

Persistent organic pollutants in soil of the central Himalaya

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Introduction

Persistent organic pollutants (POPs) are important contaminants due to their persistence in the environment and potential toxic effects on ecosystems and humans. Concerns related to these contaminants are particularly pertinent in Asia where the use of pesticides has been increasing dramatically due to changing agricultural practices and malarial vector control.¹⁻³ Based on studies in European and North American mountain regions, evidence is increasing that alpine regions function as regional convergence zones for selected POPs due to orographic cold trapping⁴. It is hypothesized that such an effect may be particularly pronounced in the Himalaya because of dramatic elevational temperature and precipitation gradients relative to contaminant source regions in its immediate vicinity and because of the regional monsoon system which has been shown to deliver particles and inorganic air pollutants to higher altitudes⁵. Since atmospheric deposition is the only plausible source of POPs in most regions, the inventory in soil is a measure of the historical atmospheric deposition. For the less volatile and highly persistent compounds, the soil inventory is a good absolute measure, whereas for the more volatile POPs it is only a relative measure of deposition since these compounds are also subject to revolatilization⁶.

An altitudinal transect of POPs in soil was undertaken to determine the effect that orographic cold trapping may play in the deposition of organic contaminants in the central Himalaya. Concentrations of the organochlorinepesticides α -hexachlorocyclohexane (α -HCH), γ -HCH, endosulfan, pp'-DDT and pp'-DDE were measured in soil sampled over altitudes ranging from 841 m to 5450 m and were normalized to the carbon content of the soil.

Materials and Methods

Soil Sample Collection. A 60 mm diameter stainless steel soil corer was used to collect soil samples to the bottom of the organic rich layer at the top of hills to minimize the effect of runoff. As much as possible, sites of similar soil and vegetation type were selected for comparison. Three soil cores were retrieved at each site and pooled. Samples were added to a sealable plastic bag and shipped to the Freshwater Institute in Winnipeg, Canada, where they remained frozen until extraction.

Figure 1: Coordinates of sampling sites in Nepal

Altitude (m)	Latitude (N)	Longitude (E)
841	27°42.571'	85°36.375'
1657	27°37.861'	85°32.532'
2638	27°44.466'	86°42.745'
3571	27°48.248'	86°42.899'
4360	27°53.380'	86°49.438'
5450	27°59.526'	86°49.790'

Soil Sample Extraction. Sodium sulphate was added to ~10 g of soil. The samples were then spiked with an internal recovery standard mixture containing polychlorinated biphenyl (PCB) congener 30 as well as mass labelled α -HCH and endosulfan. Samples were extracted using a Dionex accelerated solvent extractor using dichloromethane (DCM). Samples were exchanged into hexane and reduced in volume to 1 mL.

Soil Sample Cleanup. Samples were added to an 8 g column of 1.2% deactivated Florisil and eluted into 3 fractions using 100% hexane, 15% DCM in hexane, and 50% DCM in hexane. These were reduced to 1 mL by roto-evaporation and eventually transferred into 1 mL iso-octane using nitrogen blow-down. Samples were spiked with an aldrin internal performance standard prior to gas chromatographic injection.

Soil Sample Analysis. Samples were injected on a Varian 3800 gas chromatograph equipped with electron capture detector and a 60 m J&W DB5 column. Varian STAR graphics were used to interpret the results.

Quality assurance. Average recoveries of d6- α -HCH, d4-endosulfan and PCB 30 were 114%, 82.5% and 74% respectively. None of the compounds of interest were detected in blank samples except for pp'-DDE. Assuming a 10 g sample size and an average of 3.35% carbon we calculate a detection limit of 0.59 ng/g carbon.

Results and Discussion

Residues of pp'-DDT, pp'-DDE, α - and γ -HCH as well as endosulfan were detected in soil samples recovered from altitudes between 841 and 5450 m in Nepal. Analyzed samples were corrected for moisture content as well as surrogate recovery and normalized to the carbon content of the soil.

Table 1: Carbon Normalized Concentrations of Pesticides (ng/g carbon) and carbon content as a function of altitude

Altitude (m)	Carbon content %	α -HCH	γ -HCH	endosulfan	pp'-DDT	pp'-DDE
841	0.7	2.36	7.43	4.14	6755	6227
1657	1.5	0.86	0.68	1.70	2.50	2.59
2638	2.1	1.94	1.03	1.57	4.15	4.66
3571	5.1	0.66	0.42	0.69	1.37	2.77
4360	7.2	0.42	0.26	0.84	1.11	0.65
5450	3.5	0.57	0.63	1.16	0.17	0.30

