



Persistent Organic Pollutants Along Environmental Transects in Costa Rica, Chile, Nepal, and Botswana



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Final Report

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Appendix 2: Shunthirasingham, C., T. Gouin, Y.D. Lei, C. Ruepert, F. Wania. Further studies on current use pesticide transport to Costa Rica high altitude cloud forests. Manuscript in prep. 11 pages

Appendix 3: Shunthirasingham, C., B.T. Mmereki, M. Wellington, C. Oyiliagu, Y.D. Lei, F. Wania. Fate of pesticides in the arid subtropics, Botswana, Southern Africa. Manuscript in prep. for submission to *Environ. Sci. Technol.* 25 pages

Appendix 4: Shunthirasingham, C., R. Barra, G. Mendoza, C. Oyiliagu, Y.D. Lei, F. Wania. Spatial variability of semivolatile organic compounds in the Chilean atmosphere. Manuscript in prep. 15 pages

Appendix 5: Loewen, M., S. Sharma, C. Fuchs, F. Wang, F. Wania, D.C.G. Muir, G. Tomy. Seasonal and altitudinal trends of chlorinated pesticides in the Central Himalayan atmosphere. Manuscript in prep. 20 pages

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2 EXECUTIVE SUMMARY

2.1 What have we learned about the fate of persistent organic pollutants in tropical and subtropical environments?

Selected persistent organic pollutants (POPs), in particular organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) were quantified in air and soil samples collected in Costa Rica, Botswana, Chile and Nepal. Concentrations of these POPs in air and soil were generally very low in three of these countries (Botswana, Costa Rica, and Chile), which may be attributed to a combination of factors, including (i) relatively low historical usage of POPs in those countries specifically and in the Southern hemisphere in general, (ii) relatively favorable conditions for the degradation of POPs, such as high temperature and high OH radical concentrations, and (iii) local conditions that favor the mobilization of POPs, such as soils with low organic matter content and high temperatures. In high organic matter soils, higher POP concentrations were often detected, suggesting that a soil's retention capability is a key factor in determining levels of POPs. In tropical countries such soils are often prevalent at higher altitudes, enhancing any mountain cold-trapping effect caused by temperature dependent precipitation scavenging. Concentrations of selected POPs in air and soils of Nepal were much higher than in the other three countries. This may be attributed to: (i) continued significant usage of OCPs in Nepal itself and in neighboring India, and (ii) efficient transport of air masses from the subcontinent into Nepal during the summer monsoon. Although transport of OCPs to the higher elevations of Nepal (and even to the Tibetan plateau beyond) could be established, the highest concentrations in soil are found at middle altitudes, where there is a combination of high contaminant input (usage, high precipitation) and high contaminant retention (high organic matter soil) (Daly *et al.*, 2007). With increasing elevation in Nepal, OCP air concentrations, precipitation rates and soil organic matter decline, countering any mountain cold-trapping effect that may exist.

Active air sampling campaigns in Botswana and Costa Rica did not reveal evidence of seasonal variability in air concentrations driven by natural seasonal phenomena, such as changes in air mass origin, temperature, precipitation or flooding. Instead, for the pesticides in current use the temporal variability appears to be dominated by seasonal variable applications. In Nepal, concentrations in air were highly variable due to the monsoon, with much higher levels of most analytes during the summer, when the air masses originate in India.

2.2 What have we learned about the methods for sampling POPs in the atmosphere?

During the field studies in all four countries, passive air samplers were employed to obtain long term average air concentrations, with temporal resolution ranging from a few months to a year. The strength of relatively small networks of passive air samplers lies in their ability to map – based on a limited number of samples – spatial variability in atmospheric concentrations, which in turn reveals areas of past use, and potentially also continued use, of POPs. Similarly, the absence of major concentration variability in an area or along a transect allows to infer the absence of major contaminant sources. A year-long calibration of passive air samplers, based on both XAD-2-resin and polyurethane foam (PUF), was performed under tropical conditions in the central valley of Costa Rica by comparison with pumped Hi-Volume samples. In Maun, Botswana, XAD-based passive samplers were co-located with an active

HiVol sampler. This yielded the first kinetic data on the uptake of organic contaminants in PAS from tropical locations.

The main weakness of passive air samplers remains the uncertainty introduced to volumetric atmospheric concentrations by the air sampling rate, which may be more strongly influenced by environmental and chemical factors than had been originally anticipated. For example, the amounts of several compounds sequestered in PAS deployed along an elevation gradient in Central Chile increased with elevation, which likely can be attributed to much higher wind exposure of the samplers deployed at higher altitudes.

For relatively low capacity PAS, such as the PUF-based PAS, sampling rates that account for site and time-specific variations arising from environmental factors (wind speed, *etc.*) can be obtained from the rate of loss of so-called depuration compounds, that are spiked onto the sampling medium prior to deployment. As depuration compounds can not be present in ambient air in significant quantities, they are sometimes isotopically labeled versions of the target analytes. While this approach should in principle be also applicable to high capacity samplers, the depuration compounds would have to be much more volatile than the target analytes for notable loss to occur during the deployment period. With increasing difference in volatility, however, the assumption of identical exchange kinetics of depuration compounds and target analytes becomes increasingly tenuous.

In areas where the influence of hexachlorobenzene (HCB) sources on air concentrations can be ruled out, a new normalization method based on the assumption of a spatially and temporally constant hemispheric HCB background concentration allows the derivation of sampling rates for high capacity samplers, that are specific for a particular sampling site and sampling duration (Liu *et al.*, in press). Although this method allows for a more confident comparison of passive air sampler derived concentrations from multiple locations (*e.g.*, along an elevation gradient), this method does not account for potential differences in the sampling rate of different chemicals, a limitation it shares with the depuration compound approach.

The relatively low sampling capacity of PUF for the more volatile POPs under the high temperature conditions prevalent in tropical and subtropical countries, may additionally necessitate the correction for non-linear uptake, *i.e.*, the approach of equilibrium between sampler and atmospheric gas phase. Because this correction requires the knowledge of the temperature-dependent contaminant-specific sampler capacity, it introduces considerable, additional uncertainty.

Evidence is accumulating that some less persistent target analytes, such as chlorpyrifos, trifluralin or pendimethalin, are undergoing degradation while being sorbed to passive air sampling media (Gouin *et al.*, 2007; Hayward *et al.*, in press). Caution needs to be exercised when attempting to quantitatively interpret the amounts of these compounds sequestered in passive air samplers.

2.3 What have we learned about regulatory priorities surrounding chemical pollution?

In several of the countries (Chile, Costa Rica, Botswana), concentrations of POPs were often so low that they likely do not constitute a concern of sufficiently significant national importance to merit expending a large share of the countries' limited regulatory and scientific capacity and financial resources on dealing with them (except possibly in some contaminated

hotspots not being investigated here). In fact, it is conceivable that other issues surrounding organic contaminants are often of much higher national importance. For example, concentrations of pesticides in current use were often much higher than those of the original POPs, even in areas remote from agricultural source areas. As a result, these pesticides are more likely to lead to adverse effects on wildlife than the POPs. In Botswana, PAHs from urban air pollution and wildfires may be a more serious health concern than the presence of POPs at very low levels. It is thus probably advisable to let national concerns drive the scientific and regulatory agenda concerning organic contaminants, rather than expect substantial efforts on internationally prioritized issues, if the latter are of little concern locally.

2.4 What capacity building took place as a result of this project?

Through this project, personnel and students at the University of Botswana gained knowledge in active and passive air sampling, the trace analysis for POPs, and the interpretation of POP air concentrations. The newly acquired capacity is already being used in ongoing research projects within Botswana. Specifically, as part of a campaign involving the National Environmental Laboratory, which deployed a mobile laboratory, high-volume (HiVol) air sampling is being used in a study on urban pollution within the city of Gaborone.

The project participants at IRET, Universidad Nacional in Costa Rica also have acquired the equipment and expertise to perform active and passive air sampling for organic contaminants. This capacity is now being put to use regularly in various projects related to pesticide exposure in Costa Rica.

Capacity building of facilities and faculty at Kathmandu University (KU) has been established. Mr. Babi Kumar Kafle, a faculty member from the KU Department of Chemistry, has been trained at the pesticide laboratory at the Freshwater Institute (FWI) for a period of two months. Before Mr. Kafle's arrival in Canada, he was involved in collecting and extracting 20 water samples on SPE cartridges from three different regions of Nepal which he brought with him to FWI. Mr. Kafle was trained in all aspects of sample work-up, not only of these water samples, but also air and biological samples.

Similarly, he was trained in GC analysis of the samples, gaining insights into quality assurance and control, instrument maintenance and set-up. Mr. Kafle returned home with raw data files that were interpreted and are presented in this report (Appendix 5). KU has obtained a GC from a separate grant. UNEP funds have contributed to the facilities at KU, including fume hoods, ultra-high purity gases (for the operation of the GC), a rotary evaporator and nitrogen evaporator, among other consumable items such as organic solvents. Currently, Mr. Kafle is gaining experience operating this instrument and building the capacity of KU's pesticide analysis.

2.5 References

Daly, G.L., Y. D. Lei, C. Teixeira, D. C. G. Muir, F. Wania. Pesticides in Western Canadian mountain air and soil. *Environ. Sci. Technol.* **2007**, *41*, 6020-6025.

Gouin, T., F. Wania, C. Ruepert, L. E. Castillo. Field testing passive air samplers for current use pesticides in a tropical environment. *Environ. Sci. Technol.* **2008**, *42*, 6625– 6630.

Hayward, S.J., T. Gouin, F. Wania. Comparison of four active and passive sampling techniques for pesticides in air. Submitted to *Environ. Sci. Technol.*

Liu, W.J., D. Chen, X.D. Liu, X.Y. Zheng, W. Yang, J.N. Westgate, F. Wania. Transport of semivolatile organic compounds to the Tibetan Plateau: Spatial and temporal variation in air concentrations in mountainous Western Sichuan, China. *Environ. Sci. Technol.* in press.

3 LIST OF SEMINARS PRESENTING THE PROJECT

Wania, F. Measuring persistent organic pollutants in the atmosphere. Why do it? How to do it? What does it tell us? University of Botswana, Gaborone, Botswana, May 15, 2006.

Wania, F. Pollutants without borders - Measuring and calculating organic contaminant transport on a global scale. University of Concepcion, Chile, March 9, 2006.

Wania, F., G. L. Daly, Y. D. Lei, C. Teixeira, D. C. G. Muir, L. E. Castillo. Reconnaissance of organic contaminants in air and soil of Costa Rica. Universidad Nacional, Heredia, Costa Rica, October 24, 2006.

Wania, F. *et al.* Contaminant Amplification in the Environment - from Tropical Cloud Forests to Arctic Snow. Chinese Academy of Sciences, Research Centre for Eco- Environmental Sciences, Beijing, China, November 20, 2006, Chinese Academy of Geological Sciences, Beijing, China, November 22, 2006, and Peking University, Beijing, China, November 23, 2006.

Wania, F. *et al.* Contaminants in High Places – Pesticide Transport into Temperate and Tropical Mountains. Lectures at the Leading Edge Seminar Series, Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Canada, January 9, 2008.

Wania, F. *et al.* Contaminants in High Places – Pesticide Transport into Temperate and Tropical Mountains. EnTox, University of Queensland, Australia, Aug. 28, 2008.

Wania, F. *et al.* Contaminants in High Places – Pesticide Transport into Temperate and Tropical Mountains. Department of Environmental Science, ETH Zürich, Zürich, Switzerland, Nov. 28, 2008.

Wania, F. *et al.* POPs and other organic contaminants around the world - Results from GAPS and the UNEP Chemical project “Persistent Organic Pollutants along Environmental Transects in Costa Rica, Chile, Nepal and Botswana”. UNEP Chemicals, Châtelaine, Geneva, Switzerland, June 22, 2009.

4 LIST OF CONFERENCE CONTRIBUTION WITH PROJECT RESULTS

4.1 Conferences held

Loewen, M., S. Sharma, T. Halldorson, F. Wang, G. Tomy, F. Wania. Persistent organic pollutants in soil of the Central Himalaya. DIOXIN 2005, 25th International Symposium on Halogenated Environmental Organic Pollutants and POPs, Toronto, Ontario, Canada, August 21-26, 2005. ORAL PRESENTATION.

Wania, F. Measuring and interpreting POP air concentration gradients along environmental transects. Invited presentation at Specialty Workshop on POPs in the European Atmosphere: Concentrations, Deposition and Sources in Europe, Stresa, Italy, October 17-21, 2005. ORAL PRESENTATION.

Loewen, M.D., S. Sharma, C. Fuchs, F. Wang, F. Wania, D.C.G. Muir, G.T. Tomy. Seasonal and altitudinal trends of chlorinated pesticides in the central Himalayan atmosphere. International Symposium on POPs in Mountainous Areas, Salzburg, Austria, November 26–27, 2007. ORAL PRESENTATION.

Wania, F. *et al.* Understanding Air and Soil Concentration Changes with Altitude in Mountains at Different Latitude. International Symposium on Persistent Organic Pollutants in Mountainous Areas, Salzburg, Austria, November 26–27, 2007. ORAL PRESENTATION, INVITED.

Mmerekhi *et al.* Dispersal of Organochlorine Pesticides in Arid Regions: A survey of concentration gradients in the Soils and Atmosphere of Botswana. International Global Atmospheric Chemistry (IGAC) 10th International Conference. Bridging the scales in Atmospheric Chemistry : Local to Global 7 to 12 September 2008 in Annecy, France. POSTER.

Mmerekhi *et al.* Dispersal of Organochlorine Pesticides in Arid Regions: A survey of concentration gradients in the Soils and Atmosphere of Botswana. National Association for Clean Air (NACA) conference from 14 to 16 October 2009 at Vanderbijlpark - Gauteng, at the Emerald Casino in South Africa. POSTER **Voted the best overall poster**

Mmerekhi *et al.* Dispersal of Organochlorine Pesticides in Arid Regions: A survey of concentration gradients in the Soils and Atmosphere of Botswana. Environmental Health Conference - Our planet in crisis: Need for action 15th-19th November 2009, GICC, Gaborone, Botswana. ORAL PRESENTATION

Wania, F., H. Xiao, J.N. Westgate, Y.D. Lei, M. Loewen, X.D. Liu, W.J. Liu, D.Z. Chen, S. Sharma, C. Fuchs, F. Wang, G. Tomy, S.-C. Kang, Q.G. Zhang, W.W. Han, D.C.G. Muir, H. Hung. Cold trapping of persistent organic pollutants in the Himalayas and the Qinghai-Tibetan Plateau. DIOXIN 2009, 29th International Symposium on Halogenated Persistent Organic Pollutants, Beijing, China, Aug. 23- 28, 2009. ORAL PRESENTATION, INVITED.

Shunthirasingham, C., B.T. Mmerekhi, W. Masamba, C.E. Oyiliagu, Y.D. Lei, F. Wania. Fate of pesticides in arid regions, Botswana, Southern Africa. SETAC North America, New Orleans, Louisiana, USA, November 19-23, 2009. POSTER.

Shunthirasingham, C., Y.D. Lei, C. Ruepert, F. Wania. Current use pesticides in arboreal, fog and lake water from high altitude tropical cloud forest, Costa Rica. SETAC North America, New Orleans, Louisiana, USA, November 19-23, 2009. ORAL PRESENTATION.

4.2 Forthcoming

Wania, F. *et al.* Measuring and modelling pesticide fate in tropical and subtropical environments. 8th Iberoamerican and 5th Iberoamerican Congress on Environmental Pollution and Toxicology (CICTA-2010), Heredia, Costa Rica, November 29-December 3, 2010. ORAL PRESENTATION, INVITED.

Wania, F., C. Shunthirasingham, T.N. Brown, Y.D. Lei, B.T. Mmereki, W. Masamba, C. Ruepert, L.E. Castillo. Combining field data and fate modelling to explore differences in the transport and retention of organic contaminants in temperate, subtropical and tropical environments. SETAC Europe, Sevilla, Spain, May 2010. ORAL PRESENTATION.

5 SHORT DESCRIPTION OF APPENDICES

The detailed results of the project are summarized in five appendices, which constitute journal manuscripts at different stages of preparation.

5.1 Sub-Project Costa Rica

Appendix 1: Gouin, T., F. Wania, C. Ruepert, L. E. Castillo. Field testing passive air samplers for current use pesticides in a tropical environment. *Environ. Sci. Technol.* **2008**, *42*, 6625–6630.

This paper summarizes the results of a year-long air sampling campaign in Costa Rica's central valley, involving the comparison of XAD 2-resin and polyurethane foam based passive air samplers and an active HiVol air sampler. It yielded the first calibration of passive samplers under tropical conditions.

Appendix 2: Shunthirasingham, C., T. Gouin, Y.D. Lei, C. Ruepert, L.E. Castillo, F. Wania. Further studies on current use pesticide transport to Costa Rica's high altitude cloud forests. Manuscript in prep.

This manuscript will combine the measurements of current use pesticides in air, soil and water samples from Costa Rica, in particular (1) duplicate passive air samples placed in seven locations across the country (Carrara, Palo Verde, Santa Rosa, Monteverde, La Selva, EARTH, Belen) from October 2005 to October 2006, (2) soil samples taken in October 2006 at a number of sites along an elevation gradient on the NE side of Volcano Turrialba in the Cordillera Central, and (3) water sampled on Volcanoes Brava and Poas in February 2009 (work not funded by UNEP Chemicals). This appendix is not a complete draft of a manuscript, but contains the numerical results of the chemical analysis, which has been largely completed.

5.2 Sub-Project Botswana

Appendix 3: Shunthirasingham, C., B.T. Mmereki, M. Wellington, C. Oyiliagu, Y.D. Lei, F. Wania. Fate of pesticides in the arid subtropics, Botswana, Southern Africa. Manuscript in prep. for submission to *Environ. Sci. Technol.*

This manuscript describes the results of the analysis of soil, and passive and active air samples from Botswana for pesticides. It will be submitted for publication in early 2010. The same samples have also been analysed for PAHs and levoglucosan, a marker for biomass burning. Another manuscript on those results is currently also under preparation, but is not included in this final report.

5.3 Sub-Project Chile

Appendix 4: Shunthirasingham, C., R. Barra, G. Mendoza, C. Oyiliagu, Y.D. Lei, F. Wania. Spatial variability of semivolatile organic compounds in the Chilean atmosphere. Manuscript in prep.

This draft manuscript describes the results of the analysis for pesticides, and PAHs of passive air samplers deployed along three altitude transects in Northern, Central and Southern Chile. Only very few of the soils collected from the same sampling sites had detectable amounts of the same compounds. It is foreseen to submit this manuscript for publication in 2010.

5.4 Sub-Project Nepal

Appendix 5: Loewen, M., S. Sharma, C. Fuchs, F. Wang, F. Wania, D.C.G. Muir, G. Tomy. Seasonal and altitudinal trends of chlorinated pesticides in the Central Himalayan atmosphere. Manuscript in prep.

This draft manuscript describes the results of the analysis for pesticides of passive air samplers and soils deployed in Nepal. It is foreseen to submit this manuscript for publication in 2010. The supporting information for this appendix also includes results from the analysis for pesticides of water samples from Nepal.

Appendix 1



Gouin, T., F. Wania, C. Ruepert, L. E. Castillo.

Field testing passive air samplers for current use pesticides in a tropical environment.

Environ. Sci. Technol. **2008**, *42*, 6625–6630.

