctic, as Hg is deposited mainly in the form of Hg$_P$. A comparison of Figures 3 and 5 indicates that the peak Hg concentration in the dust layer of the snowpit from Mount Nyainqentanghla decreased from 43.2 ng L^{-1} to 19.9 ng L^{-1} from June 17, 2006 to October 16, 2006. Such differences are not necessarily due to photoreduction, as the penetration of the solar radiation to the dust layer (62.5 cm below the snow surface as of June 17, 2006) is limited (30). It is more likely due to the spatial heterogeneity of the snow deposition, as well as the postdepositional release due to snowmelting. The latter is of particular interest, given that the formation of glacier ice by snow only takes 1−2 years in the region and that intensive glacier melting has been occurring due to global warming in recent decades (31). Since the glacier melting is a major source water of Lake Nam Co, its implication for the unique ecosystem of Lake Nam Co, as well as many other remote alpine lakes on the Plateau, warrants further study.

Acknowledgments

Supporting Information Available

Two figures showing the wind trajectory analysis of the Tibetan Plateau. This information is available free of charge via the Internet at http://pubs.acs.org.

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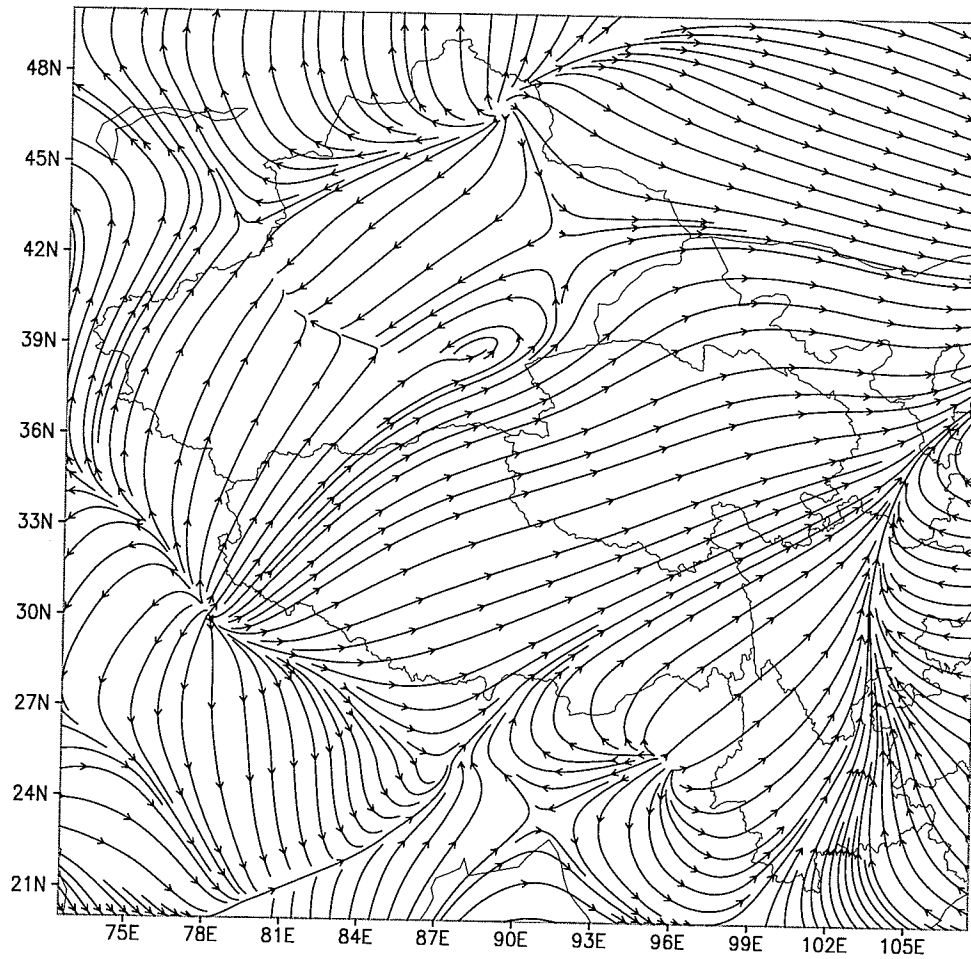
Figure S1. Average 500-hPa wind fields in winter and spring (Dec.-May; 1948-2005) over the Tibetan Plateau (data from NCEP/NCAR).

NOAA HYSPLIT MODEL
Backward trajectory ending at 00 UTC 06 Jan 06
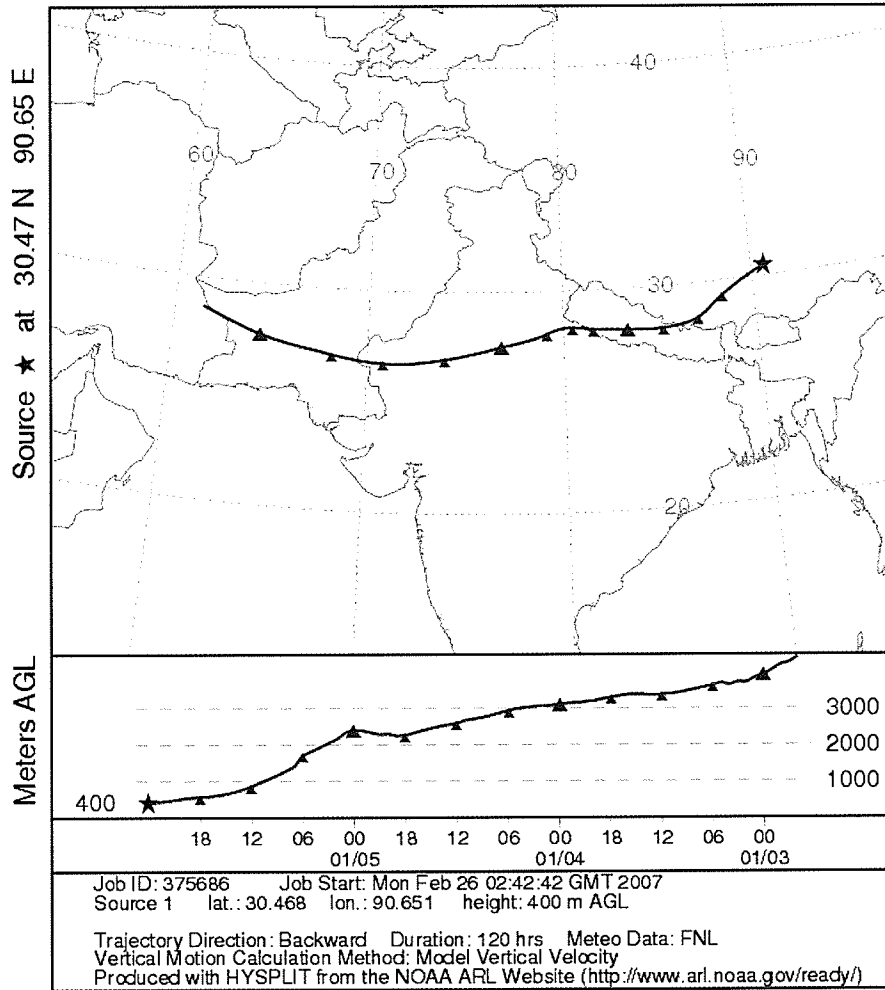### FNL Meteorological Data

Figure S2. 5-day backward wind trajectory analysis (400 hPa) showing the movement of the dust storm in January 2006, the largest dust storm over the Tibetan Plateau since the availability of satellite data. The star shows the location of the NQ1 site.