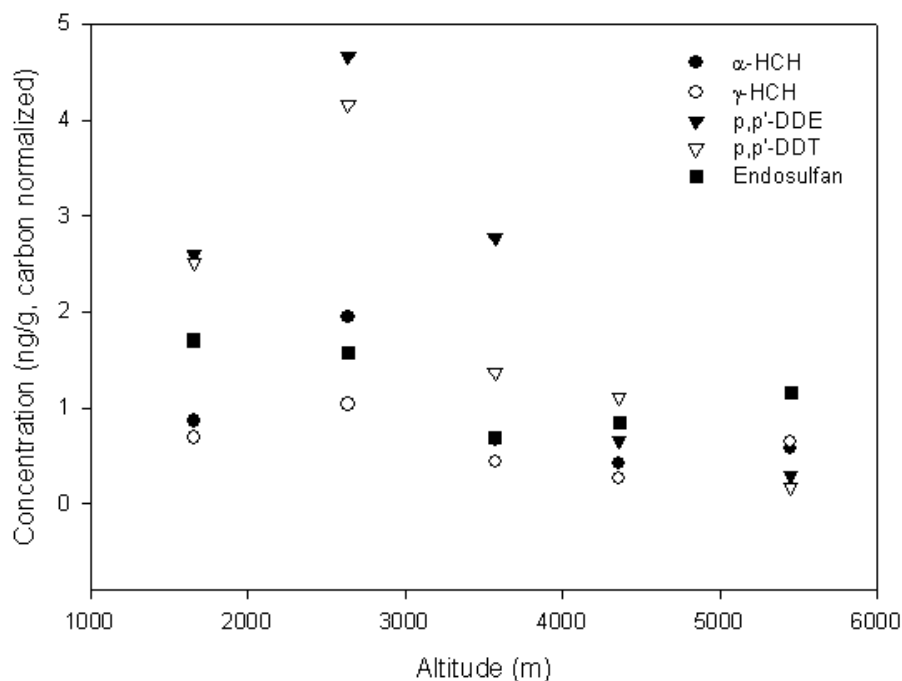


Figure 1. Soil concentrations of α -HCH, γ -HCH, endosulfan, p,p'-DDT, p,p'-DDE, as a function of altitude

Looking first at the less volatile DDT and DDE compounds (Figure 1) we find soil concentrations peaking at 2638 m and then decreasing with altitude. A look at the relatively more volatile HCH compounds yields a somewhat different trend. Once again we have observed a peak at 2638 m followed by a decrease to 4360 m and an increase to 5450 m. Similarly, endosulfan concentrations decrease to 3571 m and gradually increase to 5450 m but do not seem to peak at 2638 m.

While these measurements are the first of their kind in the Central Himalaya it is instructive to compare these results with those of other similar soil contaminant measurements in areas affected only by atmospheric deposition. HCHs, pp'-DDT, pp'-DDE and endosulfan concentrations in soil were found to be between 6 and 100 pg/g dry weight in this study, similar to the lowest observed concentrations of

selected POPs in Meijer et al.'s global study of PCBs and HCB⁷.

Correlation of our results with gradients of precipitation, temperature and vegetation type are required to further comment on the results found in this study. Soil sampling sites from 3571 m to 5450 m were however very similar in terms of vegetation (open areas with little vegetative cover and similar carbon content) and can likely be compared directly. As may be expected, concentrations of pp'-DDT and pp'-DDE decrease from 2638 m to the highest altitude sampling site. However, the observation of increased levels of the more volatile compounds at the highest elevations indicate that either re-volatilization from soil is reduced due to decreased annual temperatures at those sites, or to increased deposition rates, or both. As precipitation tends to decrease with increasing altitude in this region, reduced re-volatilization is a more likely reason for increased levels at the highest altitudes.

Analysis of these compounds in an agricultural and malaria prone area in close proximity to the current high altitude study (841 m) indicated very high levels of pp'-DDT and pp'-DDE. Concentrations of α -HCH, γ -HCH, endosulfan, pp'-DDT and pp'-DDE were observed to be 2.4, 7.4, 4.1, 6755 and 6227 ng/g carbon, respectively. This site was not included in Figure 1 as it is not reflective of atmospheric deposition of POPs. Instead it was used for comparison as a region of current pesticide usage.

It should be noted that given the very complex patterns of air movement and precipitation as well as proximity to sources of POPs contamination, results from the Central Himalayan Region may not reflect patterns of deposition in other regions of the Himalayan system. Further characterization of POPs deposition patterns should be carried out in the various regions of this mountain system. A sampling program of high altitude glacial accumulation zones in the region is underway in order to observe seasonal deposition of chemicals and to investigate HCH concentrations at even higher altitude in snow.

References

1. Sharma D. (1993) *Pesticide News* 21:15.
2. Santillo D. Johnston P. and Stringer R. (1997) *Pesticide News* 36:4-6.
3. UNEP Chemicals (2002) Central and North East Asia Regional Report; Regionally based assessment of persistent toxic substances.
4. Blais J. Schindler D. Muir D. Kimpe L. Donald D. and Rosenberg B. (1998) *Nature* 395:585-588.
5. Loewen M. Sharma S. Tomy G. Wang F. Bullock P. and Wania F. *Journal of the Aquatic Ecosystem Health and Management Society*, in press.
6. Mamontov A, Mamontova E, Tarasova E. and McLachlan M. (2000) *Environ. Sci. Technol.* 50:741-747.
7. Meijer S. Ockenden W. Sweetman A. Breivik K. Grimalt J. and Jones K. (2003) *Environ. Sci. Technol.* 37:667-672.