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Appendix 2



Further Studies on Current Use Pesticide Transport to Costa Rica's High Altitude Cloud Forests

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High concentrations of current use pesticides (CUPs) have been reported in soils from high altitude cloud forest in Costa Rica. CUPs such as endosulfan, chlorothalonil and dacthal are transported to high elevations and deposited to the ground by wet deposition such as rain and fog. Due to high precipitation, cold temperatures and high soil organic matter content, pesticides will accumulate in high altitude rain forest. This could be harming some amphibians in the cloud forest and may be one of the reasons for the observed decline of amphibian populations. Here we report on the concentration of CUPs in the air of several agricultural regions of Costa Rica, measured using duplicate year-long passive air sampler deployments. We also measured the concentration gradients of CUPs in soils sampled along an altitudinal transect on the windward side of the Volcano Turrialba to probe for the possibility of mountain cold-trapping. However, because soil concentrations are not suitable for evaluating potential toxic effects on cloud forest amphibians, we also determined whether water samples from high elevation cloud forest contain elevated level of pesticides. The levels of detected pesticides in water samples were low. Endosulfan sulfate is the most abundant pesticide in the water samples, with concentration ranging from 0.4 ng/L to 9.4 ng/L, with highest levels in the water sample from the bromeliads. Fog water contained higher levels of some of the analysed pesticides such as lindane and chlorothalonil. Pesticides such as trans-chlordane, cis-chlordane and trans-nonachlor were only detected in creek and lake water, suggesting that there were no recent atmospheric inputs to the lake. The detected levels of Σ endosulfan in the water samples are much lower than the reported LC50 value for α -endosulfan for tadpoles, suggesting that endosulfan may not have an impact on amphibian populations.

Introduction

Current-use pesticides (CUPs) are substances that are widely used in agriculture, and which have been designed to illicit a toxic effect. Generally, CUPs are used to control populations of unwanted pests, such as insects, plants, or fungi. They also have the potential, however, to negatively impact non-target species, particularly if they persist in the environment, and have the potential for long-range transport (LRT). Currently there is a lack of understanding with respect to the environmental fate and behaviour of CUPs. Given the widespread use of CUPs in tropical regions, there is an interest to better understand how these substances might be transported to tropical rainforests at high altitudes, where they may have a detrimental effect on plants and wildlife.

It is well understood that the identification of pollutant sources is the primary objective in devising effective strategies to limit the exposure of populations to potentially harmful substances. Because the atmosphere is the most important pathway in the regional and global cycling of CUPs, identifying their distribution in air is critical for better understanding source-receptor relationships. Recently, several studies have demonstrated the effectiveness of passive air samplers (PAS) to characterize the spatial distribution of a wide variety of organic pollutants, including CUPs, both regionally and globally. Of particular interest is the use of XAD-based PAS to assess the spatial distribution of organic pollutants throughout Costa Rica. Based on results from an environmental fate model Daly et al. (2007) suggest that the physical-chemical properties of a substance will strongly influence its potential to accumulate in soils at high elevations in the tropical rainforest. The implication is that substances with a $\log K_{AW}$ between -3 and -5 have a greater potential for accumulation at high altitudes. This enrichment behaviour is enhanced by the physical properties of the tropical rainforest environment, characterized by lower temperatures and high rates of precipitation, allowing for efficient scavenging to occur.

In order to assess this transport mechanism, XAD-based PAS were deployed in different regions of Costa Rica. These regions were selected based on their unique differences in meteorology, and their geographic relationship with areas of agricultural activity. For instance, the climate of the northern mountain regions, which is characterized by misty

conditions, is in contrast to the conditions present in the central valley. Thus, one of the objectives of this study is to assess the relative influence of this unique meteorology on the transport of pollutants from one region to another. This can be achieved by deploying passive air samples at key locations in different regions. Of particular interest is an investigation into differences in the levels of CUPs in air between coastal regions along the Pacific to those in the Caribbean. A second objective of the study is an examination into how CUPs are transported to high altitudes, via the neo-tropical mountain contamination process described by Daly et al. (2007). Typically, air masses in Costa Rica move from east to west, flowing from the Caribbean towards the Pacific passing through high altitude tropical rainforests. Consequently, substances with $\log K_{AW}$ between -3 and -5 thus have the potential to accumulate at higher elevations. Thus evidence of an altitudinal concentration gradient in soil will be examined through the collection of soil samples along an altitudinal gradient.

Studies have focused on rain and snow as vectors for transferring organic pollutants from the atmosphere to the ground. However, fog may be another important wet deposition pathway, in particular in areas subject to high fog frequency. This study was carried out to determine the potential importance of fog in the deposition of current use pesticides (CUPs) to a high altitude tropical cloud forest in Costa Rica. Levels of CUPs were determined in six high altitude water samples collected on volcanoes Poas and Barva. Those water samples were taken from lakes, creeks, epiphytic plants and a fog sampler.

Methods

Air Sampling. XAD-based PAS were deployed for one year from October 2005 to October 2006 at seven sampling sites (Carrara, Palo Verde, Santa Rosa, Monteverde, La Selva, EARTH, Belen), shown in Figure 1. Details on the air sampling methodology are given in Daly et al. (2007).

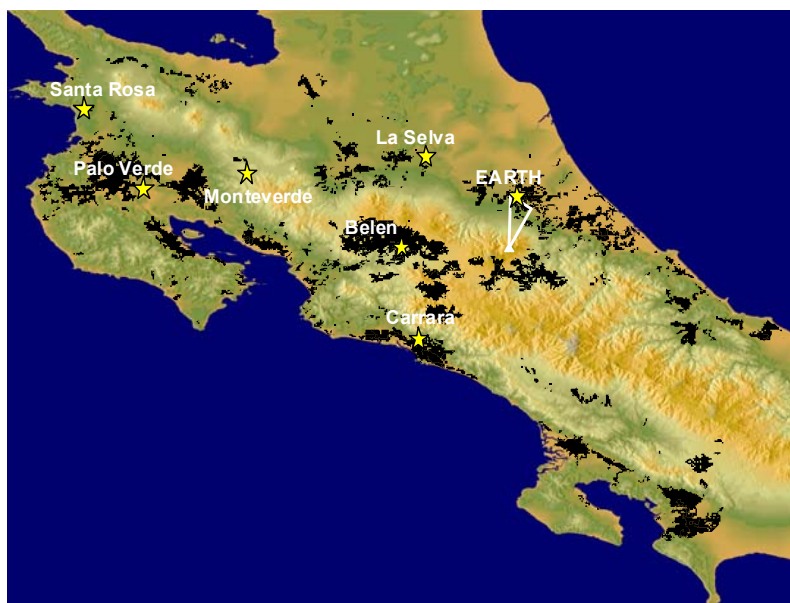


Figure 1 Sampling locations for XAD-passive samplers (stars) in Costa Rica and for soil samples collected along the eastern slope of Volcan Turrialba (triangle). Sites are shown in relation to mountainous regions (orange) and, forested areas (green), and agricultural activity (black).

Soil Sampling. Soil samples were collected in October 2006 along the eastern slope of Volcan Turrialba and at the sampling site located at EARTH. The triangle in Figure 1 illustrates the region from which soil samples were collected. Eight elevations were sampled, ranging from 30 to 3240 m above sea level. Details of the soil sampling method is given in Daly et al. (2007).

Water Sampling. Six high altitude water samples were collected on Volcanoes Poas and Barva in February 2009. Soils from these two mountains had higher residues of endosulfan sulfate and chlorothalonil than other non-agricultural soil in Costa Rica (Daly et al., 2007). High soil concentrations indicate high deposition rates of pesticides. The two volcanoes also experience persistent and rapidly moving fog as northeasterly trade winds are being orographically uplifted onto the Cordillera Central. These winds pass over intensive agricultural plantations in the Caribbean lowland and therefore, have the potential to be highly contaminated with pesticides. Water samples were collected from three lakes (Laguna Botos, Laguna Poas, Laguna Copey), from a creek (Poas creek) and from a fog sampler (Figure 2) and from bromeliads growing on the forest floor. The pools

of water that accumulate in such epiphytic plants are important breeding grounds for amphibians, such as the poison dart frog. Water samples from the lakes were collected manually from 20-30 cm beneath the surface using a glass bottle. 10 to 20 L of water was collected from each lake and stored in pressurizable stainless steel cans. The water samples were pulled through baked glass fibre filters to collect organic pollutants sorbed to particles and then through clean XAD-2 resins columns to extract organic pollutants dissolved in the aqueous phase using a peristaltic pump. The filters and XAD-2 resins were extracted with DCM and passed through sodium sulfate columns to remove water residues in DCM extracts. The extracts were volume reduced using a rotary evaporator, concentrated to around 1 ml using a gentle stream of N₂ and then solvent-exchanged into iso-octane.



Figure 2 Photographs of the fog sampler deployed on Volcano Poas (left) and of the Teflon strings that serve to force coalescence of fog droplets.

All extract were analyzed for pesticides by gas chromatograph-mass spectrometry.

Results and Discussion

Concentrations for several of the CUPs, including endosulfan, pendimethalin, and chlorothalonil, in the passive air samplers are shown in Figure 3. Generally, levels of CUPs in air are highest in the central valley region of Costa Rica, where coffee is intensively produced. It is notable, however, that elevated levels can also be observed at Palo Verde, which is an area of intensive rice production. Both pendimethalin, a pre-

emergent herbicide, and endosulfan, an insecticide, are observed to be elevated at Palo Verde in comparison to other sites outside the central valley. In the intensive banana and pineapple growing regions along the Caribbean coasts, chlorothalonil, used to combat fungal disease in bananas is seen to be elevated. Areas with less intensive agricultural activity, such as Monteverde, Santa Rosa, and Carrara all show much lower levels of these CUPs. These results are thus useful in defining the potential source regions of CUPs in Costa Rica.

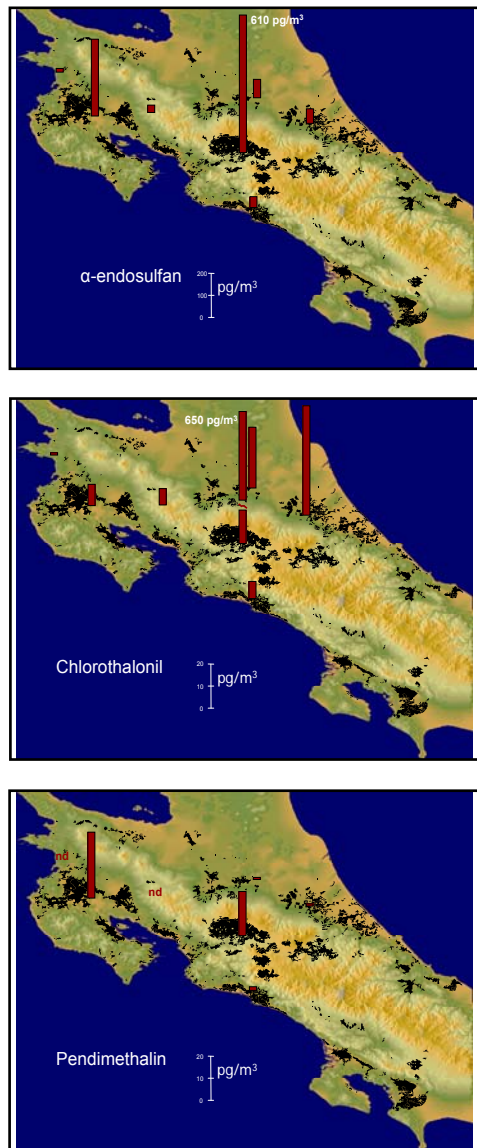


Figure 3 Average concentrations in air of α -endosulfan, chlorothalonil, and pendimethalin derived from XAD-PAS, between October 2005 and October 2006.

To understand the potential transport mechanisms of CUPs to the high altitude tropical rainforest, soil samples collected along an altitudinal transect were collected and analyzed. Figure 4 illustrates results for endosulfan sulfate, a degradation product of endosulfan. The results suggest a concentration gradient with altitude, which is consistent with the theory of tropical mountain contamination potential, suggested by Daly et al. (2007). Concentrations of other CUPs were generally much lower than those observed for endosulfan sulfate, and are not reported here, suggesting inefficient transport of these substances occurs.

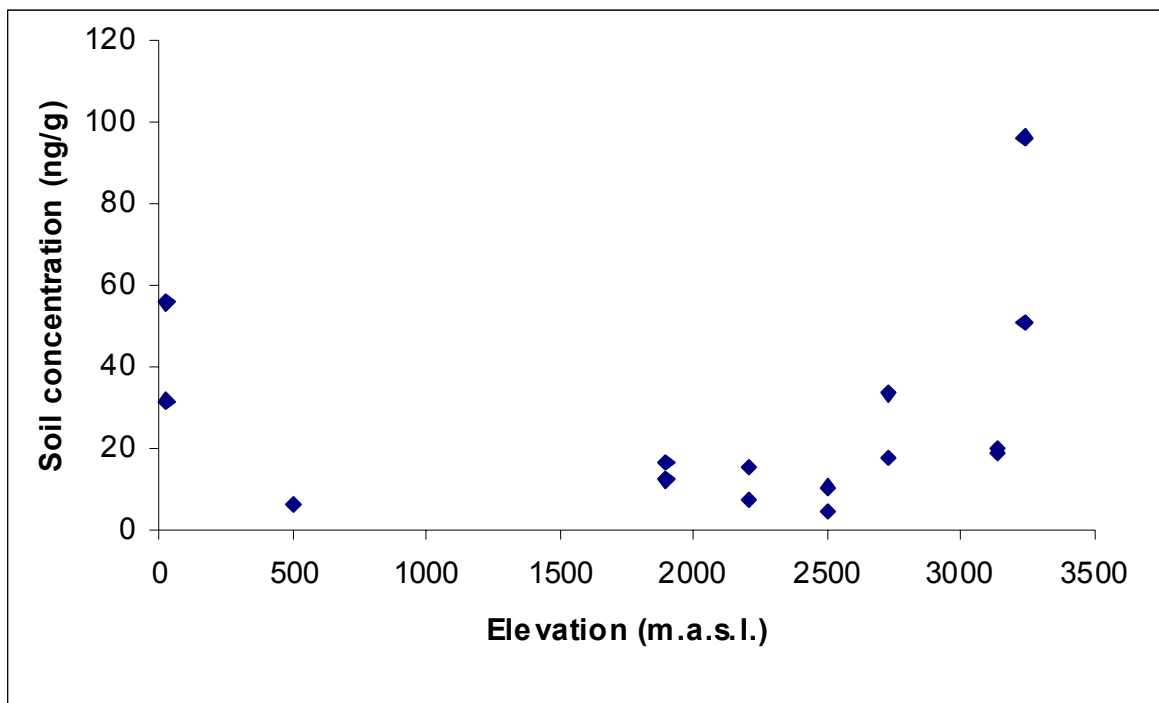


Figure 4 Soil concentration data along an altitudinal gradient between the sampling site at EARTH (30 m above sea level) and the summit of Volcan Turriabla (3240 m above sea level) for endosulfan sulfate.

The box and whisker plot in Figure 5 shows the level of pesticides in the water samples. The pesticides are arranged in sequence of decreasing median: endosulfan sulfate is the most abundant analyte in water, followed by β -endosulfan and lindane. High concentrations of endosulfan sulfate are consistent with elevated levels in soil samples from volcanoes Barva and Poas (Daly et al., 2007).

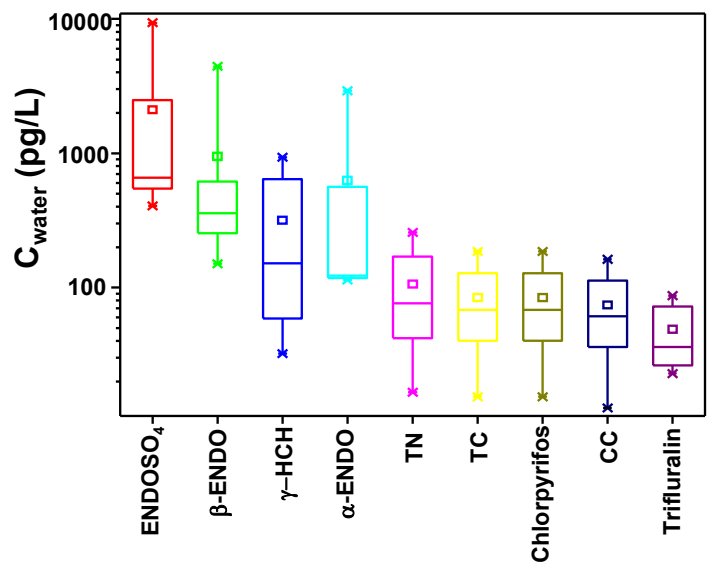


Figure 5 Box and whisker plot of the concentrations of the most frequently detected pesticides in water samples taken on Volcanoes Poas and Barva in February 2009

Total concentrations of endosulfan (sum of the parent compounds α - and β -endosulfan and degradation product endosulfan sulfate) in six water samples are shown in Figure 6. The highest levels of Σ endosulfan were measured in the samples from the bromeliads. High levels of Σ endosulfan in natural organic matter (some of it alive) from arboreal water suggest bioaccumulation of this pesticide in invertebrates. Fog water contained higher levels of Σ endosulfan than lake and creek water.

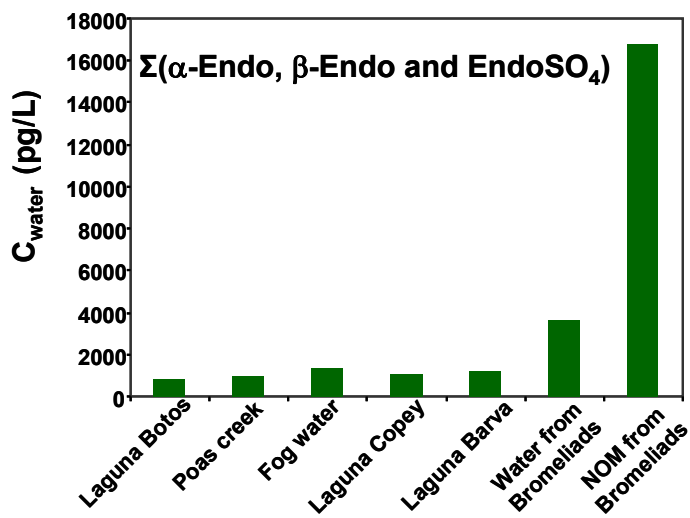


Figure 6 Concentration of the sum of endosulfan in Costa Rican water samples.

The amounts of endosulfan are higher than those of its degradation product endosulfan sulfate in air, suggesting that endosulfan composition in the atmosphere is similar to that in the technical pesticide mixture. However, soils contained a greater abundance of the degradation product than the parent compound, presumably because microbes have converted endosulfan to endosulfan sulfate, which is more persistent than the parent compound. Lake and creek water samples have a composition in between these two extremes (Figure 7). In fog water, similar amounts of α -endosulfan, β -endosulfan and endosulfan sulfate were detected, indicating that equals amounts of parent and degradation product are being deposited onto the ground. This also suggests that some of the conversion into endosulfan sulfate occurs already in the atmosphere.

