

Pesticides in soil and air from various regions and altitudes in Costa Rica

Gillian Daly¹, Frank Wania¹, Ying D Lei¹, Luisa E Castillo², Derek CG Muir³

¹University Of Toronto

²Universidad Nacional

³National Water Research Institute

Introduction

Central America has a significant agricultural industry - major crops are coffee, sugarcane, pineapple and banana. It also has a history of using organochlorine pesticides, many of which are now classified as persistent organic pollutants (POPs) under the Stockholm Convention. Tropical agriculture is often very chemical-intensive. E.g., the per hectare use of plant protection products is higher in Costa Rican agriculture than in the highly industrialised agriculture of the Netherlands. Pesticides that have been banned in industrialised countries sometimes continue to be used for public health and agriculture in tropical countries¹. At the same time, Central America is a region of exceptionally high biodiversity, with very highly valued ecosystems, including in economic terms². The Central American mountain regions in particular are home to biologically highly diverse forest ecosystems. Plantations with high usage of plant protection agents are often in immediate vicinity and/or upwind of protected areas, such as National Parks and Biological Reserves.

About 10% of Costa Rica's total land area is used for crop production, and pesticide imports up to 9000 metric tons annually have been reported³. In Costa Rica, organochlorine pesticides were primarily used for agricultural purposes, while DDT could only be used for malaria control⁴. DDT and a series of other OC pesticides (e.g. aldrin, dieldrin) were banned for use in 1988, while chlordane, heptachlor, endosulfan and a series of other organochlorine compounds were restricted in their use³. Persistent organochlorine pesticide residues have been measured in a variety of media in Costa Rica, including insect larvae⁵ and human milk⁶. Current use pesticides (CUPs), such as those used in large quantities on banana plantations (e.g. the organophosphorus pesticides terbufos and chlorpyrifos) have been measured primarily in the aquatic environment⁷. Pounds and Crump⁸ hypothesized a decade ago, that the disappearance of the endemic golden toad and of the local populations of the harlequin frog in Costa Rica's Monteverde Cloud Forest Preserve may be related to atmospheric contaminants scavenged by mist and cloud water in montane areas.

Here we report on an ongoing study aimed at assessing the geographic variation of POPs and CUPs in the atmospheric and soil environment of Costa Rica. A particular focus of this work is to understand POP distribution along tropical altitudinal gradients.

Materials and Methods

Air and soil samples were taken at twenty-three locations in Costa Rica (Table 1). The sampling sites were mostly located in protected areas, such as National Parks, Biological Reserves and research stations, where it can be assumed that no pesticides had been used in the past. The network includes sites on the Caribbean and Pacific coast of Costa Rica, as well as sites ranging over 3400 m in elevation.

Table 1 Name, elevation and geographical coordinates of the sampling station in Costa Rica.

1 Volcan Barva	2642 m	N 10°8.5'	W 84°7.3'
2 Carara	54 m	N 9°46.8'	W 84°36.3'
3 Manuel Antonio	55 m	N 9°22.9'	W 84°08.6'
4 Playa Naranjo	2 m	N 10°46.8'	W 85°40.0'
5 Santa Rosa	308 m	N 10°50.4'	W 85°37.1'

EMV - POPs in Mexico, Central and South America

6 Maritza	600 m	N 10°57.4'	W 85°29.7'
7 Volcan Cacao	1139 m	N 10°55.6'	W 85°28.1'
8 San Gerardo, Guanacaste	625 m	N 10°52.8'	W 85°23.3'
9 Palo Verde	17 m	N 10°20.6'	W 85°20.4'
10Monteverde West	1527 m	N 10°17.9'	W 84°48.2'
11Monteverde East	1500 m	N 10°35.9'	W 84°80.1'
12VolcanPoas	2704 m	N 10°11.1'	W 84°13.8'
13La Selva Biological Station	53 m	N 10°25.9'	W 84°0.2'
14E.A.R.T.H.	50 m	N 10°12.8'	W 83°35.7'
15Cahuita	1 m	N 9°44.1'	W 82°50.2'
16KeKöldi	227 m	N 9°38.3'	W 82°46.8'
17Talamanca	87 m	N 9°38.4'	W 82°52.1'
18Belen	935 m	N 9°97.5'	W 84°18.5'
19SanRafael de Muertes de Oca	1330 m	N 9°56.5'	W 84°01.2'
20Cot, Oreamuno Cartago	1831 m	N 9°53.4'	W 83°52.8'
21Prusia	2689 m	N 9°57.2'	W 83°52.9'
22Volcan Irazu	3390 m	N 9°58.8'	W 83°50.2'
23Esperanza	2880 m	N 9°41.5'	W 83°52.0'

The five stations numbered 4 to 8 in Table 1 represent an elevational transect of more than a 1000 m in the Guanacaste Conservation Area in the Northwestern part of Costa Rica. Whereas stations 4 to 7 are facing towards the Pacific, station 8 is located on the continental divide and is influenced more strongly by weather from the Caribbean side. Similarly, stations 10 and 11, although in relatively close proximity, are on different sides of the continental divide and often experience dramatically different weather conditions. Standley and Sweeney⁵, reported distinctly different contamination with organochlorine pesticides in mayfly larvae and vegetation collected on the eastern and western slopes of the Guanacaste Conservation Area. The five stations numbered 18 to 22 constitute an elevational gradient on the west-facing slope of volcano Irazu, ranging from the heavily populated central valley to the summit more than 2000 m higher.