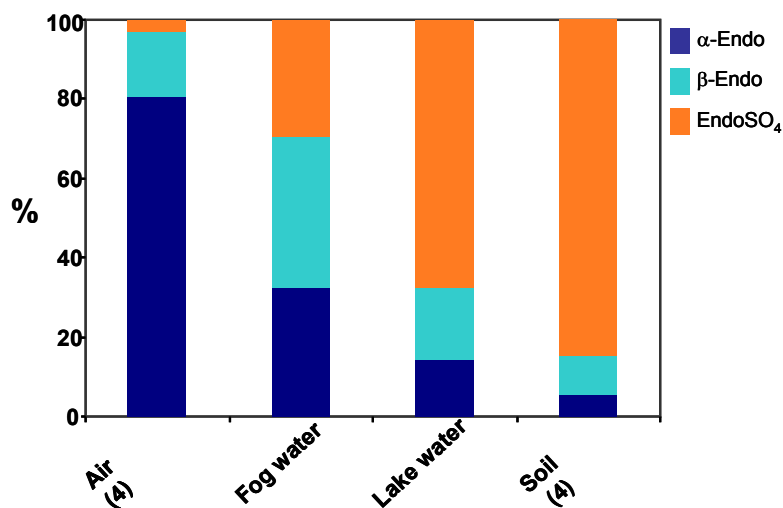


Figure 7 Relative abundance of α - and β -endosulfan and endosulfan sulfate in air, fog water, lake water and soil from Costa Rica. Air and soil data are taken from Daly et al. (2007)

The chlordanes (CC, TC and TN) were found in very low levels in the lake and creek water samples and they were not detected in the fog and bromeliad samples (Figure 8). This indicates there are no recent atmospheric inputs. Fog and bromeliads samples provide a measure of recent pesticide deposition. Concentrations of chlordanes in Poas creek are much lower than in Poas Lake (Laguna Botos) water samples. Poas creek is downstream of Laguna Botos. Thus, soils act as a filter for these compounds during the flow of water from the lake to the creek sampling site. However, this was not observed

for endosulfan, the level of endosulfan was higher in creek water than in the lake water, suggesting that endosulfan was directly deposited into Poas creek via wet deposition.

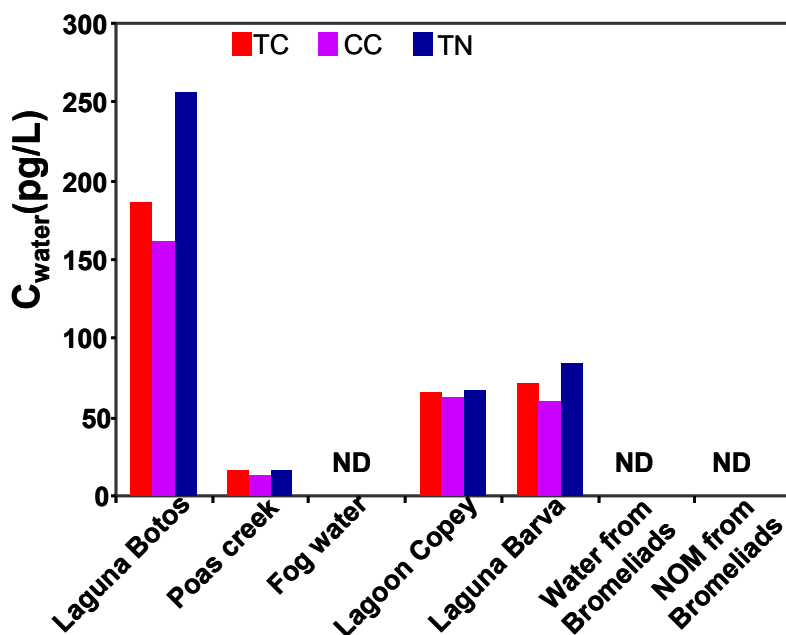


Figure 8 Concentration of chlordanes in Costa Rican water samples.

Acknowledgements

We are grateful to Liisa Jantunen and Terry Bidleman for advise on extraction of pesticides from water and for lending us their water sampling equipment. We also acknowledge Diana and Seiling for their assistance with water sampling in Costa Rica. A CGCS Graduate Student Award provided travel funding for CS.

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Appendix 3



Fate of Pesticides in the Arid Subtropics, Botswana, Southern Africa

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Despite a history of pesticide usage, only few data exist on the concentrations in air and soil of Southern Africa. In order to add to the understanding of the processes controlling the fate of organic contaminants in arid regions, the levels, spatial trends, and seasonal variability of pesticides was studied in air and soil from Botswana. XAD resin-based passive air samplers (PAS) were deployed at 15 sites across the country from May 2006 to May 2007. Soil samples were collected from the vicinity of nine of the PAS sampling sites. In addition, 27 24 hour-high volume air samples were collected in Maun, at the southeastern edge of the Okavango Delta, every two weeks for one year. Levels of pesticides in PAS were low, with α -endosulfan and lindane being most abundant. Concentrations in soils were extremely low and only a soil with a high organic carbon contained notable amounts of dieldrin and traces of other pesticides. In particular, air and soil from the Okavango Delta had very low levels even though the area had repeatedly been sprayed with DDT and endosulfan in the past. Air samples from Eastern Botswana, where the majority of the population lives, contained higher levels. Higher air concentrations of α -endosulfan occurred during summer and higher HCB levels in winter. This seasonality was related with neither minor seasonal changes in temperature nor hydrological seasonal events such as the rainy season or the flooding of the Okavango Delta. Thus, the observed spatial and seasonal patterns are more likely related to pesticide usage pattern than to environmental factors or historical use. High temperature and low organic matter content limit the uptake capacity of Botswanian soils for pesticides. No evidence was found that sorption to dry mineral matter plays a major role. Arid soils in subtropical regions are therefore neither a major reservoir of organic contaminants nor do they constitute a significant long-term source of pesticides to the atmosphere.

Brief: The limited uptake capacity of warm, organic matter poor soils in subtropical Botswana leads to short environmental residence times and low concentrations of organochlorine pesticides, even in areas treated with DDT and endosulfan in the past.

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Introduction

Organochlorine pesticides (OCPs) have been widely used around the world to boost agricultural crop yield and food production, and to control vector-borne diseases. Reliable reports on the usage of OCPs in Africa are limited, but the use of pesticides in Africa is generally believed to be low compared to agricultural applications elsewhere (Batterman et al., 2008, Rosendahl et al., 2008). Studies on pesticide occurrence in environmental samples from Africa are also scarce. The few reported studies have focused on a limited number of sampling sites and often were confined to short periods of time. From these studies, it is difficult to obtain information on the spatial variability of OCPs, identify their temporal trends, or to gain an understanding of the fate of OCPs in low latitude environments.

Botswana, located at around 22°S and 24°E, is a thinly populated, land-locked country in Southern Africa occupying an area of 582,000 km² (Thomson et al., 2005). Botswana's climate is characterized by high temperature throughout the year; temperatures in the summer are above 35 °C; winter temperatures are known to fall to 0°C, with frost occurring the occasional night between June and August (Thomson et al., 2005). Rain fall varies from 650 mm in the northern part of the country to less than 250 mm in the southwestern region in the Kalahari (Thomson et al., 2005). A large alluvial fan with a wetland, the Okavango Delta, is situated in the northwest of the country and has substantial biodiversity (Daka et al., 2006). The Delta is the world's largest inland wetland, with a surface area of 25,000 km² and wetland area of 12,000 km² (Mbongwe et al., 2003, Kgori et al., 2006). The Okavango Delta brings water from the central Angola highlands into Botswana and, after cutting through Namibia's Caprivi Strip, enters northwestern Botswana (DeMotts et al., 2009). Seasonal flooding takes place in the Okavango as result of the interaction of local, regional and basin-wide influences (DeMotts et al., 2009). Floods occur between May and October (dry season) and rainfall occurs in the summer months (Kgori et al., 2006, DeMotts et al., 2009). The climate of the Okavango Delta is characterized as semi-arid, with rain fall rates varying between 400 and 600 mm (DeMotts et al., 2009). Maximum and minimum temperatures in the Okavango Delta area range from 30.5 to 33.7°C and 14.8 to 19.2°C, respectively (Mbongwe et al., 2003).

In the Okavango Delta area, malaria and sleeping sickness are more prevalent, therefore the area was repeatedly sprayed with a range of pesticides in the past (Mbongwe et al., 2003). Dieldrin was used in 1964, which was followed by dichlorodiphenyltrichloroethane (DDT) between the

years of 1967 and 1970 (Daka et al., 2006). Between 1972 and 1991, endosulfan was used by itself and then as a mixture with deltamethrin starting in the 1990s (Daka et al., 2006). Since 2001, deltamethrin by itself has been used in the Okavango Delta area to control tsetse fly populations (Daka et al., 2006). DDT and endosulfan were extensively used in the past to control disease vectors, however, the total amounts used of DDT, endosulfan and deltamethrin in the Okavango Delta area for the purpose of controlling vector-borne diseases is not known. Approximately 5000 to 10,000 kg of DDT was used in the Okavango Delta area per year in the early 1990s (Mbongwe et al., 2003). DDT was used in Botswana for over 50 years until it was banned in 1997 (Mbongwe et al., 2001). Currently, pesticides are being widely used in the urban and peri-urban areas of Gaborone and Francistown to control pests on vegetables (Obopile et al., 2008). Insecticides represent the majority of pesticides used in Botswana and the majority of these are organophosphates (Obopile et al., 2008).

Despite the history of OCPs usage in Botswana, only limited data exist on the concentrations of OCPs in air, sediments and biota (Daka et al., 2006, Mbongwe et al., 2001, Mmualefe et al., 2009, Pozo et al., 2006, 2009). To our knowledge no data exist on the concentrations of OCPs in soils. Thus, a very limited understanding of the processes controlling the fate of OCPs in Botswana exists and very little is known about the atmospheric dispersal of DDT and endosulfan from known application areas under subtropical, arid conditions, even though Mbongwe et al.'s (2001) study highlighted the importance of vaporization and atmospheric transport. Clearly, the dry, hot conditions prevalent in Botswana can influence the distribution and degradation of pesticides in the atmosphere as well as in soils. The objectives of this study were: (i) to use soil sampling and a passive air sampling technique on a regional scale to probe the extent of dispersal of DDT, endosulfan and their degradation products from known past and present source areas in Okavango Delta, and (ii) to contrast OCP air concentrations during periods of low and high water levels in the Okavango Delta. Goss et al. (2004) suggested that adsorption to mineral surfaces becomes important for the uptake of organic chemicals in dry soils with low organic carbon (OC). An aim of this study was also to examine if the mineral surfaces play a role in uptake process of organic pollutants in soils with low OC.

Experimental Section

Air and Soil Sampling Sites. A field campaign was conducted in 2006/2007 in Botswana to collect air and soil samples. Air samples were collected using both passive and active samplers. The sampling sites are shown in Figure S1 and their coordinates are listed in Table S1. Duplicate XAD resin-based PAS were deployed at 15 sites across Botswana for one year between May 2006 and May 2007. Ten of the passive air sampling sites were located in the Okavango Delta area and the other five sites were in Eastern Botswana, where the majority of the population resides.

Passive Air Samplers. XAD-PAS have been previously used to determine the spatial variability of POPs on a regional (Gouin et al., 2008, Daly et al., 2007a, 2007b), continental (Shen et al., 2004, 2005, 2006), and global scale,(Shunthirasingham et al., submitted). They consist of a stainless steel mesh cylinder, filled with XAD-2 resin and suspended in a stainless steel shelter with an open bottom (Wania et al., 2003). The XAD resin has a large uptake capacity for semi-volatile organic chemicals, preventing them from reaching equilibrium between the resin and the atmospheric gas phase over periods from several months to over one year (Wania et al. 2003). Therefore, XAD-PAS are suitable to obtain annually averaged air concentrations of pesticides (Wania et al., 2003). In this study, a short XAD PAS, with half the length of the original design (Wania et al., 2003) was used. The XAD-resin PAS was prepared as described previously (Wania et al., 2003).

High Volume (HiVol) Sampler. Twenty-seven HiVol samples were collected every two weeks at the Harry Oppenheimer Okavango Research Centre in Maun between July 2006 and August 2007. During the average sampling time of 24 hours approximately 770 m³ air were pulled through a glass fiber filter (GFF), which had been baked at 450°C overnight prior to use, to collect the particulate phase and then through a glass cartridge containing XAD-2 resin placed between layers of polyurethane foam (PUF) plugs to collect the gaseous phase. After sampling, the cartridges and GFFs were wrapped in solvent-rinsed aluminum foil. All the HiVol samples and PAS were stored in a freezer and shipped to Canada at the end of the sampling period, where they were kept frozen until analysis.

Soil Sampling. Soils were sampled in May 2006 in the vicinity of the PAS sampling site in Gaborone and at eight of the sites in the Okavango Delta. Each soil sampling site was divided

into a grid and 9 samples were collected with an auger, reaching a depth of 25 cm, which were then mixed with a clean steel shovel and bucket (Daly et al., 2007). For each site, two sub-samples were collected and wrapped in aluminum foil that had been baked at 450°C. Soil water and OC content, determined as described by Daly et al. (2007), ranged from 5 to 25% and from below detection level (BDL) to 8.8% (Table S1), respectively.

Extraction and Clean-up of Samples. After spiking with recovery standards, all air samples were Soxhlet-extracted with dichloromethane (DCM) for 20-22 hours. PUF-XAD-PUF sandwiches and GFF were extracted separately to determine the distribution of pesticides between gas and particle phase and the second PUF plug from several sandwiches was extracted separately in order to quantify breakthrough. The volume-reduced extracts were passed through baked sodium sulfate to remove any water residue (Gouin et al., 2008). 30 g of wet soil was mixed with baked sodium sulfate, ground, spiked with recovery standards and then extracted with DCM for 22 hours (Daly et al., 2007). Duplicate soil samples for each location were extracted in order to determine the reproducibility of extraction and quantification. Soil extracts were cleaned on alumina columns. The final volume of the extracts was 1 ml, and 100 ng of mirex was added for volume correction.

Analysis of Extracts. The extracts were analyzed for α - and γ -hexachlorocyclohexane (HCH), *cis*- (CC) and *trans*-chlordane (TC), *trans*-nonachlor (TN), heptachlor (HEPT), heptachlor epoxide (HEPX), aldrin, dieldrin, *p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDD, *o,p'*-DDD, *p,p'*-DDE, *o,p'*-DDE, α - and β -endosulfan, endosulfan sulphate, pendimethalin, trifluralin, dacthal, chlorothalonil and chlorpyrifos using an Agilent 6890 gas chromatograph (GC) with a DB-5 column (60 m, 0.25 mm i.d., 0.25 μ m film thickness) coupled to a 5973 mass selective (MS) detector with a negative chemical ionization source operating in selected ion mode. The detailed conditions used for quantification of pesticides in air and soils extracts are described in Gouin et al. (2008).

Quality control and assurance. Field blanks were collected for both HiVol and passive samples. After placing a GFF and a PUF-XAD-PUF cartridge in the HiVol sampler, the sampling media were immediately removed again without ever drawing air and stored in solvent-rinsed foil. Field blanks for PAS were collected at a few sites by taping a closed container with an XAD-filled mesh cylinder onto the post holding the exposed PAS for the one year of sampling. The field blanks underwent the same shipping, handling and storage as the exposed samplers except that

blanks were never exposed to air. Laboratory blanks and field blanks were processed in the same way as the exposed samples to determine the level of contaminants introduced during extraction and clean-up and by handling, shipping and storage, respectively. The average blank values were low, except for HCHs in HiVol blanks, which indicated that lindane contamination had occurred. As lindane also contains impurities of α -HCH, it was also elevated in those blanks. Consistent with these blanks, concentrations of α -HCH and γ -HCH were greatly elevated in HiVol samples from February 23, 2007 onwards, suggesting that samples taken after that date were contaminated with lindane. These data are therefore not reported. All other data were corrected using the average of lab and field blanks (HCHs in HiVol samples from before Feb. 23 were corrected using only the average of the lab blanks). Method of detection limits (MDLs) were calculated as three times the standard deviation for the compounds that were detected in blank samples and for those that were not detected in the blanks, MDLs were calculated by using three times the instrument detection limits. Only chlorpyrifos was detected in the back PUF-disk extracts. The amount found was less than 4% of that on the front PUF-disk/XAD-2 extracts, suggesting that the breakthrough for this pesticide was not significant.

Results

Passive Air Samplers. The blank-corrected average concentrations (ng/PAS) of duplicate PAS and coefficients of variation (CV) are reported in Tables S3 and S4. Agreement between duplicates is very good, with CVs ranging between 3 and 19 %. Chlorpyrifos is the exception with a CV of 50%. Whereas chlorpyrifos was only detected in trace amounts in a few PAS, it was present at much higher levels in the HiVol samples (Table S4), suggesting that it may have undergone degradation while to the XAD resin during long periods of time. This is consistent with earlier findings by Gouin et al. (2008). Generally, the levels of pesticides in the PAS extracts are low and ranged from below MDL (BMDLs) to 41 ng/PAS (Tables S3 and S4). HCB, α - and γ -HCH, chlorothalonil, endosulfan and its degradation product, endosulfan sulfate, were detected in all PAS, whereas TC, CC, TN, and dacthal were found in some PAS. Dieldrin was only detected in two air samples from the most populated area of Botswana. Although the Okavango Delta area had been sprayed repeatedly with DDT in the past, only one of the PAS from the Delta area, Nokaneng, contained *o,p'*-DDE at level of 15.5 ng/PAS (Table S4). Failure

to detect DDT in any of the air samples indicates that there is no recent use of DDT within the country, which agrees with the ban of DDT in Botswana.

A box and whisker plot illustrate the levels and the variability of pesticides in the PAS deployed across the country (Figure 1). α -endosulfan is the most abundant pesticide in the atmosphere of Botswana, followed by HCB, and lindane. Highest concentrations were recorded for α -endosulfan and lindane. HCB shows a uniform distribution (Figures 1 and 2); levels ranged from 4.5 to 8.8 ng/PAS (Table S2), with higher levels recorded for samples from the most populated areas of Botswana (Figure 2). The uniform concentrations of HCB across the country agree with other studies reporting such a distribution on continental, and regional scales (Shen et al., 2005, Jaward et al., 2004, Daly et al., 2007, Liu et al. 2010) and is a result of the very high residence time of HCB in the atmosphere. In contrast, lindane had the greatest variability across the country (Figure 1), with levels ranging from 0.4 to 41 ng/PAS (Table S3). Higher levels were found in PAS from the more populated parts of Botswana, such as Francistown and Maun Airport. γ -HCH is more abundant than α -HCH; the α -/ γ -HCH ratio varies between 0.04 and 0.9 (Figure S2), indicative of the ban of technical HCH in Botswana. Higher levels of endosulfan were also found in PAS from the more populated areas of Eastern Botswana and lower levels in the Okavango Delta despite historical use. β -endosulfan, which is a less abundant isomer in the technical mixture, and the metabolite endosulfan sulfate, were detected at low levels relative to α -endosulfan. The α -/ β -endosulfan ratio ranges between 4.3 and 45.6 and averages 16.4 (Figure S2), which is higher than in the technical endosulfan (2.3). The high ratio indicates that that β -endosulfan may be degraded faster than α -endosulfan. Air sample from Eastern Botswana also contained higher levels of chlorothalonil than air samples from the Okavango Delta. The observations of higher levels in Eastern Botswana agree with Obopile et al. (2008), who indicated that most pesticide use in Botswana was for controlling pests on vegetables in the Gaborone and Francistown areas. Chlordanes showed a distribution pattern different from that of α -endosulfan, chlorothalonil and lindane, such that sites that contained high levels of these pesticides had low levels of chlordanes (Figure 2). Chlordanes in air samples are dominated by TC (Table S3 and Figure 2). TC/CC ratios varied between 1.4 and 2.2 and averaged 1.84, which is higher than in technical chlordane (1.16) (Figure S2).

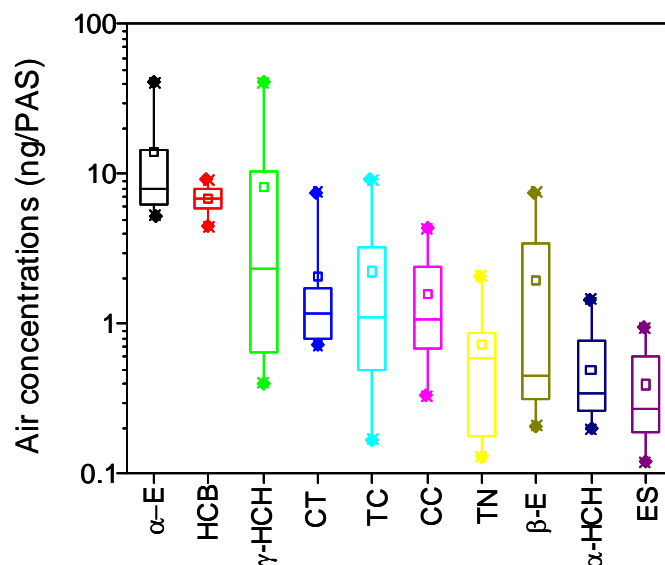


Figure 1 (A) Box and whisker plot of concentrations (ng/PAS) of pesticides in passive air samplers deployed across Botswana. The boxes in this plot represent the interquartile range, containing 50% of the data. The upper and the lower edges of the box indicate the 75th and 25th percentile of the data set, respectively. The median and the mean is represented by the horizontal line in the box and the square, respectively.

HiVol Samples. Pesticides concentrations in all 27 HiVol samples are reported in Table S5. HCB, α -HCH, γ -HCH, chlordanes, chlorpyrifos and endosulfan and endosulfan sulfate were detected consistently in the HiVol samples. In several samples, dacthal, chlorothalonil and HEPT were also found. The pesticides were mainly observed in the gas phase extracts (in PUF/XAD-2 sorbent). The GFF extracts contained extremely low levels of these pesticides. Only chlorpyrifos and TC were consistently detected in the particle phase. The vapor pressure of the pesticides ranges from 0.0007 to 0.025 Pa at 25 °C (Shen et al., 2005, Xiao et al. 2004), which is sufficiently high for them to partition into the gas phase. The dominant pesticides in the HiVol samples are chlorpyrifos, α -endosulfan and γ -HCH. The sample taken on August 30, 06 contained very high concentration of chlorpyrifos (Figure 3), indicating its usage in the proximity of the sampling site during this period. Elevated levels of γ -HCH, chlordanes, HCB and chlorpyrifos were observed in air sample taken on November 2, 06 and July 15, 07 (Figure 3), whereas the air sample from May 20, 07 had high levels of endosulfan, HCB and chlordanes. In general, higher levels of HCB were found in air samples taken during winter, whereas the

opposite was observed for endosulfan, which had generally higher levels during the rainy summer season (Figure 3), likely caused by higher usage for controlling mosquito.

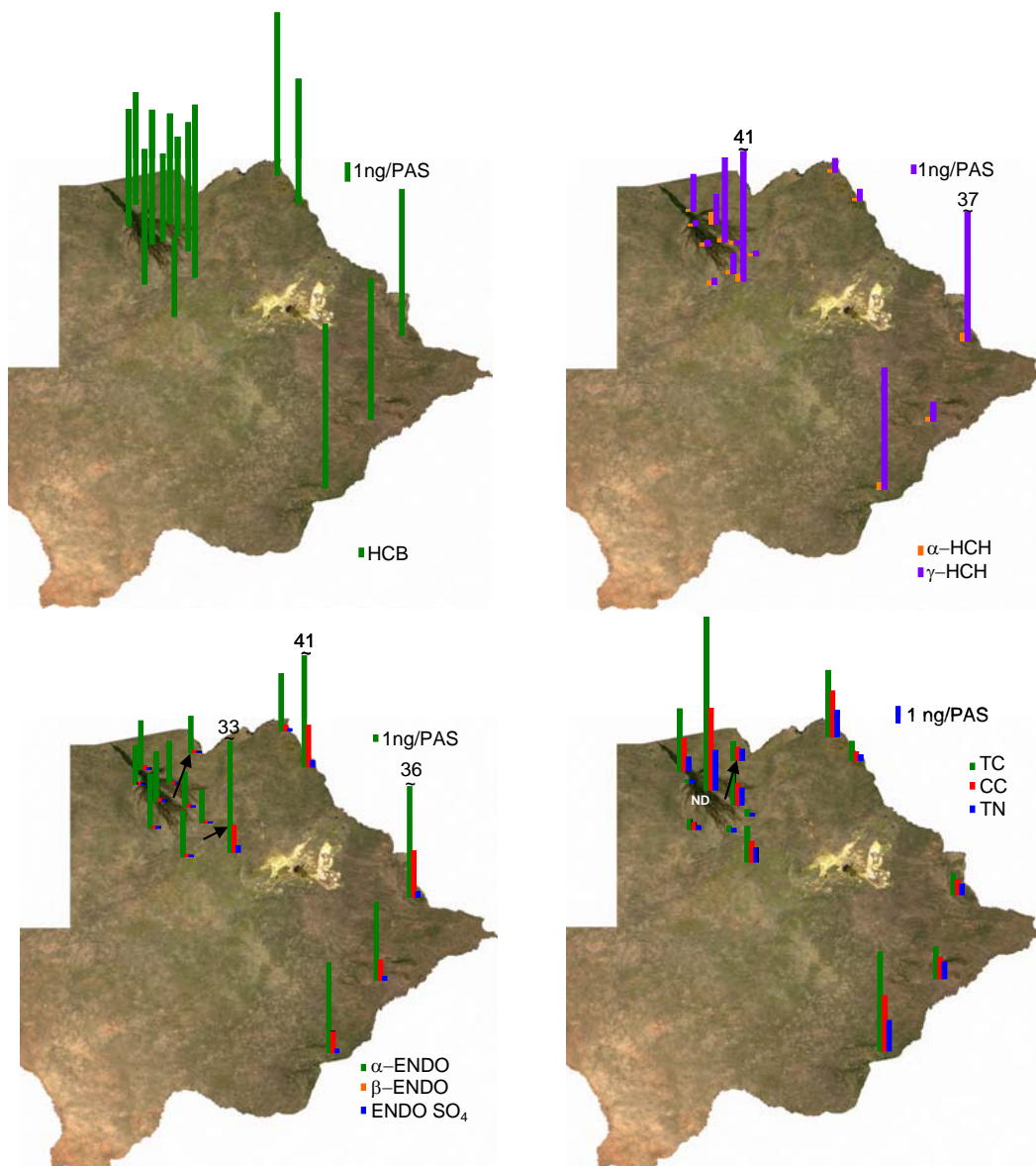


Figure 2 Spatial patterns of HCB, α -HCH, γ -HCH, TC, CC, TN, α -endosulfan, β -endosulfan and endosulfan sulfate in the Botswanian atmosphere, as recorded by passive air samplers deployed for one year in 2006/7.

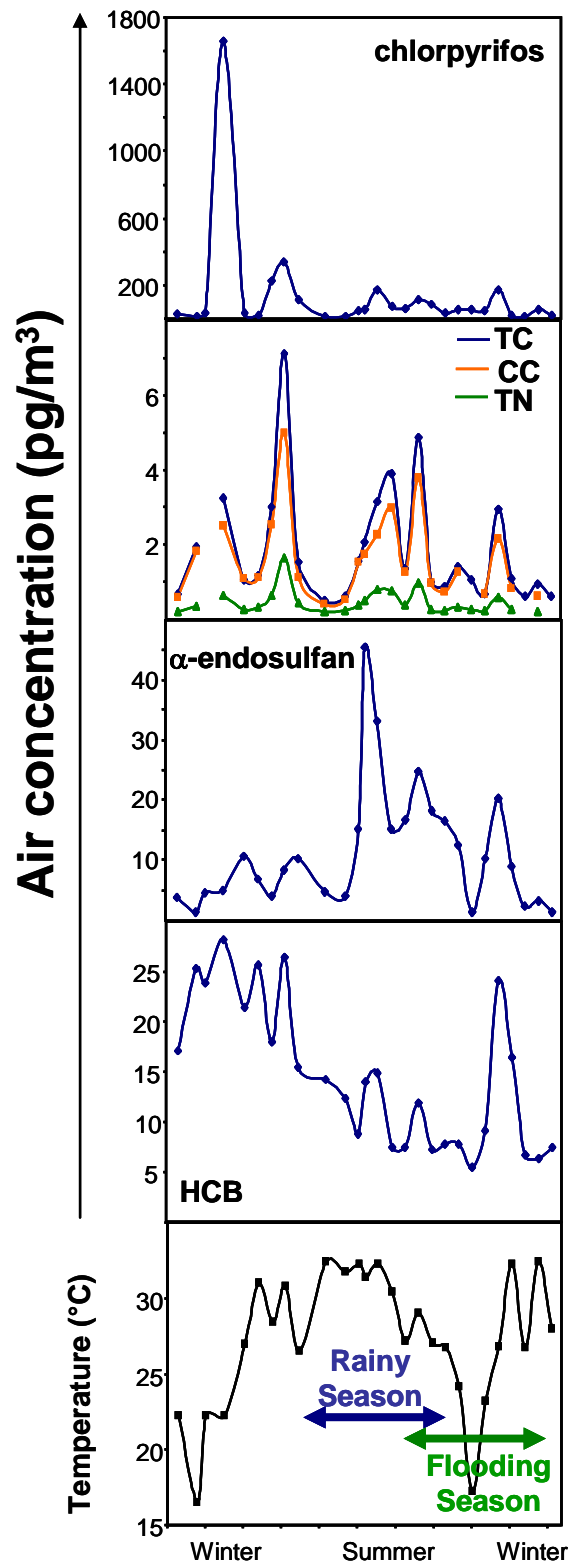


Figure 3 High volume air concentrations (pg/m^3) of TC, CC, TN, α -HCH, γ -HCH, chlorpyrifos, α -endosulfan, β -endosulfan and endosulfan sulfate at Maun site.

Soils. Concentrations of pesticides in soils from Botswana (blank corrected average of two samples in units of pg/g dry soil are given in Table S6) were extremely low, including in historical use areas. Only soils with a notable amount of OC contained dieldrin and traces of other pesticides (Figure S3). In particular, the soil from Seronga, which had the highest amount of OC (Table S1), had higher levels of dieldrin and DDT and its metabolites (Figure S3) than any other soil and also contained trace levels of HCHs, HCB and chlordanes. Extremely low levels of dieldrin were also detected in Gaborone, Nxaraga, Nokangeng and Sehitwa soils. The second highest concentrations of DDT and its metabolites were observed in Sehitwa soil. Nokangeng also contained very low levels of DDT-related substances. The DDT composition in the soils was dominated by DDE. DDE had also been the most abundant DDT component in water and biota samples from the Okavango Delta (Mbongwe et al., 2004). High DDT/DDE ratios in soils between 3 and 4 indicate that the DDT in the soils has aged (Shen et al., 2005). Soil from Eagle Island had a slightly higher amount of γ -HCH and traces of α -HCH. The PAS from this location also had the highest lindane levels among the sampler deployed in the Okavango Delta area. This suggest that lindane had recently been used at Eagle Island, presumably at the nearby tourist camp. Low levels of chlordanes were detected in soil from Nokangeng, which agrees with the PAS from this location. HCB and chlorothalonil were found in extreme low levels in a few soils samples, whereby the Nxaraga soil had higher HCB levels than any other soil. Despite the detection of endosulfan and its metabolite in all PAS, they were not detected in any of the soil.

Discussion

Do spatial patterns reflect historical or current pesticide use? Even though the Okavango Delta area had repeatedly been sprayed with DDT and endosulfan in the past for vector control, the observed spatial pattern suggest that there is no or little “memory” of the OCP usage in soils and air. Levels in air and soil samples from the Delta were generally very low, when compared to other world regions (Pozo et al., 2009, Meijer et al., 2003, Kurt-Karakus et al., 2006). This lack of memory is in contrast to temperate soils, which were found to retain substantial pesticide residues indicative of use that occurred decades ago (Meijer et al., 2003, Kurt-Karakus et al., 2006). OCPs persist for long time periods (e.g. the half-life of dieldrin 28 yr, α -HCH 7 yr and DDT 2.8 yr, Meijer et al., 2001). Not only were the levels in air or soil from the Okavango very low, but also fish from this region contained less DDT-related substances than fish from

temperate region (Mbongwe et al. 2003). Most pesticides had lower levels in the Delta than in the Eastern part of the country. Some pesticides were found in higher levels in samples from the Delta area, such as dieldrin in Seronga soil and chlordane in air sample from Nokangeng. Even when levels in the Delta are higher, as in the case of lindane at Eagle Island, it is more likely due to relatively recent use than historical applications. Spatial distribution of pesticides in the populated part of Botswana is also largely determined by current usage rather than historical use.

The results suggested that the residence time of OCPs in the soils of the arid subtropics is shorter than in temperate areas. Higher soil temperature in the arid regions may induce higher degradation and volatilization compared to temperate regions. The degradation rates of pesticides can increase by a factor of 2 for a 10 °C increase of soil temperature and volatilization rates by a factor of 3-4 for the same temperature difference (Laabs et al., 2002). Because of the short half lives of OCPs in soils in the arid environment, this type of soils is not likely to be a reservoir for the pesticide or a significant long term source of pesticides to the atmosphere like temperate soils.

Does the high storage capacity of dry mineral soil influence the fate of OCPs in arid regions? Based on laboratory experiments, it has been suggested that dry mineral soils have tremendous capacity for organic substances such as the OCPs (Goss et al., 2004). Goss et al., (2004) predicted sorption to mineral matter to be dominant in dry soils with low OC content. Botswana has an abundance of such soils. Yet, measured pesticides concentrations are very low in low OC soils in Botswana and in particular much lower than in the one soil containing notable amounts of OC. This may be due to low OC content of soils and the high soil temperature, which leads to high evaporative and degradative loss of OCPs in arid regions. The other reason may be that the Okavango Delta soils are wet throughout the year due to the “out of sync” of the flooding and rainy seasons (Figure 3). This means that mineral surfaces are occupied by water molecules, and therefore do not have the capacity for retaining OCPs. Overall, there is no evidence that suggests that the high sorptive capacity of mineral soils notably affects the fate of OCPs in subtropical areas. Soils in arid regions are not major reservoirs of organic pollutants. The intermittent humidification of these soils (rain, flooding, morning dew) may result in temporary collapses of the storage capacity, which results in the rapid loss by volatilization.

What controls seasonality of air concentrations in the arid subtropics? The seasonality of air concentrations of pesticides in temperate regions is often controlled by seasonal temperature

fluctuations (Hoff et al., 1998 and Lee and Jones, 1999, Hoff et al., 1992, Cortes et al., 1998). As the temperature increases during summer, the levels of pesticides also increase due to volatilization from surfaces. During winter time, low temperatures cause a decrease as the pesticide is deposited to the ground. However, no such correlation between temperature and air concentrations was observed in Botswana, where the seasonal temperature variability is minor. Instead the seasons in the Okavango Delta are mainly determined by hydrological events, namely rain and flooding (Figure 3). Because the water flooding the Okavango is not due to local precipitation, but falls several hundreds of kilometers away, the flooding occurs as the rainy season comes to an end. Only endosulfan and HCB exhibited some seasonal variation in air concentrations, but neither had an obvious relationship with the timing of the hydrological events. In particular, no peak in air concentrations was observed at the beginning of the wet season, which would have been expected if pesticides adsorbed to mineral surfaces are replaced by water molecules and released into the atmosphere by volatilization as the soils become wet after a period of drought. This may be because rainy season and flooding season are “out of sync”, and there is therefore no season that soils in the Okavango Delta would be expected to be completely dried out for a long time. As a result no obvious seasonality that could be linked with soil moisture is apparent. Those seasonal trends that are observed for HCB and endosulfan tend to be more likely related to seasonal usage pattern than to seasonal events in the environment.

The fate of organochlorine pesticides in the arid subtropics. It appears that the residence time of OCPs in arid subtropics is very short. Presumably the low uptake capacity of the environment is due to the high temperatures and the low organic matter content of the soils. The OCPs are therefore not easily retained by these soils. Furthermore, high irradiance (no clouds, low latitude, and high OH radical concentrations (Mandalakis et al., 2003)) may result in greater atmospheric degradation of pesticides compared to in temperate region.

Supporting Material

Additional tables of passive, active and soil sampling sites, physical-chemical properties, and degradation properties of pesticides, the passive air sampler, high volume sampler and soil concentrations and figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Supporting Information for
Fate of Pesticides in the Arid Subtropics, Botswana, Southern Africa

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Table S1 Latitude, longitude of each sampling site, length of passive air sampling period in days, and organic carbon (OC) content of soils sampled in Botswana in percent. BDL stands for below detection limit.

Number	Name	Latitude	Longitude	Sampling length	% OC
1	Gaborone	24° 39' S	25° 54' E	370	BDL
2	Mayalapye	23° 05' S	26° 49' E	331	No soil sample
3	Francistown	21° 10' N	27° 30' E	330	No soil sample
4	Pandamatenga	18° 31' S	25° 39' E	370	No soil sample
5	Kasane	17° 49' S	25° 09' E	371	No soil sample
6	Eagle Island	19° 32' S	23° 02' E	299	BDL
7	Xakanaxa	19° 10' S	23° 23' E	370	1.82
8	Maun	19° 54' S	23° 31' E	370	BDL
9	Maun Airport	19° 58' S	23° 25' E	341	No soil sample
10	Stanley	19° 35' S	23° 15' E	295	3.34
11	Sehitwa	20° 47' S	22° 71' E	307	BDL
12	Nokaneng	19° 66' N	22° 18' E	307	BDL
13	Nxaraga	19° 32' S	23° 10' E	370	3.63
14	Guma	18° 57' S	22° 22' E	370	No soil sample
15	Seronga	18° 49' S	22° 24' E	370	8.75

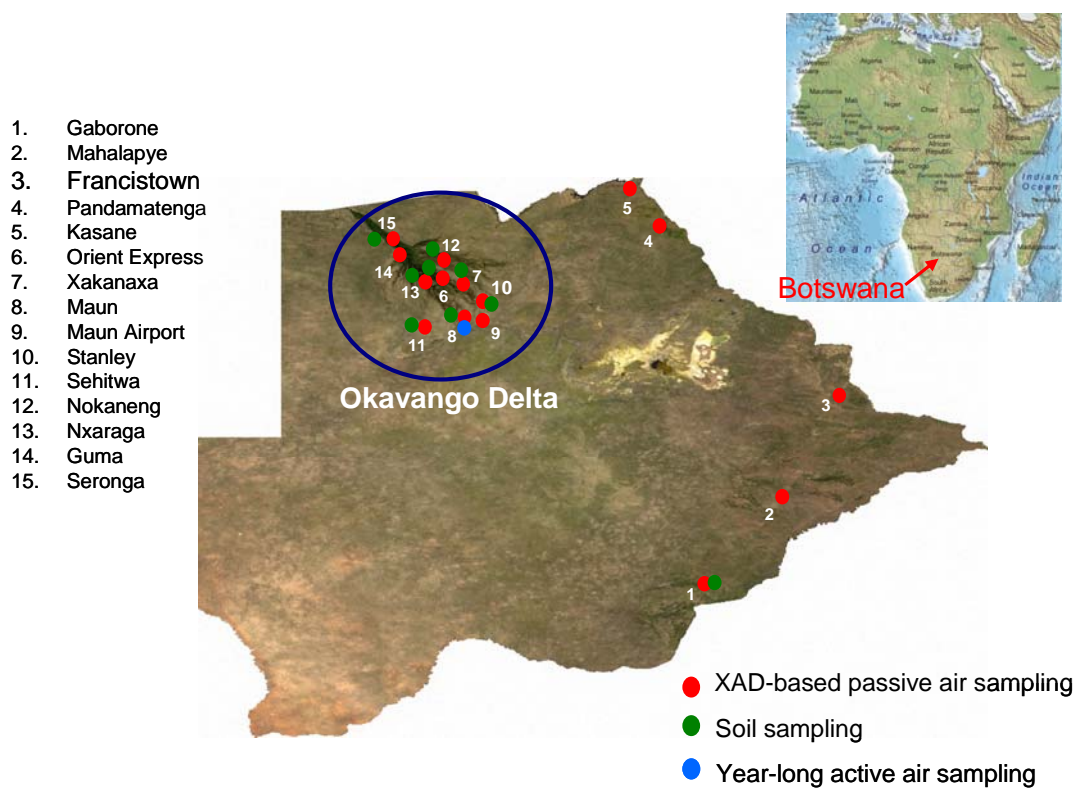


Figure S1 Map showing the passive air (red markers) and soil (green markers) sampling sites. The high volume air sampler was operated at Maun (blue marker, site #8).