Air Sampling. Air was sampled at all 23 sampling locations from February 2004 to February 2005 using the XAD-resin based passive air sampling system by Wania et al.⁹. When deployed for a one year period, annually averaged air concentrations can be derived from the amount of chemical sequestered in the resin. The sampling container is a long thin cylinder made of a fine stainless steel mesh held in shape by two end caps and filled with the resin sorbent material. The container is placed in a shelter, which consists of a steel can with an opening at the bottom (Fig. 2). Air exchange in the can is mostly through the bottom opening. Duplicate samplers were installed at approximately 1.5 m above the ground at each site, and field blanks (samplers that remained in the storage tubes and were taped to the post) were left at a selected number of sampling sites.



Fig. 3 Soil auger used to collect soil samples.



Fig. 2 Passive air sampler housing.

Soil Sampling. Soil has been shown to contain the bulk of the POP inventory in terrestrial ecosystems¹⁰. It also has proven useful for mapping the spatial variability of POP deposition on a regional scale¹¹. 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 subject to revolatilization¹¹. Soil was sampled to a depth of 25 cm or to the bottom of the organic matter rich soil layer (A horizon) at 21 sampling sites (all except 11 and 18) in February 2004. Ten soil samples were taken with a soil auger (Fig. 3) in an approximate grid surrounding the location of the air sampler. These samples were then homogenized in a

bucket, and two subsamples were taken for analysis. The subsamples were wrapped in pre-cleaned (baked) aluminum foil, sealed in plastic bags, and transported to the laboratory where they were stored at -20 °C.

Chemical Analysis. For extraction, 15 g aliquots (wet weight) of soil were mixed with anhydrous sodium sulfate and ground to a fine, grainy consistency. The mixtures were transferred to thimbles (Whatman) and extracted by Soxhlet for 20 hours using dichloromethane. The thimbles had been pre-cleaned by Soxhlet for 4 hours using the same solvent. Extracts were reduced in volume and transferred into iso-octane by rotary evaporation, before further blow-down with N₂ to 2 mL. A 3 g neutral Al₂O₃ (6% added water) clean-up column was used with 1:1 dichloromethane/hexane as an eluent. Further rotary-evaporation and blow-down with N₂ produced a final sample volume of 1 mL. Chemical analysis is performed by GC-MS. The air samples are analyzed as described in ref. ⁹. Soil moisture content was determined by weighing soils before and after drying for 15 hours at 75-80 °C. Moisture contents varied widely from 0 to 78%, with a mean of 32%. The organic carbon content of ground and dried soil is determined with an elemental analyzer after acidification with 10 % HCl to remove carbonates.

Results and Discussion

Soil and air was sampled successfully throughout various regions of Costa Rica and is currently being analyzed for CUPs and POPs. Regional weather patterns and emission sources (agricultural and urban areas) will be used to explain the observed spatial contamination patterns in air and soil.

Acknowledgements

We thank Dr. Tom Harner and all the members of his group at the Meteorological Service of Canada for use of the lab and advice on extraction techniques. We are appreciative of the assistance of Andrea Suarez Serrano and Diego Arguello Murillo in Costa Rica, as well as the staff of the numerous parks and conservation areas where we set up our stations. We are grateful for funding from a Canon National Parks Scholarship and the Natural Sciences and Engineering Research Council of Canada.

References

¹Carvalho F.P., Montenegro-Guillen R., Villeneuve J.P., Cattini C., Tolosa I., Bartocci J., Lacayo-Romero M., and Cruz-Granja A. (2003) *Chemosphere* 53: 627-636.

- ²Echeverria J., Hanrahan M., and Solorzano R. (1995) *Ecol. Econ.*3: 43-52.
- ³ Von Duzeln J. (1991) In: Chemistry, Agriculture and the Environment (Richardson M. L., Ed.), Royal Society of Chemistry Press, 410-428.
- ⁴ Castillo L. E., de la Cruz E., and Ruepert C. (1997) *Environ. Toxicol. Chem.* 16: 41-51.
- ⁵ Standley L. J., and Sweeney B. W. (1995) *J N AM Benthol. Soc.* 14: 38-49.
- ⁶ Umana V., and Constenla M. (1984) *Rev. Biol. Trop.* 32: 233-239.
- ⁷ Castillo L. E., and Ruepert C. (2000) *Environ. Toxicol. Chem.* 19: 1942-1950.
- ⁸ Pounds J. A., and Crump M. L. (1994) *Conservation Biology*8: 72-85.
- ⁹ Wania F., Shen L., Lei Y.D., Teixeira C., and Muir D.C.G. (2003) *Environ. Sci. Technol.* 37: 1352-1359.
- ¹⁰ Harrad S.J., Sewart A.P., Alcock R.E., Boumphrey R., Burnett V., Duarte-Davidson R., Halsall C.J., Sanders G., Waterhouse K.S., Wild S.R., and Jones K.C. (1994) *Environ. Pollut.* 85: 131-146.
- ¹¹ Mamontov A.A., Mamontova E.A., Tarasova E.N., McLachlan M.S. (2000) *Environ. Sci. Technol.* 34:741-747.