Table S2 Average concentrations of duplicate PAS (ng/PAS) that were deployed at 15 sites across Botswana for the pesticides that were detected in all PAS. (HCB: hexachlorobenzene, HCH: hexachlorocyclohexane, CT: chlorothalonil, α -E: α -endosulfan, β -E: β -endosulfan, ES: endosulfan sulfate, BMDL: below method of detection limit, ND: not detected).

Location	HCB	α -HCH	γ -HCH	CT	α -E	β -E	ES
Gaborone	8.8 ± 0.7	0.8 ± 0.1	15.1 ± 1.4	7.6 ± 0.6	14.6 ± 0.7	3.5 ± 0.5	0.51 ± 0.03
Mayalapye	7.6 ± 0.3	0.43 ± 0.01	2.3 ± 0.1	4.4 ± 0.0	12.7 ± 0.5	3.25 ± 0.02	0.60 ± 0.01
Francistown	7.9 ± 0.3	0.9 ± 0.1	36.6 ± 1.8	5.84 ± 0.01	35.6 ± 0.3	7.5 ± 0.2	0.88 ± 0.02
Pandamatenga	6.7 ± 0.1	0.24 ± 0.04	1.39 ± 0.01	1.33 ± 0.02	40.9 ± 1.4	6.7 ± 0.1	0.9 ± 0.1
Kasane	8.7 ± 0.6	0.3 ± 0.02	1.6 ± 0.2	1.6 ± 0.1	9.3 ± 0.1	0.9 ± 0.1	0.300 ± 0.002
Eagle Island	4.7 ± 0.3	0.4 ± 0.2	10.4 ± 0.7	0.8 ± 0.0	5.87 ± 0.02	0.29 ± 0.04	0.15 ± 0.01
Xakanaxa	5.4 ± 0.1	0.3 ± 0.1	0.40 ± 0.01	0.7 ± 0.1	5.63 ± 0.3	0.34 ± 0.02	0.190 ± 0.002
Maun	6.9 ± 0.2	0.3 ± 0.1	2.45 ± 0.02	1.25 ± 0.05	7.36 ± 0.3	0.35 ± 0.01	0.20 ± 0.02
Maun Airport	9.2 ± 0.2	0.84 ± 0.1	40.7 ± 1.8	1.7 ± 0.1	33.2 ± 1.1	4.31 ± 0.1	0.95 ± 0.005
Stanley	4.47 ± 0.02	0.3 ± 0.1	0.56 ± 0.01	0.77 ± 0.02	5.3 ± 0.1	0.21 ± 0.01	0.12 ± 0.02
Sehitwa	7.3 ± 0.9	0.4 ± 0.1	0.8 ± 0.2	1.160 ± 0.003	8.7 ± 0.6	0.32 ± 0.04	0.27 ± 0.04
Nokaneng	5.9 ± 0.2	1.47 ± 0.03	3.7 ± 0.2	0.920 ± 0.005	6.9 ± 0.3	0.30 ¹	0.19 ¹
Nxaraga	7.2 ± 0.2	0.30 ± 0.01	0.6 ± 0.1	1.16 ± 0.02	8.1 ± 0.3	0.45 ± 0.05	0.27 ± 0.01
Guma	6.2 ± 0.6	0.20 ± 0.02	0.6 ± 0.1	0.8 ± 0.1	6.2 ± 0.2	0.32 ± 0.03	0.16 ± 0.02
Seronga	6.0 ± 0.5	0.24 ± 0.04	4.6 ± 0.6	1.01 ± 0.01	7.9 ± 0.0	0.5 ± 0.1	0.19 ± 0.01
CV (%)	5	19	8	7	3	8	6
MDL (ng/PAS)	0.23	0.14	0.12	0.18	0.10	0.07	0.05

Table S3 Average concentrations of duplicate PAS (ng/PAS) that were deployed at 15 sites across Botswana for the pesticides that were detected in a few PAS. (TC: *trans*-chlordane, CC: *cis*-chlordane, TN: *trans*-nonachlor, CF: Chlorpyrifos, BMDL: below method of detection limit, ND: not detected).

Location	TC	CC	TN	Dieldrin	o,p'-DDE	CF	Dacthal
Gaborone	5.2 ± 0.2	2.90 ± 0.03	1.59 ± 0.1	ND	ND	1.2 ± 0.6	0.33 ± 0.02
Mayalapye	1.7 ± 0.1	1.1 ± 0.1	0.87 ± 0.04	ND	ND	ND	0.25 ± 0.04
Francistown	1.10 ± 0.03	0.8 ± 0.1	0.54 ± 0.02	11.7 ± 0.8	ND	0.87 ^a	0.1 ± 0.0
Pandamatenga	1.0 ± 0.1	0.5 ± 0.1	0.31 ± 0.01	18.6 ± 1.8	ND	0.74 ^a	BMDL
Kasane	3.5 ± 0.2	2.43 ± 0.02	1.39 ± 0.04	ND	ND	0.59 ^a	0.10 ± 0.01
Eagle Island	1.00 ± 0.05	0.69 ± 0.04	0.6 ± 0.1	ND	ND	ND	ND
Xakanaxa	ND	ND	ND	ND	ND	ND	ND
Maun	0.4 ± 0.0	ND	0.13 ± 0.01	ND	ND	ND	0.07 ¹
Maun Airport	1.86 ± 0.04	1.08 ± 0.05	0.7 ± 0.1	ND	ND	0.47 ^a	0.13 ± 0.02
Stanley	0.3 ± 0.1	ND	0.18 ± 0.02	ND	ND	ND	BMDL
Sehitwa	0.50 ± 0.1	0.33 ± 0.03	0.18 ± 0.03	ND	ND	0.44 ^a	ND
Nokaneng	9.2 ± 0.4	4.3 ± 0.2	2.1 ± 0.1	ND	15.5 ± 0.5	ND	ND
Nxaraga	ND	ND	ND	ND	ND	0.73 ¹	0.11 ± 0.02
Guma	0.17 ± 0.01	ND	0.160 ± 0.003	ND	ND	ND	ND
Seronga	3.3 ± 0.1	1.7 ± 0.1	0.730 ± 0.004	ND	ND	0.65 ¹	0.10 ± 0.02
CV(%)	7	7	7	9	3	50	12
MDL (ng/PAS)	0.05	0.07	0.09	0.50	0.40	0.20	0.07

a: only detected in one the duplicates

Table S4 Maximum and minimum air temperature (T in °C), and maximum and minimum air humidity (rh in percent), and concentrations (pg/m³) of pesticides in 24 hour high volume air samples collected once every two weeks for one year at Maun, Botswana, during the sampling period. (HCB: hexachlorobenzene, HCH: hexachlorocyclohexane, TC: *trans*-chlordane, CC: *cis*-chlordane, TN: *trans*-nonachlor, α -E: α -endosulfan, β -E: β -endosulfan, ES: endosulfan sulphate, CF: Chlorpyrifos, DT: dacthal, CT: Chlorothalonil, HEP: heptachlor, BMDL: below method of detection limit, ND: not detected, NA: not available).

Date		T _{min}	T _{max}	rh _{mi}	rh _{ma}	HCB	α -HCH	γ -HCH	TC	CC	TN	α -E	β -E	ES	CF	DT	CT	HEP
130706	PUF/XAD	NA	NA	NA	NA	17	ND	3.8	0.7	0.6	0.2	3.8	0.3	ND	29	0.2	0.8	ND
	GFF					ND	ND	0.6	0.2	ND	ND	ND	ND	ND	1.4	ND	ND	ND
020806	PUF/XAD	-5.0	37.9	21	47	25	0.3	2.2	1.9	1.8	0.4	1.2	ND	ND	13	BMDL	1.4	3.5
	GFF					ND	ND	ND	0.4	ND	ND	ND	ND	ND	0.8	ND	ND	ND
110806	PUF/XAD	9.9	34.6	20	51	24	ND	1.5	ND	ND	ND	4.5	ND	ND	31	ND	1.7	ND
	GFF					ND	ND	ND	ND	ND	ND	0.5	ND	ND	ND	BMDL	2.3	ND
300806	PUF/XAD	NA	47.6	10	52	28	0.7	4.7	3.3	2.5	0.6	4.9	ND	ND	1700	ND	0.5	5.2
	GFF					ND	ND	0.1	0.5	0.4	ND	ND	ND	ND	150	ND	ND	ND
210906	PUF/XAD	14.9	39.0	18	50	21	0.4	2.0	1.1	1.1	0.3	11	0.5	0.1	36	0.1	2.3	ND
	GFF					ND	ND	ND	ND	ND	ND	ND	ND	0.1	2.9	ND	1.1	ND
061006	PUF/XAD	22.5	39.6	19	61	26	0.6	5.5	1.2	1.1	0.3	6.9	0.5	0.1	19	0.1	1.1	ND
	GFF					ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
201006	PUF/XAD	20.2	36.6	18	50	18	1.3	4.6	3.0	2.5	0.6	4.0	ND	ND	230	0.1	0.9	4.2
	GFF					ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
021106	PUF/XAD	21	40.6	20	38	26	0.9	18	7.1	5.0	1.7	8.3	0.4	0.2	340	0.2	1.1	ND
	GFF					ND	ND	BMDL	ND	ND	ND	ND	ND	ND	0.3	ND	ND	ND
171106	PUF/XAD	18.0	35.0	31	52	15	0.7	6.4	1.5	1.1	0.5	10	0.6	0.2	110	0.2	1.5	ND
	GFF					ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
151206	PUF/XAD	20.9	43.9	13	72	14	0.4	1.4	0.5	0.4	0.2	4.7	0.2	0.1	12	BMDL	ND	ND
	GFF					ND	ND	ND	ND	ND	ND	ND	ND	ND	0.1	ND	ND	ND
050107	PUF/XAD	20.0	43.5	16	89	12	0.3	1.8	0.6	0.5	0.2	3.9	ND	ND	11	BMDL	ND	ND
	GFF					ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
190107	PUF/XAD	20	44.6	16	87	8.7	ND	2.4	1.6	1.6	0.4	15	ND	0.2	48	ND	ND	2.4
	GFF					ND	ND	ND	ND	ND	ND	ND	ND	ND	BMDL	ND	ND	ND

Table S4 continued

Date		T _{min}	T _{max}	rh _{mi}	rh _{ma}	HCB	α-HCH	γ-HCH	TC	CC	TN	α-E	β-E	ES	CF	DT	CT	HEP
260107	PUF/XAD	19.1	43.6	18	48	14	0.6	3.4	2.1	1.8	0.5	45	2.3	0.6	55	0.4	1.9	2.7
	GFF					ND	ND	ND	ND	ND	ND	ND	ND	ND	0.26	ND	ND	ND
080207	PUF/XAD	22	42.6	NA	NA	15	0.8	5.0	3.2	2.3	0.8	33	2.3	0.4	170	0.2	ND	ND
	GFF					ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
230207	PUF/XAD	19.3	41.5	NA	NA	7.4			3.9	3.0	0.8	15	0.5	0.4	76	BMDL	ND	4.8
	GFF					ND			ND	ND	ND	ND	ND	ND	0.4	ND	ND	ND
090307	PUF/XAD	22.4	32	41	87	7.5			1.4	1.3	0.4	17	0.8	0.2	57	BMDL	ND	1.3
	GFF					ND			ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
230307	PUF/XAD	20	38	NA	NA	12			4.9	3.8	1.0	25	1.3	0.3	110	0.2	ND	4.7
	GFF					ND			ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
060407	PUF/XAD	15.1	39	18	50	7.2			1.0	1.0	0.3	18	0.9	0.3	83	BMDL	ND	1.6
	GFF					ND			ND	ND	ND	ND	ND	ND	BMDL	ND	ND	ND
200407	PUF/XAD	17.6	35.8	26	70	7.8			0.9	0.7	0.2	17	0.4	0.3	36	0.1	1.0	ND
	GFF					ND			ND	ND	ND	ND	ND	ND	0.6	ND	ND	ND
040507	PUF/XAD	31.5	16.8	22	49	7.8			1.4	1.3	0.3	13	0.3	0.2	55	ND	ND	ND
	GFF					ND			0.2	ND	ND	ND	ND	ND	1.9	ND	ND	ND
180507	PUF/XAD	6.6	27.9	21	34	5.4			1.1	ND	0.3	1.3	ND	ND	51	ND	ND	3.7
	GFF					ND			0.2	ND	ND	ND	ND	ND	2.1	BMDL	ND	ND
010607	PUF/XAD	11.6	34.8	19	55	9.1			0.7	0.7	0.2	10	ND	ND	46	0.1	ND	ND
	GFF					ND			ND	ND	ND	ND	ND	ND	0.9	ND	BMDL	ND
150607	PUF/XAD	17.4	36.2	26	70	24			3.0	2.2	0.6	20	0.5	0.2	170	0.2	2.7	5.0
	GFF					ND			ND	ND	ND	ND	0.2	0.1	0.9	ND	BMDL	ND
290607	PUF/XAD	22	42.6	19	55	17			1.1	0.8	0.3	9.0	ND	ND	21	0.1	1.0	2.1
	GFF					ND			ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
130707	PUF/XAD	13.5	40	18	47	6.7			0.6	ND	ND	2.4	ND	ND	12	ND	0.9	ND
	GFF					ND			0.2	ND	ND	ND	ND	ND	1.3	ND	ND	ND
270707	PUF/XAD	24	40.9	18	65	6.3			0.9	0.63	0.2	3.2	ND	ND	56	ND	ND	3.5
	GFF					ND			ND	ND	ND	ND	ND	ND	1.1	ND	ND	ND
100807	PUF/XAD	15.6	40.4	20	46	7.5			0.6	ND	ND	1.4	ND	ND	20	ND	1.0	1.5
	GFF					ND			0.2	ND	ND	ND	ND	ND	2.2	ND	ND	ND

Table S5 Average concentrations (pg/g dry soil) of detected pesticides in nine soils samples from Botswana (BMDL: below method of detection limit, ND: not detected).

Pesticides	Gaborone	Maun	Nxaraga	Nokangeng	Eagle Island	Stanley	Sehiwta	Seronga	Xakanaxa
HCB	BMDL	BMDL	0.008 ± 0.001	ND	ND	ND	0.024 ± 0.009	0.024 ± 0.009	BMDL
α-HCH	ND	ND	ND	ND	0.009 ± 0.002	ND	ND	0.008 ± 0.002	ND
γ-HCH	ND	ND	ND	ND	0.99 ± 0.02	ND	ND	0.007 ± 0.001	ND
TC	ND	ND	ND	0.16 ± 0.01	ND	ND	ND	0.006 ± 0.000	ND
CC	ND	ND	ND	0.12 ± 0.01	ND	ND	ND	0.007 ± 0.000	ND
TN	0.006 ± 0.001	ND	ND	0.12 ± 0.01	0.020 ± 0.004	ND	ND	0.009 ± 0.001	ND
Dieldrin	0.06 ± 0.02	0.06 ± 0.02	0.10 ± 0.04	0.36 ± 0.08	ND	ND	0.03 ^a	381 ± 34	ND
Aldrin	ND	ND	ND	ND	ND	ND	ND	2.13 ± 0.05	ND
p,p'-DDT	ND	ND	ND	ND	ND	ND	1.2 ^a	2.5 ± 0.5	ND
p,p'-DDE	ND	ND	ND	0.84 ± 0.04	0.26 ± 0.04	ND	4.0 ± 0.6	10.2 ± 1.2	ND
o,p'-DDT	ND	ND	ND	0.038 ± 0.012	ND	ND	0.2 ^a	0.5 ± 0.1	ND
o,p'-DDE	ND	ND	ND	0.023 ± 0.002	ND	ND	0.04 ^a	0.092 ± 0.006	ND
o,p'-DDD	ND	ND	ND	ND	ND	ND	ND	0.20 ± 0.04	ND
CF	ND	ND	ND	ND	ND	ND	0.009 ± 0.003	ND	ND
CT	0.008 ± 0.00	0.009 ± 0.005	0.01 ± 0.00	ND	ND	ND	ND	0.008 ± 0.001	0.010 ± 0.004

a: only detected in one the duplicates

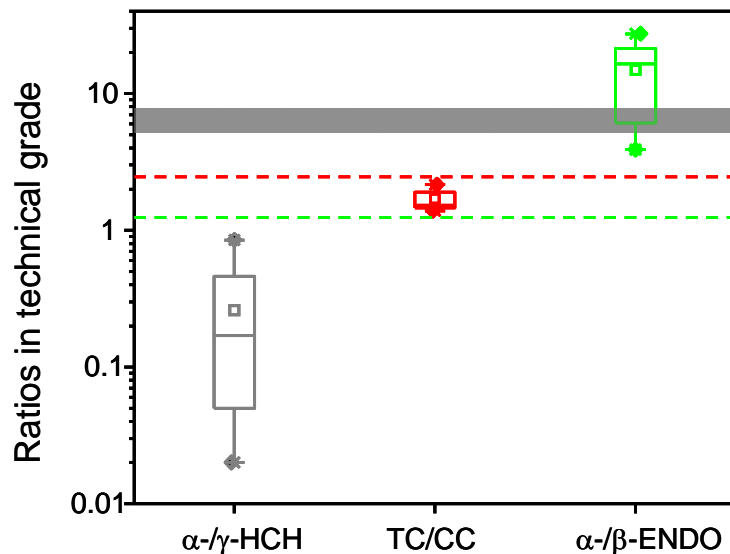


Figure S2 Box-and-whisker plot of α -/ γ -HCH, TC/CC and α -/ β -endosulfan ratios in passive air samples from Botswana. The gray band, red-dotted and green-dotted lines indicate the ratio in technical HCH (range from 4.7 to 8), chlordane (1.17) and endosulfan (2.3), respectively.

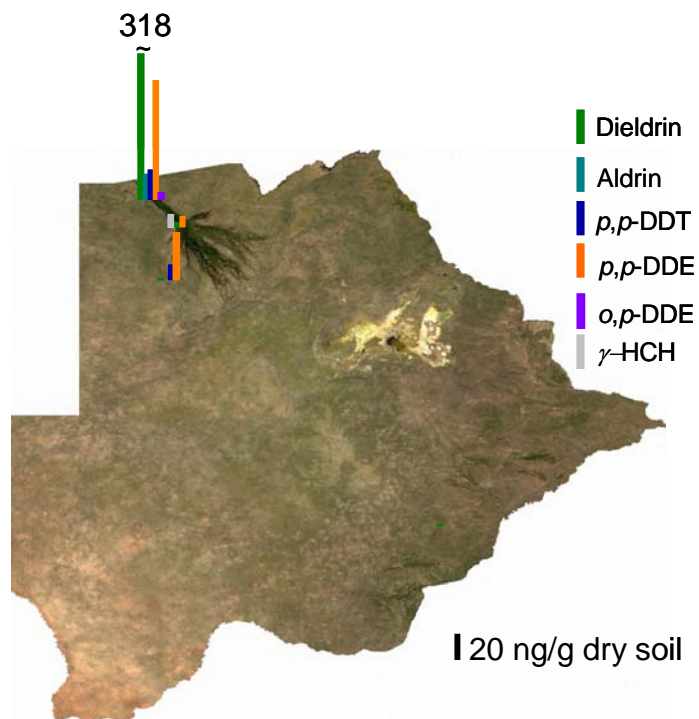


Figure S3 Map showing the average concentrations (ng/g dry soil) of dieldrin, aldrin, γ -HCH and DDT and its metabolites in Botswanian soils.

Appendix 4



Spatial variability of semivolatile organic compounds in the Chilean atmosphere.

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In an effort to characterize the spatial variability of pesticides, polychlorinated biphenyls, and polycyclic aromatic hydrocarbons in the Chilean atmosphere, XAD-based passive air samples (PAS) were deployed for 12 months along three elevational gradients in Northern, Central and Southern Chile, for a total of 20 sampling sites, ranging in elevation from 10 to 4400 m and ranging over 26 degrees of latitude. Levels of pesticides in air from Chile are very low. Only hexachlorobenzene, α - and γ -hexachlorocyclohexane, endosulfan I and chlorothalonil were present in all of the samples. The concentrations of these five pesticides in air decreased from North to South, with much steeper gradients for chlorothalonil and endosulfan. HCB had largely uniform air concentrations with latitude and altitude, and can thus be used to derive sampler specific sampling rates, that account for differences in uptake kinetics due to environmental factors such as altitude and temperature. Chlorothalonil levels were greatly elevated in air samplers deployed in urban locations. Remarkably, endosulfan concentrations in air tend to increase with elevation, in particular in Central Chile. Since endosulfan is particularly susceptible to mountain cold-trapping, such gradients may reflect the re-volatilisation of endosulfan that had been preferentially deposited at higher altitudes. PCB concentrations were also low (0.2 to 11 ng/PAS), with slightly higher levels in the two urban sampling sites in Concepcion and Arica. PCB- 52 is the only congener present in all samples, with levels that are remarkably uniform across the country.

Introduction

Chile is a South American country with an extraordinary latitudinal extension (4630 km, 18 ° to 56 °S) resulting in highly variable climate with extremely dry desert climate in the north, Mediterranean climate in the central region (around 30 cm of precipitation per year), and cool and damp climate in the south (up to 5 m of precipitation per year). Equally staggering are the elevation changes, ranging from sea level to 6880 m (Nevado Ojos del Salado) over a mere 200 km distance. Similar to the latitudinal changes, vertical

gradients are also steep gradients of precipitation and temperature. The Chilean atmosphere is under Pacific influence and local sources of organic contaminants are relatively minor. Chile thus is the ideal location to study latitudinal and altitudinal gradients in organic contamination in the Southern hemisphere.

Very little information on persistent organic pollutants (POPs) in the environment of Chile exists. Focardi et al. (1996) noted the presence of PCBs, DDT and its metabolites, HCH isomers and HCB in fish and birds from different locations in the Biobio river basin. Barra et al. (2001ab) reported the concentrations of a variety of organochlorine pesticides in the sediments of four Chilean lakes, and Palma-Fleming et al. (1998) identified similar contaminants in the sediments of the Valdivia river estuary. Mandalakis and Stephanou (2002) recently reported PCBs levels in urban particles sampled in Santiago and Temuco, noting levels comparable to other urban areas around the world. The sum of PCBs was higher in human adipose tissue from Siena (Italy) than in that from Concepcion (Chile) by an order of magnitude (Mariottini et al., 2000).

Even fewer studies allow the analysis of latitudinal trends: The International Mussel watch programme included a number of Chilean coastal locations (Sericano et al., 1995), and noted higher concentrations of PCBs in Punta Arenas in the very South of the country compared to mussels from lower latitudes. Confirming these findings, Barra et al. (2002) found much higher concentrations in the southernmost part of Chile, when studying PCBs in sessile marine bivalves along a latitudinal transect. This has been attributed to higher precipitation rates and colder temperatures in the South. Munoz and Becker (1999), on the other hand reported higher concentrations of PCBs and OC pesticides in gull eggs from central Chile than in eggs from the southernmost part of the country. Pozo et al. (2004) reported concentrations of PCBs, PBDEs and selected organochlorine pesticides in Chilean air. Levels were generally low, but endosulfan was prevalent and showed a decreasing concentration gradient from the north to the south of Chile. Over the last few years, Barra et al. have conducted some preliminary work on elevation gradients in Chile (Grimalt et al., 2004; Barra et al., 2005). For example, they analysed for PAHs, PCBs and HCHs in soils, superficial water, and snow along an altitudinal gradient in the Laja River Basin of South Central Chile (Barra et al., 2005). When analyzing selected POPs in mosses from the Chilean Andes, Grimalt et al. (2004)

observed that most compounds exhibit higher concentrations with increasing elevation above sea level.

In this study we set out determine and interpret the changes in air concentrations of semivolatile organic compounds along three altitudinal gradients, situated at three different latitudes within Chile. We hoped to gain insight into the atmospheric background contamination with POPs in the Southern hemisphere.

Methods

Sampling. Year-long, duplicate passive air samples (PAS) were taken along three elevational gradients in Northern, Central and Southern Chile, for a total of 20 sampling sites, ranging in elevation from 10 to 4400 m and ranging over 26 degrees of latitude (Figure 1). The 20 sampling sites represent a wide variety of landscapes (Figure S1). The PAS consist of a stainless steel mesh cylinder, filled with XAD-2 resin and suspended in a stainless steel shelter with an open bottom (Wania et al., 2003). In this study, a short XAD PAS, with half the length of the original design (Wania et al., 2003) was used. The XAD-resin PAS was prepared as described previously (Wania et al., 2003).

The transect in Northern Chile (“Altiplano de Arica”, 18°S), deployed from July 2006 to July 2007, included six sampling sites between Arica (48 m) and Lago Chungara (4400 m). The transect in Central Chile (“Araucaria”, 38°S), deployed from March 2006 to March 2007, included seven sites between Lago Llu Llu (10 m) and Paso Pino Hachado (1874 m), and an additional sampling site on the campus of the University of Concepcion. The transect in Southern Chile (“Rio Cisne”, 44°S), deployed from February 2006 to February 2007, included five sites between Puerto Cisne (50 m) to Alto Rio Cisne (700 m), and an additional sampling site in the vicinity of the town of Coyhaique.



Fig. 1 Location of the three sampling transects along elevation gradients within Chile.

Soil samples were taken at each of the PAS sampling sites. Northern Chilean soils were taken in July 2006, Central Chilean soils were taken in March 2006, and Southern Chilean soils were taken in February 2006. Each soil sampling site was divided into a grid and 9 samples were collected with an auger, reaching a depth of 25 cm, which were then mixed with a clean steel shovel and bucket (Daly et al., 2007). For each site, two sub-samples were collected and wrapped in aluminum foil that had been baked at 450°C.

Analysis. After spiking with recovery standards, the PAS were Soxhlet-extracted with dichloromethane (DCM) for 20-22 hours. The volume-reduced extracts were passed through baked sodium sulfate to remove any water residue (Gouin et al., 2008). The final volume of the extracts was 1 ml, and 100 ng of mirex was added for volume correction. The extracts were analysed for their content of four-ring polycyclic aromatic hydrocarbons, PCBs (54 congeners) and organochlorine pesticides. The list of analytes included hexachlorobenzene (HCB), chlordane (cis- and trans-chlordane, trans-nonachlor), heptachlor (and heptachlorepoxyde), dieldrin, aldrin, DDT (and metabolites), endosulfan and endosulfan sulfate, α - and γ -hexachlorocyclohexane, dacthal, chlorothalonil, trifluralin, and pendimethalin.

The soil samples were extracted and first analysed for PCBs in Chile, then send to Canada for additional analyses for pesticides and PCBs.

Results and Discussion

The concentrations of semivolatile organic compounds in the passive air samplers (in units of ng/PAS) are given in [Tables S1](#) to [S3](#). The concentration of organochlorine pesticides in the Chilean atmosphere is exceptionally low ([Table S1](#)). Only five compounds were present in air from all Chilean sampling sites: HCB, α - and γ -HCH, endosulfan I and chlorothalonil. In Central Chile, traces of heptachlor and chordanes were detected at a single site (“Fundo el Vergel”) near the town of Angol, which is in an agricultural area in the central valley. At the lower end of the transect in Northern Chile, i.e. in the town of Arica, dieldrin, chlordane and heptachlor were present. DDT-related substances and aldrin were not detected in any air sample from Chile. All of the samplers deployed in urban locations in Chile (Coyhaique, Concepcion, Angol, Arica) showed relatively high levels of chlorothalonil, suggesting wide-spread use of this fungicide.

For the five pesticides that were detectable in air from all Chilean sampling sites, [Figure 2](#) displays the geometric mean concentrations for each part of the country in ng/PAS. They all show a latitudinal gradient with higher levels in the North, although the gradients are very different for different chemicals. The gradient is very steep for chlorothalonil with concentrations in the North being 30 times higher than in the South and very weak for HCB, with less than 30 % difference between the average concentrations in the North and the South.

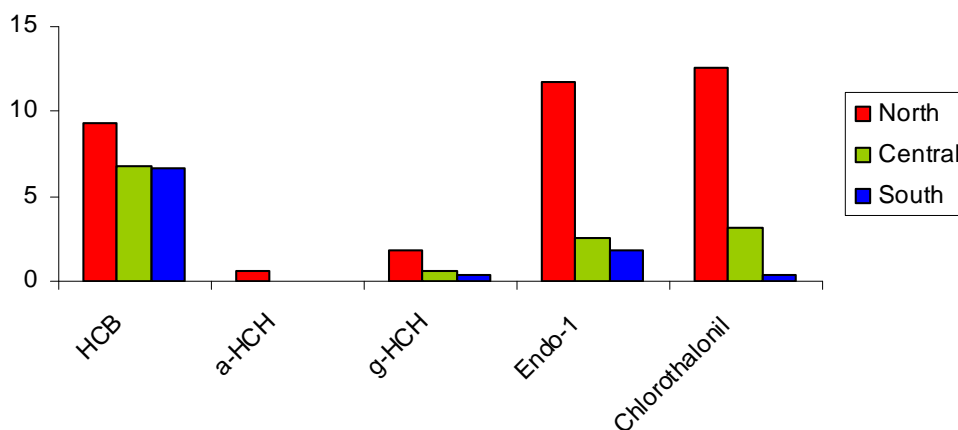


Figure 2 Latitudinal gradients in the concentrations of five organochlorine pesticides in the Chilean atmosphere.

HCB levels were also uniform along each transect (black bars in [Figure 3](#)), which is consistent with both other studies on the spatial variability of atmospheric HCB concentrations and the very long atmospheric residence time of HCB. This consistency of sequestered amounts of HCB can be used to derive sampler specific sampling rates (Liu et al., 2010). By dividing the amount of HCB sequestered in each PAS by the sampling duration and the hemispheric average concentration, which is assumed to be constant in space and time, we can obtain a sampler-specific R , which then can be used to calculate volumetric air concentrations for the other analytes. This way we indirectly account for the environmental factors (temperature, pressure, wind speed and turbulence) that could affect R , and we can be more confident in comparing levels of the same chemical between sites at different altitude and latitude (Liu et al., 2010). The choice of the constant HCB air concentration affects the numerical value of R and the calculated volumetric concentrations for the other SVOCs, but it does not affect relative differences

in concentration in space and time. this approach assumes that all analytes have uptake rates similar to HCB, which may not be the case (12). These *R* values thus have to be considered approximations and differences in the concentrations between different chemicals have to be interpreted with this uncertainty in mind (Liu et al., 2010).

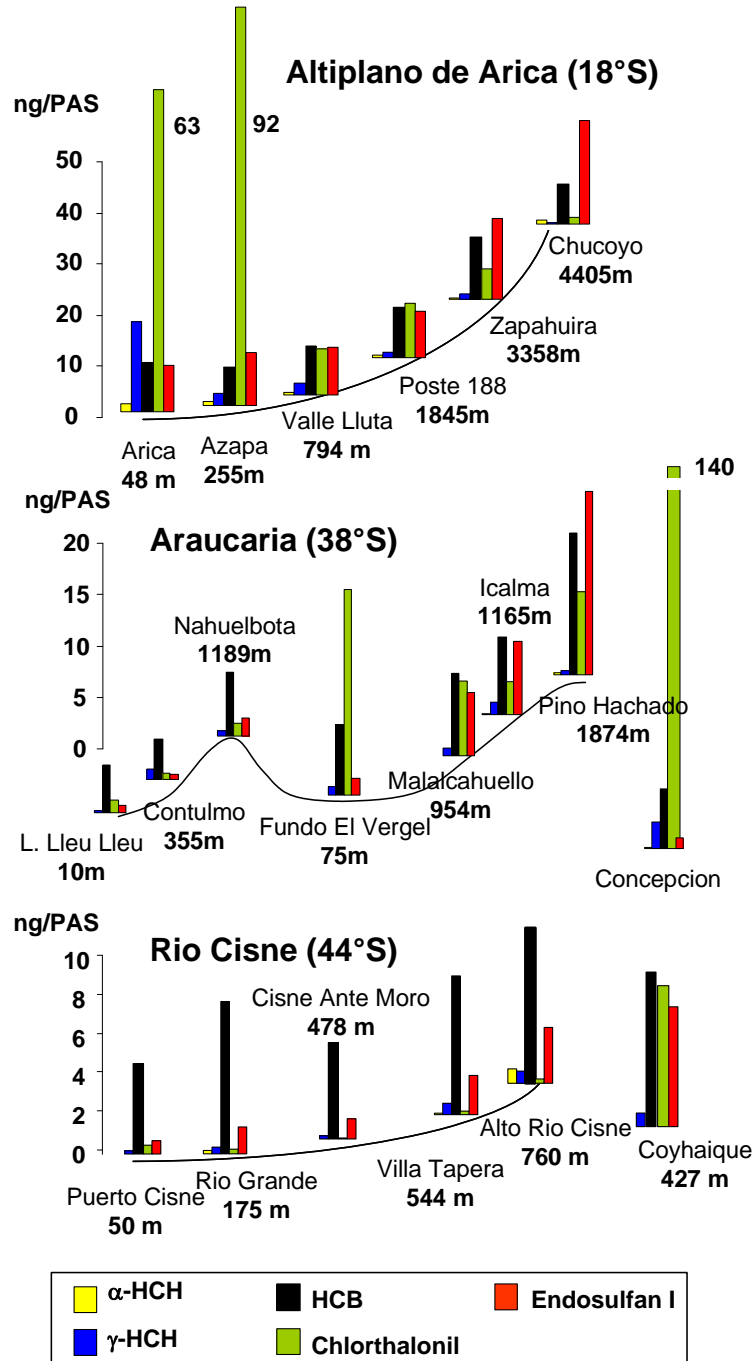


Figure 3 Concentrations of five organochlorine pesticides along three elevation gradients in Northern, Central and Southern Chile.

Comparing the concentrations along the various transects, it appears that there is a consistent trend of increasing Endosulfan-I concentration with altitude in all parts of Chile. Since HCB, which likely has uniform air concentration along a transect, does generally not show such a trend, the pattern for endosulfan can not be explained by faster uptake caused by higher wind at higher altitude (Except possibly at Paso Pino Hachado, which had unusually high HCB levels in PAS and is exceptionally windy). Since endosulfan is particularly susceptible to mountain cold-trapping (Wania and Westgate, 2008, Dlay et al., 2007), such gradients may reflect the revolatilisation of endosulfan that had been deposited to a greater extent at higher altitudes.

Concerning the PAHs in passive air samplers, it is obvious that activities in the immediate vicinity of the sampling site may skew the results. While it is easy to explain higher levels of the four-ring PAHs in the samplers deployed at Concepcion and Arica, which are both urban locations, the origin of similarly high levels at the remote sites of Icalma, Contulmo, and Rio Grande is less obvious. Icalma is a small border settlement, Contulmo is a small protected nature reserve, and Rio Grande is a remote farm. Possibly the burning of refuse and home heating at these places is responsible for higher PAH levels in the air of these sites. In the case of Cotulmo, the sampler was placed fairly close to the road. Truly remote sites, i.e. sites that have neither houses nor major roads in the vicinity (such as Poste 188, Paso Pino Hachado, Cisne ante Moro), are likely more reflective of true background concentrations for PAHs.

PCB concentrations were low (sum of 54 PCB congeners 0.2 to 4 ng/PAS), with slightly higher levels in the two urban sampling sites in Concepcion (11 ng/PAS) and Arica (6.5 ng/PAS). Despite the low levels, the agreement between duplicates is excellent. Nahuelbota is the only site with larger differences between the two duplicates. Only 13 congeners are detected in at least one sampling location, and only eight congeners are detected in at least two samples. PCB- 52 is the only congener present in all samples, and is thus best suited for spatial comparisons. Its levels that are remarkably uniform across the country. The differences in PCB-52 concentration between the three transects is very minor, and there is also no apparent relationship of its concentration with elevation in any of the three transects.

The lighter congener (esp. 18, but also 8, 17, 16+32) are only detected at the urban sites (Arica and Concepcion). If they are present, levels tend to be relatively high (above 1 ng/PAS for individual congeners). This may indicate that they are present only near sources and have very limited atmospheric residence times and thus travel distance. Interestingly, the heavier congeners (esp. 110, but also 99) seem to be present only at relatively wet places not far from the ocean, such as the lower range of the Rio Cisne transect and the coastal mountains of the Araucaria transect. No PCBs heavier than 153 were detected in any sample.

PCBs and OCPs were below detection limits in virtually all of the soil samples from Chile. Only the lowest sampling site along the Rio Cisne transect contained traces of several PCB congeners.

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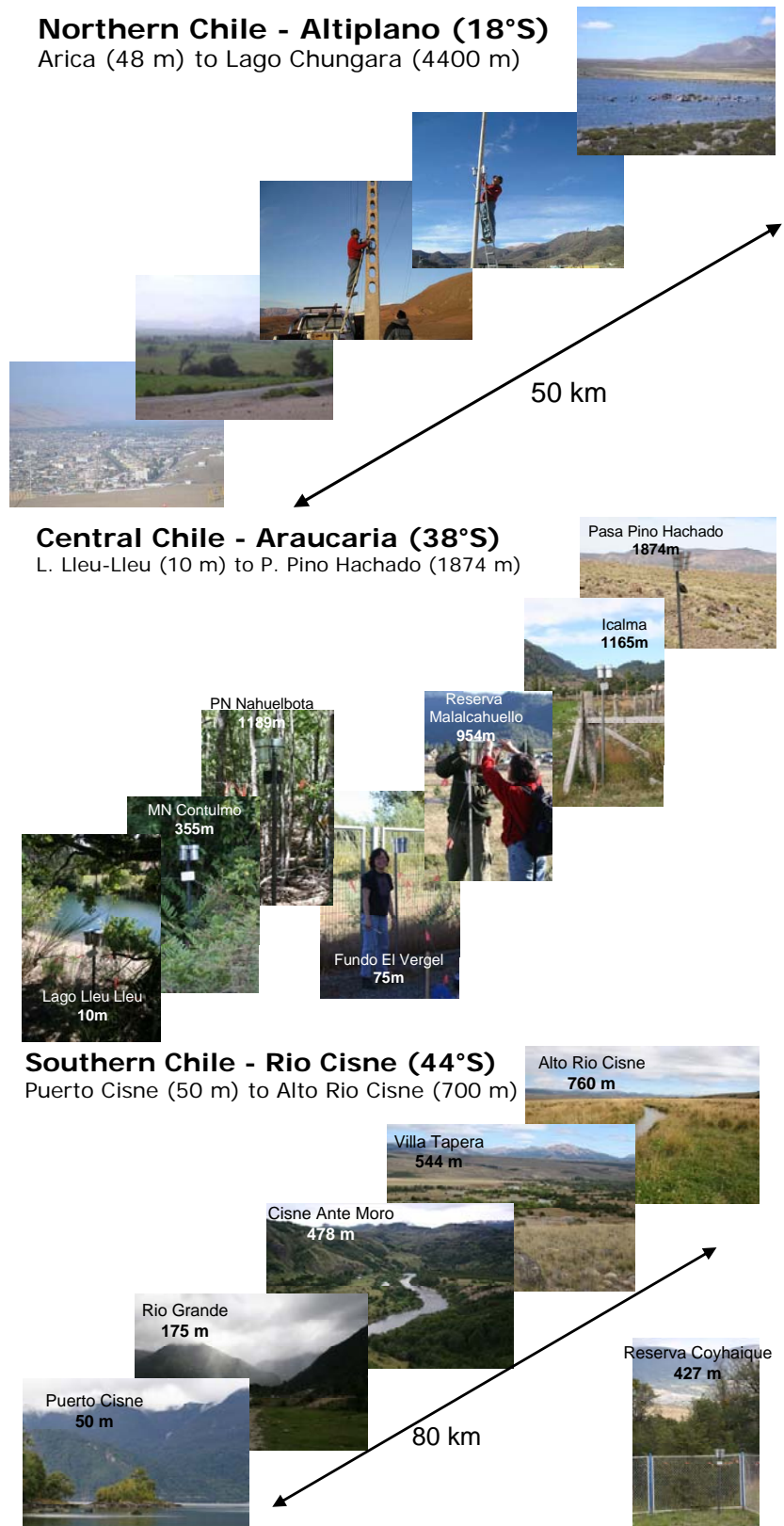


Figure S1 Photographs showing the landscape at each of the 20 passive air sampling sites across Chile

Table S1. Air concentrations (average of duplicates in ng/PAS) of pesticides classified under the Stockholm Convention in Chile.

Location	Latitude	Longitude	Elevation (m a.s.l.)	HCB	HEPT	HEPX	TransC	CisC	trans- nonachlor	Dieldrin	p,p'- DDE	p,p'- DDT
Altiplano de Arica												
Arica	18° 29' S	70° 182' W	48	9.5	1.2	ND	0.9	0.2	0.2	26.0	ND	ND
Valle Azapa	18° 34' S	70° 11' W	255	7.5	ND	ND	0.2	ND	ND	30.4	ND	ND
Valle Lluta	18° 24' S	70° 00' W	794	9.6	ND	ND	0.1	ND	ND	ND	ND	ND
Poste 188	18° 29' S	69° 54' W	1845	9.7	ND	ND	ND	ND	ND	ND	ND	ND
Zapahuira	18° 20' S	69° 35' W	3358	12.1	ND	ND	ND	ND	ND	ND	ND	ND
Chucuyo	18° 13' S	65° 19' W	4405	7.9	ND	ND	ND	ND	ND	ND	ND	ND
Araucaria												
Lago Lleu Lleu	38° 07' S	73° 23' W	10	4.7	ND	ND	ND	ND	ND	ND	ND	ND
MN Contulmo	38° 00' S	73° 11' W	355	3.9	ND	ND	ND	ND	ND	ND	ND	ND
PN Nahuelbota	37° 49' S	72° 57' W	1189	6.2	ND	ND	ND	0.5	ND	ND	ND	ND
Fundo El Vergel	37° 49' S	72° 39' W	75	6.8	5.9	0.9	0.9	BMDL	BMDL	ND	ND	ND
Malalcahuello	38° 29' S	71° 34' W	954	8.0	ND	ND	ND	ND	ND	ND	ND	ND
Icalma	38° 48' S	71° 16' W	1165	7.6	ND	ND	ND	ND	ND	ND	ND	ND
Pasa Pino Hachado	38° 39' S	70° 53' W	1874	13.8	ND	ND	ND	ND	ND	ND	ND	ND
Concepcion	36° 49' S	73° 02' W	33	5.8	ND	ND	0.1	ND	ND	ND	ND	ND
Rio Cisne												
Puerto Cisne	44° 44' S	72° 39' W	50	4.6	ND	ND	ND	ND	ND	ND	ND	ND
Rio Grande	44° 39' S	72° 15' W	175	7.8	ND	ND	ND	ND	ND	ND	ND	ND
Cisne Ante Moro	44° 39' S	71° 48' W	478	5.0	ND	ND	ND	ND	ND	ND	ND	ND
Villa Tapera	44° 38' S	71° 40' W	594	7.2	ND	ND	ND	ND	ND	ND	ND	ND
Alto Rio Cisne	44° 29' S	71° 18' W	760	8.0	ND	ND	ND	ND	ND	ND	ND	ND
Reserva Coyhaique	38° 28' S	71° 34' W	954	8.0	ND	ND	ND	ND	ND	ND	ND	ND

BMDL = below method of detection limit

ND = not detected

Table S2. Air concentrations (average of duplicates in ng/PAS) of PAHs and non-Stockholm Convention pesticides in Chile.

Location	α -HCH	γ -HCH	endo I	endo II	endoSO ₄	trifluralin	Chloro-thalonil	Pendi-methalin	FLT	PYR	BaA	CHR
Altiplano de Arica												
Arica	1.6	17.7	9.1	2.1	0.1	0.1	62.8	ND	193	102	2.88	7.89
Valle Azapa	0.8	2.3	10.4	2.1	0.2	0.1	91.9	ND	118	44.7	4.01	6.12
Valle Lluta	0.5	2.5	9.2	0.8	0.2	0.1	9.2	ND	58.8	ND	3.30	3.74
Poste 188	0.5	1.0	9.0	0.7	0.4	0.1	10.7	ND	BMDL	ND	4.24	ND
Zapahuira	0.3	1.0	15.9	0.4	0.3	ND	5.9	ND	31.4	ND	4.45	ND
Chucuyo	0.7	0.4	20.2	0.2	0.3	BMDL	1.2	ND	17.7	ND	4.23	ND
Araucaria												
Lago Lleu Lleu	BMDL	0.2	0.7	ND	ND	ND	1.2	ND	42.1	ND	ND	1.59
MN Contulmo	BMDL	1.0	0.5	ND	ND	0.2	0.6	ND	124	52.0	0.69	2.24
PN Nahuelbota	BMDL	0.5	1.7	ND	BMDL	0.1	1.2	ND	19.0	ND	ND	0.65
Fundo El Vergel	BMDL	0.9	1.6	0.1	ND	10.4	20.0	51.8	34.0	ND	ND	1.17
Reserva Malalcahuello	BMDL	0.7	6.2	0.2	0.1	ND	7.2	ND	50.5	ND	ND	2.18
Icalma	BMDL	1.2	7.1	0.3	0.1	ND	3.3	ND	204	54.0	2.90	5.45
Pasa Pino Hachado	BMDL	0.4	17.8	0.8	0.4	0.1	8.1	ND	5.48	ND	ND	0.72
Concepcion	BMDL	2.6	1.1	ND	ND	0.8	130.5	ND	519	210	6.13	23.0
Rio Cisne												
Puerto Cisne	BMDL	0.2	0.7	ND	ND	BMDL	0.5	ND	73.3	23.9	0.23	2.22
Rio Grande	BMDL	0.4	1.4	ND	ND	0.2	BMDL	ND	247	81.0	1.64	4.17
Cisne Ante Moro	BMDL	0.2	1.0	ND	ND	ND	BMDL	ND	5.51	ND	ND	ND
Villa Tapera	BMDL	0.6	2.0	ND	ND	0.1	BMDL	ND	50.1	ND	2.53	1.73
Alto Rio Cisne	0.8	0.7	2.9	BMDL	BMDL	BMDL	BMDL	ND	107	ND	2.47	2.32
Reserva Coyhaique	BMDL	0.7	6.2	0.2	0.1	ND	7.2	ND	24.2	ND	ND	0.90

BMDL = below method of detection limit

ND = not detected

Table S3. Air concentrations (average of duplicates in ng/PAS) of PCBs.

Location	8	18	17	16+32	33	52	44	70	95	99	110	149	153	Σ PCB
Altiplano de Arica														
Arica	ND	3.78	ND	ND	ND	1.39	1.19	ND	ND	ND	ND	0.26	ND	6.63
Valle Azapa	ND	0.93	ND	ND	ND	0.57	ND	ND	ND	0.67	ND	ND	ND	2.17
Valle Lluta	ND	ND	ND	ND	ND	0.48	ND	ND	ND	ND	ND	ND	ND	0.48
Poste 188	ND	0.28	ND	ND	ND	0.27	ND	0.15	0.20	0.60	ND	ND	ND	1.40
Zapahuira	ND	ND	ND	ND	ND	0.60	ND	ND	ND	ND	ND	ND	ND	0.60
Chucuyo	ND	ND	ND	ND	ND	0.48	ND	0.15	0.24	0.40	ND	ND	ND	1.08
Araucaria														
Lago Lleu Lleu	ND	ND	ND	ND	ND	0.31	ND	0.11	ND	ND	ND	ND	ND	0.36
MN Contulmo	ND	ND	ND	ND	ND	0.63	ND	0.27	ND	0.55	0.82	ND	ND	2.00
PN Nahuelbota	ND	ND	ND	ND	ND	0.54	ND	0.18	0.58	0.60	0.88	0.33	0.21	2.31
Fundo El Vergel	ND	ND	ND	ND	ND	0.66	ND	0.27	ND	ND	ND	ND	ND	0.80
Reserva Malalcahuello	ND	ND	ND	ND	ND	0.33	ND	ND	ND	ND	ND	ND	ND	0.33
Icalma	ND	ND	ND	ND	ND	0.35	ND	ND	ND	ND	ND	ND	ND	0.35
Pasa Pino Hachado	ND	ND	ND	ND	ND	0.20	ND	ND	ND	ND	ND	ND	ND	0.20
Concepcion	3.18	2.43	1.07	0.44	0.69	0.83	0.79	0.28	ND	0.82	ND	0.28	0.37	11.18
Rio Cisne														
Puerto Cisne	ND	ND	ND	ND	ND	0.57	0.40	0.21	0.60	0.32	0.73	0.26	ND	3.10
Rio Grande	ND	ND	ND	ND	ND	1.07	ND	0.47	0.76	0.75	1.20	ND	ND	4.25
Cisne Ante Moro	ND	ND	ND	ND	ND	0.67	0.47	0.33	ND	0.79	0.81	ND	ND	3.06
Villa Tapera	ND	ND	ND	ND	ND	0.38	ND	ND	0.36	ND	ND	ND	ND	0.56
Alto Rio Cisne	ND	ND	ND	ND	ND	0.49	ND	0.20	ND	ND	ND	ND	ND	0.69
Reserva Coyhaique	ND	ND	ND	ND	ND	0.52	0.40	0.14	0.31	0.37	0.38	ND	ND	2.11

ND = not detected

Bold font = one duplicate was ND

Appendix 5



Seasonal and Altitudinal Trends of Chlorinated Pesticides in the Central Himalayan Atmosphere

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XAD-resin based passive air samplers were used to measure the concentrations of hexachlorobenzene (HCB), endosulfan I, α - and γ -hexachlorocyclohexane (α - and γ -HCH), p,p'-DDE and p,p'-DDT over an altitudinal transect from 174 to 5605 m a.s.l in Nepal (27°34'-27°60'N, 84°29'-86°50'E). In malaria prone agricultural regions in the lower reaches of the transect, where some of those organochlorine pesticides are used extensively, very high air concentrations up to several thousand pg/m³ and soil concentrations of pp'-DDT in the μ g/g carbon were observed. Concentrations in the high altitude range of the study region, where no pesticide usage takes place, were on the order of tens to hundreds of pg/m³ air and ng/g carbon in soil, similar to those found in North American mountains. HCB which had similar levels at different altitudes and during different seasons, and could therefore be used to derive sampler specific uptake rates. Concentration of the other pesticides were generally higher in summer (May to October) than in winter (November to April), and tended to decline with slightly with elevation. gradients with altitude displayed large differences between summer and winter. 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. Carbon normalized soil concentrations tend to decline above 2600m a.s.l. following the gradient of precipitation.

Brief: In lower altitudes of Nepal, exceptionally high air and soil concentrations of DDT-related substances were observed. This, in combination with high abundance of the parent compound DDT relative to the metabolite DDE, indicates recent usage. The pesticides clearly are transported atmospherically into the higher reaches of the Himalaya.

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 also observed in the world's highest mountain range (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 (OCPs), 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 OCP most frequently detected at high concentrations in the global atmosphere (17). HCB 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 industrial areas in China (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 an 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 on 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 OCPs 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 200 μ l and spiked with an aldrin performance standard (Accustandard, New Haven, CT, USA). One μ l of each sample was injected onto a Varian GC/ECD (Missisauga, Canada) equipped with a 60m J&W DB-5 capillary column (Agilent Technologies, Missisauga, Canada) and analyzed for several OCPs.

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/m³ for HCB, α -HCH, γ -HCH and p,p'-DDE, respectively, based on an air sampling rate of 0.52 m³/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 174 m a.s.l to 5400 m a.s.l. using a 60 mm ID corer to the bottom of the organic layer. The pooled samples were double wrapped in sealable plastic bags, sent to the Freshwater Institute 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. Samplers were deployed in three distinct regions (Table 1, Figure 1a). Region A, at low elevation, subtropical in climate, and with high summer time precipitation, is malaria prone and has agriculture in close proximity. One duplicate sampler was placed at 174 m in Chitwan National Park. Region B had two sampling sites, Dhaitar at 841 m and Tulichour at 1881 m. Dhaitar, again with subtropical climate, is typified by intensive agriculture and is also malaria prone. As it is accessible by road and in close proximity to Kathmandu, and therefore a large market, pesticide usage is very high. Although Tulichour is not far from Dhaitar, road access is very limited and it is not malaria prone due to the elevation. Pesticide usage is much lower. It has slightly higher precipitation rates and snow can fall in the winter. Five sites, ranging in elevation from 2638 to 5605 m a.s.l., are in remote Solo Khumbu (region C). Pest problems at this high altitude are limited, and access to pesticides is also extremely limited due to long distance to a road head (6 days walk for a porter). Precipitation rates decline with altitude in region C (Figure 1b).

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

Region	Site Name	Northern Latitude	Eastern Longitude	Altitude (m a.s.l.)	Deploy date in 2004	Retrieval/ 2 nd deploy date in 2005	1 st sampling duration (days)	2 nd retrieval date in 2005	2 nd sampling duration (days)	Soil carbon content (%)	Vegetation
A	Chitwan Park	27°34.605'	84°29.839'	174	Oct. 23	May 1	190	Nov. 4	187		Tropical Forest
B	Dhaitar	27°42.571'	85°36.375'	841	Oct. 21	Apr. 27	188	Nov. 1	188	0.7	Agricultural
	Tulichour	27°41.568'	85°33.013'	1881	Oct. 20	Apr. 27	187	Nov. 1	188	1.5	Agricultural
C	Phakding	27°44.466'	86°42.745'	2638	Oct. 28	May 2	186	Nov. 8	190	2.1	Forested
	Namche	27°48.248'	86°42.899'	3571	Oct. 30	May 4	186	Nov. 10	190	5.1	Forested
	Dingboche	27°53.380'	86°49.438'	4360	Nov. 1	May 5	185	Nov. 12	191	7.2	Alpine
	Lobuche	27°57.657'	86°48.789'	5061	Nov. 3	May 7	185	Nov. 13	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	May 7	185	Nov. 13	190		None

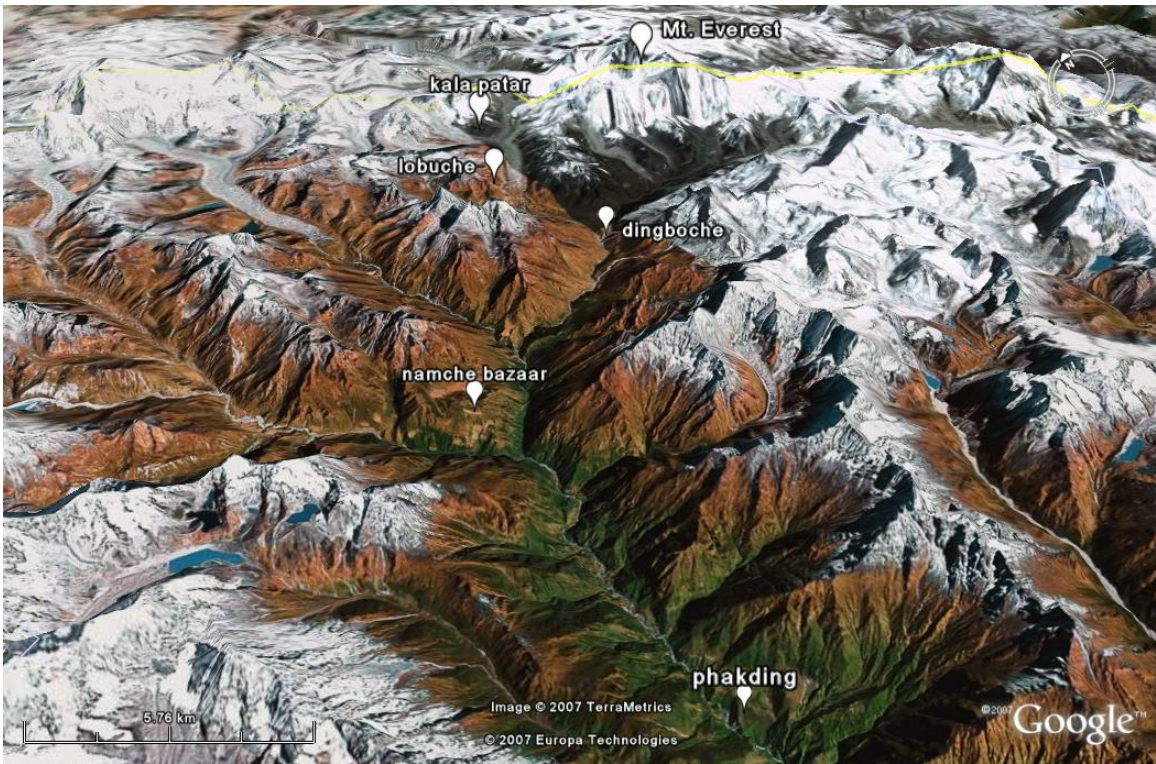


Figure 1a&b: a: Sampling regions in Nepal. b: Remote sampling region in the Central Himalaya. Mt. Everest is labelled for reference.

Results and Discussion

Air Concentrations. The analysis of the passive air sampler extracts yields sequestered amounts of the target chemicals in units of ng/sampler. In order to convert these amounts into volumetric air concentrations, it needs to be divided by the length of sampler deployment in days and the air sampling rate R in units of m^3 air per day. This conversion introduces considerable uncertainty, because R may to some extent be influenced by environmental factors such as atmospheric pressure, temperature and wind speed, and because it may be slightly different between different chemicals. To avoid that uncertainty, some studies have chosen to compare the unconverted sequestered amounts rather than the volumetric air concentrations derived from them. This option is not available, when comparing samplers deployed at sampling sites that vary very widely in altitude and exposure to wind. Two approaches have been presented to allow for a comparison of concentrations derived from passive air samplers deployed at widely different altitude. In the first it is assumed that molecular diffusion of the analytes across an air boundary layer is limiting uptake and thus determines R . Then, all of the factors that may influence chemical diffusivity are explicitly taken into consideration. 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 (See Figure S1). Figure S2 presents the atmospheric concentrations that were calculated using this approach.

An alternative approach has recently been proposed by Liu et al. and used in the interpretation of PAS data from the Eastern edge of the Tibetan Plateau (39). It is based on the assumption that in the absence of major sources of hexachlorobenzene, this chemical will achieve highly uniform air concentrations in space and time because of its exceptionally high atmospheric residence time, which in turn is a result of a very slow reaction rate with OH radicals and of a volatility that prevents dissolution in water droplets and sorption to solid atmospheric aerosol. The amounts of HCB sequestered in the air samplers from this study were indeed remarkably uniform with altitude and between seasons. In fact, HCB was the only analyte that did not show large differences in the sequestered amount with altitude and season. By dividing the amount of HCB sequestered in each PAS by the sampling duration and the hemispheric average concentration,

which is assumed to be constant in space and time, we can obtain a sampler-specific R , which then can be used to calculate volumetric air concentrations for the other analytes (39). This way we indirectly account for the environmental factors (temperature, pressure, wind speed and turbulence) that could affect R , and we can be more confident in comparing levels of the same chemical between sites at different altitude and season (39). The choice of the constant HCB air concentration affects the numerical value of R and the calculated volumetric concentrations for the other analytes, but it does not affect relative differences in concentration in space and time. This approach assumes that all analytes have uptake rates similar to HCB, which may not be the case. These R values thus have to be considered approximations and differences in the concentrations between different chemicals have to be interpreted with this uncertainty in mind (39). Figure 2 presents the atmospheric concentrations that were calculated using this approach, assuming a hemispheric average HCB concentration of 72 pg/m^3 .

It is presumably the mixing ratio of HCB in air that remains constant with altitude and not the actual volumetric concentration, which will be lower at lower atmospheric pressure. The approach thus yields concentrations normalized to standard atmospheric pressure conditions. This facilitates comparison of the data with air concentrations reported in the literature (39). HCB, α -HCH, γ -HCH, endosulfan I, p,p'-DDE and p,p'-DDT were detected in all air samples in both the agricultural areas at low elevation and in the remote central Himalaya. In both regions, endosulfan was the most abundant organochlorine pesticide. 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).

In Figure 2, blue lines indicate the levels during winter, red lines show summer time concentrations. Large differences are apparent between samplers deployed (i) in the agricultural areas and the remote region of Nepal, (ii) during summer and winter season, and (iii) at different elevations (Figure 2).

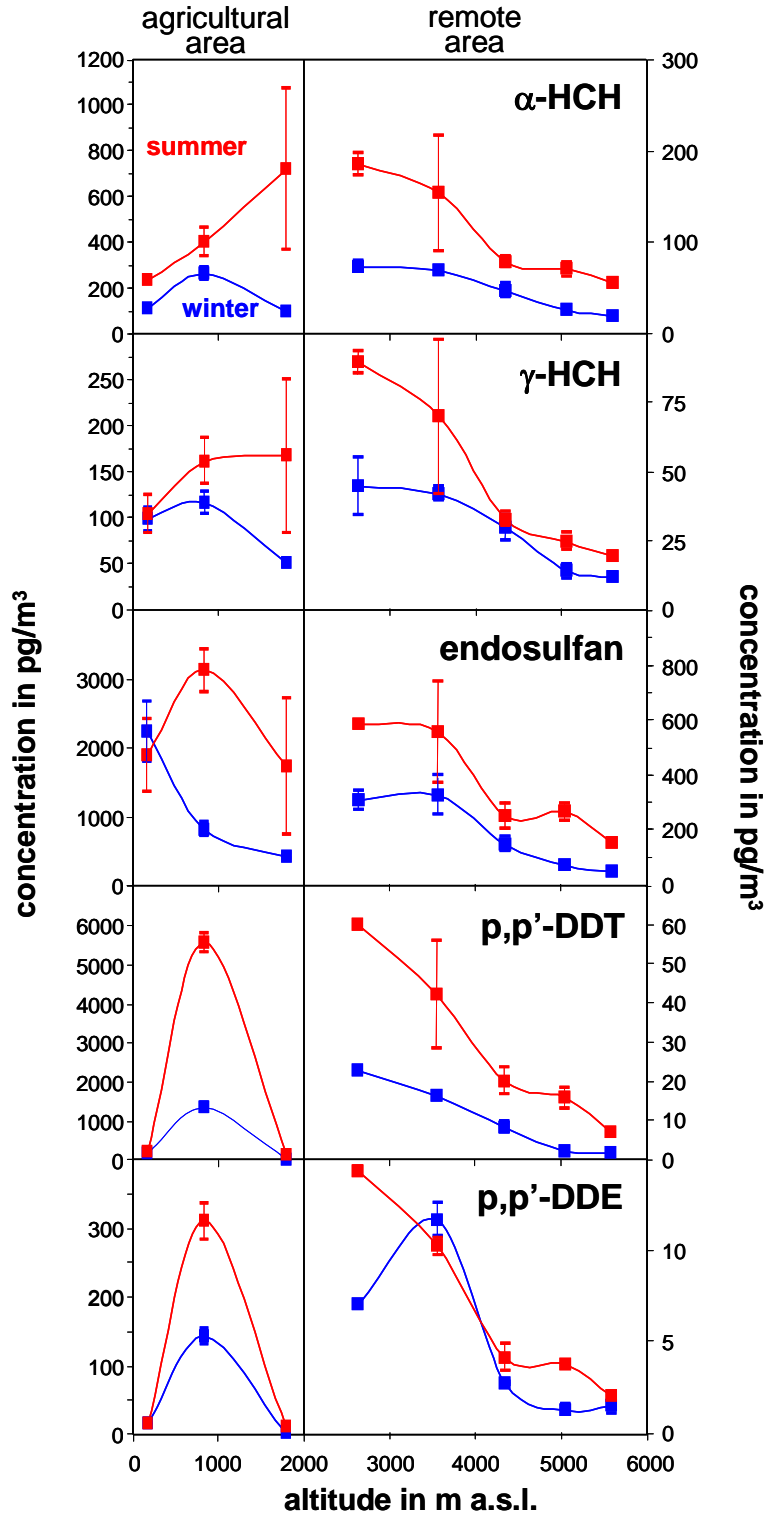


Figure 2 Concentrations of five organochlorinated pesticides in Nepalese air during summer and winter, as derived from PAS deployed for two sequential 6-month period at different elevations.

Differences between air concentrations measured in low altitude agricultural regions and the remote central Himalaya. As expected based on the local usage of pesticides, the concentrations of the OCPs were higher in the agricultural regions at low altitude than in the remote Solo Khumbu region. The differences between the concentrations in the agricultural area to the remote area was much larger for p,p'-DDT (more than 20-fold) than for p,p'-DDE and endosulfan (approximately 6-fold) and the HCHs (approximately 3-fold). However, the differences for the p,p'-DDT and p,p'-DDE were strongly influenced by an extremely high concentration value measured at Dhaitar during summer. With over 5000 pg/m³ this site had the highest p,p'-DDT level reported globally (17). Without that value, there would be only a 9-fold and 2-fold difference between agricultural area and remote region for p,p'-DDT and p,p'-DDE, respectively. All the chemicals decreased in concentration with altitude in Solo Khumbu, with summer time declines being steeper than those during winter.

Differences between summer and winter season. In remote areas, winter concentration were lower than summer concentrations for all chemicals except p,p'-DDE which had similar concentrations in either season. In the source regions at lower altitude, seasonal differences were less pronounced, except that the one high concentration for p,p'-DDT and p,p'-DDE at Dhaitar skewed the summer time values for those substances to high values. 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. Concentrations that are declining slightly with elevation is what we would expect, if the monsoon blows air from the Gangetic plains into the mountains.

Soil Concentrations. Figure 3 shows soil concentrations normalized for carbon content and moisture. 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 summer time air concentrations of HCH increase between these two sites. Highest concentrations of all the chemicals from the 1880m a.s.l. site and upwards were found at the forested site at 2360m a.s.l. with generally declining concentration at higher altitudes. As in air, p,p'-DDT and p,p'-DDE had the largest gradients in concentration with

elevation. Whereas the high concentrations in low elevations are clearly due to recent usage, the peak concentration at 2600 m a.s.l. may be a result of the relatively high precipitation rate at these elevations. Deposition of the OCPs at higher altitude is expected to decline with altitude because of the decline in precipitation rate at higher altitude.

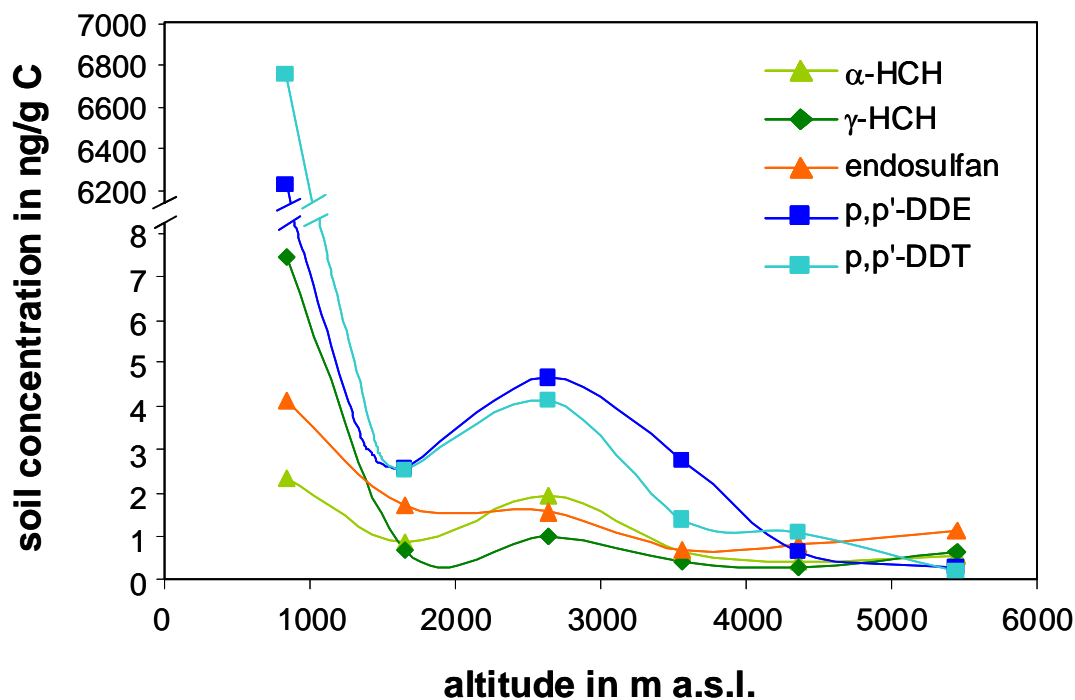


Figure 4: Pesticide concentrations in soil on a ng/g carbon dry weight basis as a function of altitude.

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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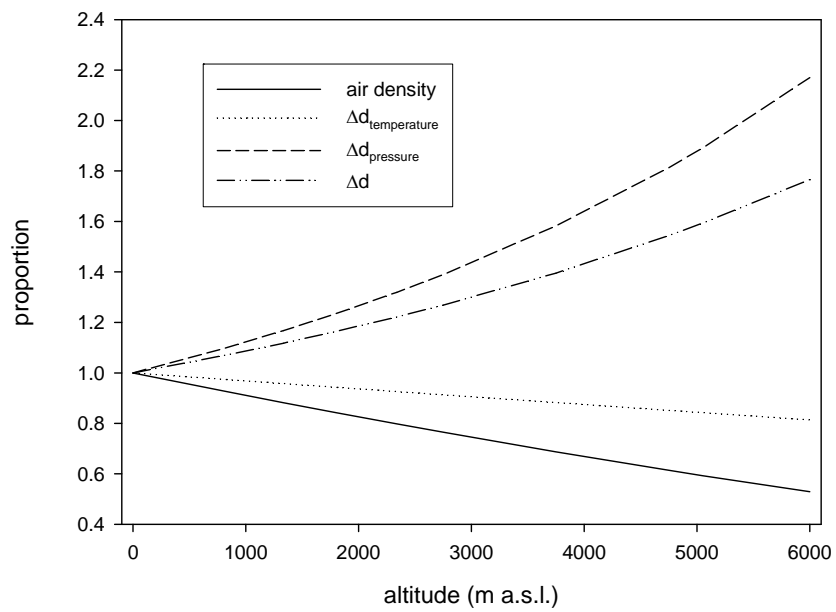


Figure S1: Change in diffusivity due to temperature and pressure. Δd is the sum of these phenomena. Air density is shown for reference.

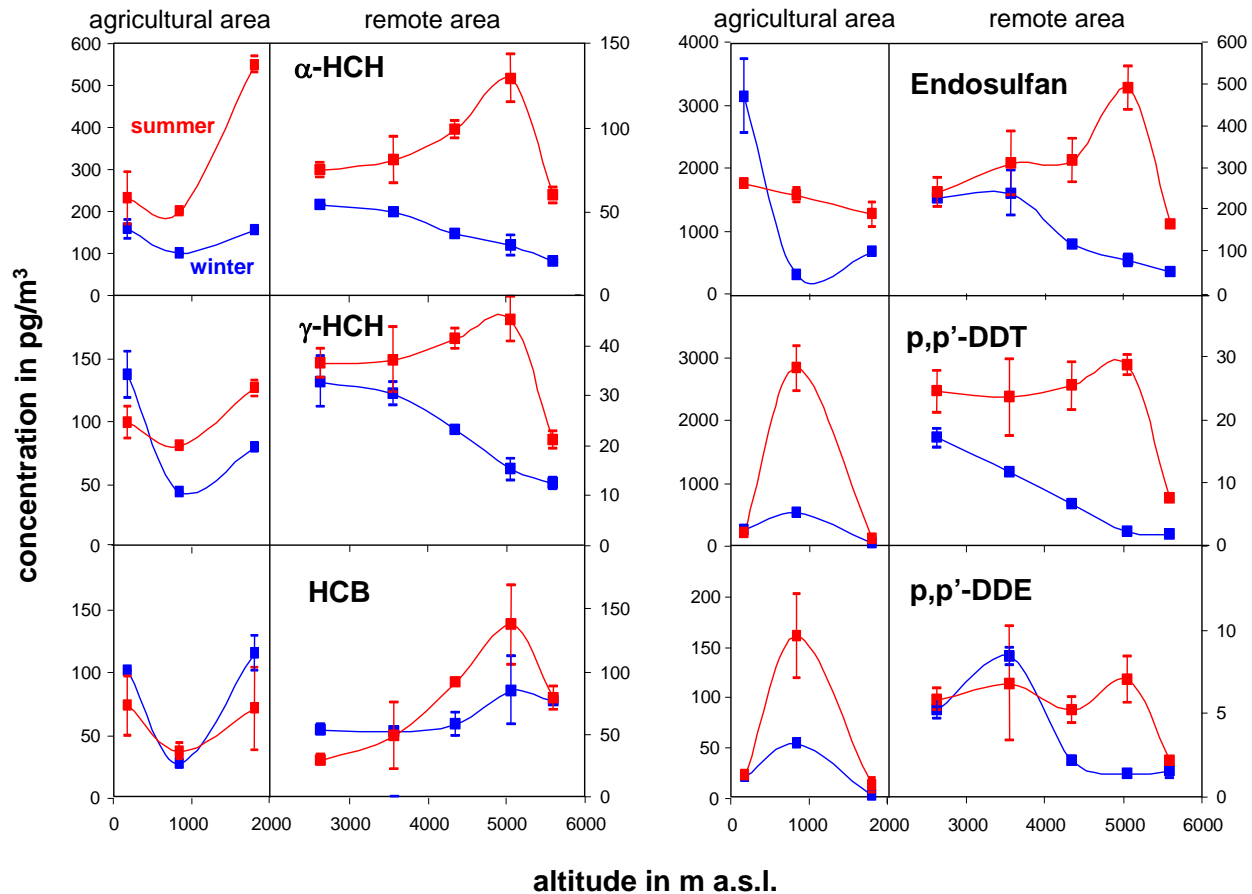


Figure S2 Seasonal and altitudinal trends in the atmospheric concentrations of HCB, α and γ -HCH, endosulfan, p,p'-DDT and p,p'-DDE in current use and remote regions of the central Himalaya. The whiskers indicate range of duplicates.

Analysis of Water Samples for POPs

20 water samples were collected from three different regions of Nepal and extracted on SPE cartridges. The regions included Rauhatat, an agricultural area near the Indian border, Pokhara, an agricultural region west of Kathmandu. and Panauti, near Kathmandu University, which is located 30 km east of Kathmandu. In the Table S1 below, minimum, maximum and average water concentrations are reported for the three sampling regions, separately. Water concentrations of DDTs and metabolites were quite low with a few sites having higher concentrations. HCB, HCHs and endosulfan were detected in most water samples with concentrations similar to those found in the Great Lakes region of Canada. Only endosulfan showed more varied concentrations across the regions indicating its current use status. These data will be the subject of a manuscript authored by Mr. Kafle and will be the main chapter in his M.Phil. thesis. This will be the first such observations from the Himalayan region using current QA/QC protocols.

Table S1 Concentrations of pesticides in Nepalese water samples in units of ng/L

Name)	Panauti (n=7)			Rauthahat (n=6)			Pokhara (n=7)		
	Min	Max	Av	Min	Max	Av	Min	Max	Av
α -HCH	ND	0.72	0.35	0.038	0.64	0.31	0.0202	0.36	0.17
γ -HCH	0.0063	0.94	0.35	0.0036	0.78	0.27	0.0101	1.20	0.50
HCBz	0.047	0.71	0.27	0.062	0.50	0.19	0.0623	0.21	0.14
endosulfan 1	0.0027	1.6	0.44	ND	0.62	0.12	ND	0.16	0.046
p,p'-DDE	ND	0.0059	0.0021	ND	ND	ND	ND	ND	ND
p,p'-DDT	0.015	0.29	0.090	ND	0.13	0.056	ND	0.098	0.028
o,p'-DDE	ND	0.057	0.014	ND	0.024	0.0079	ND	ND	ND
o,p'-DDT	ND	0.23	0.061	ND	0.38	0.17	ND	0.18	0.048
oxychlordane	ND	0.020	0.0041	ND	0.041	0.019	ND	ND	ND
t-chlordane	0.0069	0.059	0.017	ND	0.022	0.0094	ND	0.016	0.0060
c-chlordane	ND	0.0087	ND	ND	0.0090	0.0020	ND	ND	ND
t-nonachlor	ND	0.026	0.0075	ND	0.043	0.016	ND	0.017	0.0063